CRE-
CHEMICAL
REACTION
ENGINEERING

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Thanks to all of You :

Kinetics

Reaction :–

When a component losses its identity to form a new identity. Chemical rxn can be of following type.

1) **Decomposition rxn :–** When a big molecule breaks into smaller molecules.

eg→ Electrolysis of water

$$2H_2O \longrightarrow 2H_2 + O_2 .$$

2) **Synthesis rxn :–** When two or more smaller molecules combined together to form a big molecule.

eg→ $A + B \rightarrow AB$
$C + O_2 \rightarrow CO_2$
} When two smaller molecules combine in such a way that third comp is not formed.

3) **Isomerization Rxn :–**

When molecular structure of the molecule is changed w/o being combined or decomposed.

$$CH_3-CH_2-CH_2-CH_3 \Rightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}}$$

Rate of rxn

Based on unit volume of rxn mixture,

for homogeneous rxn system →

$$r_i = \frac{1}{V}\frac{dN_i}{dt}, \quad \frac{mol}{m^3 \cdot s}$$

Rxn mixture contains Reactants, pdts. inerts.

Based on unit interfacial area of two fluid system,

for heterogeneous system →

$$r_i'' = \frac{1}{S}\frac{dN_i}{dt}, \quad \frac{mol}{m^2 \cdot s}$$

S = interfacial surface area

Based on unit weight of solid in fluid-solid system,

rxn mixture contains fluid

$$r_i' = \frac{1}{W}\frac{dN_i}{dt}, \quad \frac{mol}{kg \cdot s}$$

For homogeneous rxn system :-

where the rxn mixture contains only one phase.

ex→ $N_2(g) + H_2(g) \longrightarrow NH_3(g)$

$$\boxed{r_i = f(\text{temp}^r, \text{conc}^n)}$$

Reactant ⟶ Product.

$A \longrightarrow B$

$$(-r_A) \text{ or } (r_{A-}) = -\frac{1}{V}\frac{dN_A}{dt}$$

$dN_A = N_{Af} - N_{A0}$
$= -ve.$

rate of formation of B $r_B = \frac{1}{V}\frac{dN_B}{dt}$

or

rate of rxn based on B

$dN_B = dN_{Bf} - N_{B0}$
$= +ve$

Power Law :-

$aA + bB + cC \longrightarrow Pdt$

$$r_i = k C_A^{\alpha} C_B^{\beta} C_C^{\gamma} \ldots$$

$$\boxed{r_i = k \pi C_i^{\alpha_i}}$$

$n = \Sigma \alpha_i$ → overall order of rxn

k = sp. rxn rate or rate constant.

C_i = Conc^n of 'i'

α_i = Apparent order of reactant

⇒ $A + B \longrightarrow Pdt$

$$\boxed{-r_A = k C_A^{\alpha} C_B^{\beta} = -\frac{1}{V}\frac{dN_A}{dt}}$$

Elementary rxns :-

which proceeds in single step

$aA + bB \longrightarrow C_1$

$$-r_A = k C_A^{\alpha} C_B^{\beta}$$

⇒ $aA + bB \longrightarrow C$

Non-Elementary rxn :—

which proceeds in more than one rxn.

$$aA + bB \rightarrow C$$

(slowest) ⇒ $\frac{a}{2}A + \frac{b}{3}B \rightarrow C^*$ (rds) $\quad -r_A = k C_A^{\alpha} C_B^{b}$ $\quad \alpha = a/2,\ \beta = b/3$

⇒ $C^* + \frac{a}{3}A \rightarrow D^*$

⇒ $D^* + 1/2\,B \rightarrow C$

⟹ rxn rate

Calculated for rate determining step

⇒ rate determining step is the slowest step in the rxn mech.

$$-r_A = k C_A^{\alpha} \cdot C_B^{\beta}$$

$$\alpha = a\ ,\ \beta = b$$

Molecularity :—

⇒ No. of molecules atoms, ions or moles, colliding in the rate determining step.

⇒ It is theoretical quantity.

• It can not be zero or fractional value. : molecules collides completely not in parts.

⇒ It is only, 1, 2 or 3.

It is related to only elementary rxn,

$$A + 2B \rightarrow P$$

Molecularity = 3

$$-r_A = k C_A C_B^2$$

$$n = 3$$

Molecularity = Overall order of rxn = Sum of stoicheometry coeff

Order of rxn

The order of the rxn refers to the powers to which the concn are raised in the kinetic rate law.

→ It is an experimental qty:
→ It can be zero, fractional value or -ve
→ It can be whole number,

$$aA + bB \rightarrow C$$

$$-r_A = k C_A^{\alpha} C_B^{\beta}$$

$$\boxed{n = \alpha + \beta}$$

Zero order rxn :- $n = 0$

Photosynthesis rxn,

First order rxn :- $n = 1$

Radioactive decomposition

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2$$

$$r \propto \frac{1}{C_{CO}}$$

$$r \propto C_{CO}^{-1}$$

$$\boxed{n = -1}$$

$$CH_3CHO \rightarrow CH_4 + CO$$

$$r \propto C_{CH_3CHO}^{3/2}$$

$$n = 3/2$$

Q. What will be the over all order of rxn.

$$r = k C_A^{0.3} C_B^{1.5}$$

$$n = 0.3 + 1.5 = 1.8$$

⊗ $A + 2B \rightarrow 3R + S$, rate of rxn is define as. $r = k C_A C_B^2$, then what will be the rate of rxn $2A + 4B \rightarrow 6R + 2S$

$$r = k C_A C_B^2$$

Relative rate of rxns :-

$$aA + bB \longrightarrow cC + dD$$

$$-r_A =$$

$$-r_b = \frac{b}{a}(-r_A)$$

$$r_C = \frac{c}{a}(-r_A)$$

$$r_D = \frac{d}{a}(-r_A)$$

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

Q.) for the rxn $3A + 4B \rightarrow 2C + 5D$

$$\boxed{\frac{-r_A}{3} = \frac{-r_B}{4} = \frac{r_C}{2} = \frac{r_D}{5}}$$

Rate Constant :- (k) Sp. rxn rate.

→ k is strongly temp^r dependent term.

$$\boxed{\text{Units of } k = (\text{time})^{-1}(\text{conc}^n)^{1-n}}$$

! n = order of rxn

for first order rxn

$$\text{unit of } k = s^{-1}$$

for second order rxn

$$\text{unit of } k = s^{-1}(\text{mol/L})^{-1} = \text{L/s mol}$$

Q.) for the rxn $A + 3B \rightarrow 2C$

$$-r_A = k C_A C_B^3$$

$$\text{Unit} = s^{-1}(\text{mol/L})^{-3} = s^{-1}\frac{l^3}{\text{mol}^3}$$

Q.) for a rxn, rate constant is given as $k = 3\frac{mol}{m^3 \cdot s}$, n = ?

$s^{-1}, \left(\frac{mol}{L}\right)^3$

n = 4

—

Arrhenius theory :-

$$k \propto \exp(-E/RT)$$

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

k_0 has same unit as k

$k_0 \rightarrow$ Pre exponential factor.

$\rightarrow$ frequency factor

$k_0 \neq f(T)$

E = Activation Energy, J/mol

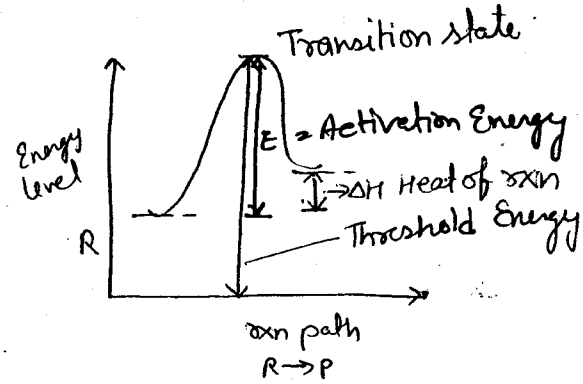
R = Universal gas constant, J/mol.K

$T \Rightarrow$ Absolute temp, K

Threshold energy is actually

Required energy + additional energy

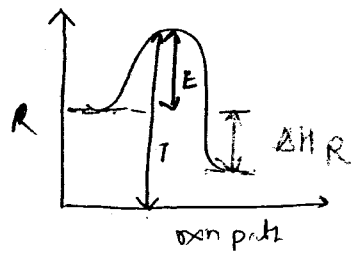
Threshold Energy = Activation Energy + Energy of molecules



$$\Delta H_R = \Sigma H_{Pdt} - \Sigma H_{React}$$

$\Delta H_R > 0 \Rightarrow$ Endothermic rxn

$\Delta H_R < 0$ Exothermic.



$$k_1 = k_0 e^{-E/RT_1}$$

$$k_2 = k_0 e^{-E/RT_2}$$

Assumption :

Activation energy is constant for temp range.

$$\ln k_1 = \ln k_0 - E/RT_1 \quad \text{—(1)}$$

$$\ln k_2 = \ln k_0 - E/RT_2 \quad \text{—(2)}$$

eqn (2) − (1)

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

* Collision Theory

→ Based on kinetic theory of gases.

Sep 16,14

collision

2.) at 500 k, the rxn rate was 10 times faster than that of at 400k,

for gaseous rxn we collision theory.

Sol^n

$$k = k_0 T^{1/2} e^{-E/RT}$$

$$\ln k = \ln k_0 + \tfrac{1}{2}\ln T - \frac{E}{RT}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{1}{2}\ln\left(\frac{T_2}{T_1}\right) + \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln(10) = \tfrac{1}{2}\ln\left(\frac{500}{400}\right) + \frac{E}{R}\left(\frac{1}{400} - \frac{1}{500}\right)$$

$$R = 1.987 \text{ cal/mol.k}$$

$$\boxed{E = 8702.08 \text{ cal/mol}}$$

$$k \propto T^{1/2} \cdot e^{-E/RT}$$

$$\boxed{k = k_0 T^{1/2} e^{-E/RT}}$$

Transition State Theory :-

→ Based on Statistical Mechanics.

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

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

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

⇒ $n = 0$ for AT

⇒ $n = 1/2$ for C.T

⇒ $n = 1$ for TST

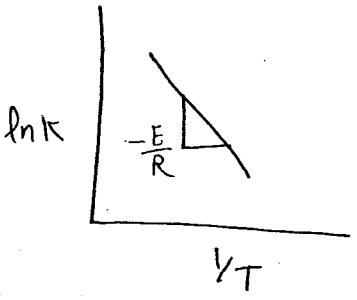
* Effect of temp^r

Arrhenius Theory –

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

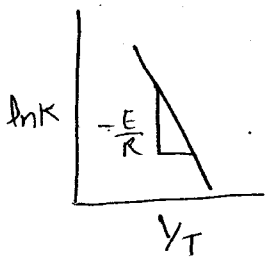
$$\ln k = \ln k_0 - E/RT$$

$$y = c + mx$$



⇒ For higher value of Activation Energy

Temp^a Sensitive rxn.



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

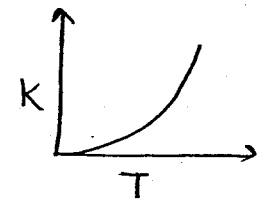
T ↑ K ↑

T ↓ K ↓

$e^{-\infty} \to 0$

$e^{0} \to 1$

Ans) $K = k_0 e^{-E/RT}$



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

$r \propto k$

$$\ln\left(\frac{r_2}{r_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Q.) The E_A of a bimolecular rxn is abt 9150 cal/mol. How much faster will this rxn takes place at 500 K then at 400 K. 10

$R = 1.987 \frac{cal}{mol\,K}$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{9150}{R}\left(\frac{1}{400} - \frac{1}{500}\right)$$

$$= \frac{4.575 \times 4.18}{8.314}$$

$$\ln\left(k_2/k_1\right) = 2.302$$

$$\frac{k_2}{k_1} = 9.998$$

$$\boxed{k_2 \simeq 10 k_1}$$

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Collision theory

Rxn only those molecules take part which have gone through a successful collision.

valid for only - molecularity greater than one.

It is failed for the unimolecular rxns.

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

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

Q→ for the gaseous phase rxn. The rate exp is given as $-\frac{dC_A}{dt} = kC_A^n$
Then what will be rate exp in terms of partial pressure A.
for the low pressure condition.

$$-\frac{dC_A}{dt} = kC_A^n$$

$PV = nRT$

$\frac{P}{RT} = \frac{n}{V} = C$

$$-\frac{dP_A}{dt} = ?$$

$\propto P_A^n (RT)$

$PV = nRT$

$\frac{P}{RT} = C$

$$-\frac{d}{dt}\left(\frac{P_A}{RT}\right) = k\left(\frac{P_A}{RT}\right)^n$$

$$\boxed{-\frac{dP_A}{dt} = \frac{k P_A^n}{(RT)^{n-1}} = k(RT)^{1-n} P_A^n}$$

Rxn Mixture

Constant Volume Rxn Systems

The vol of rxn mixture does not change with the rxn progression
(Constant density System)
(Liq phase)

Variable Volume Rxn Systems

The vol. of the rxn mixture is changed with the rxn progression.
(Variable density System)
(Gas rxn)

Constant Volume Systems:—

Concentration:— (c)

moles of solute / volume of solution.

for A,

$$C_A = \frac{N_A}{V}$$

$$N_A = C_A \cdot V$$

*** $$r_i = \frac{1}{V}\frac{dN_i}{dt}$$ general form of rate eqn

$$N_i = C_i V$$

$$r_i = \frac{1}{V}\frac{d}{dt}(C_i \cdot V)$$

$$= \frac{1}{V}\left(V\frac{dC_i}{dt} + C_i\frac{dV}{dt}\right)$$

for constant volume system.

Initial concentration

$$C_{A_0} = \frac{N_{A_0}}{V_0}$$

Final Concentration

$$C_A = \frac{N_A}{V}$$

for constant vol. system.

$V = V_0$

$dV = 0$

$$r_i = \frac{1}{V}\left[V \cdot \frac{dC_i}{dt}\right]$$

$$\boxed{r_i = \frac{dC_i}{dt}}$$

for reactant A

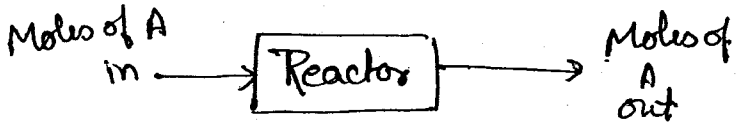
$$\boxed{-r_A = -\frac{dC_A}{dt}}$$

for pdt P

$$\boxed{r_P = \frac{dC_P}{dt}}$$

Conversion (X) :—

$$X_A = \frac{\text{Moles of A reacted}}{\text{Initial moles of A fed to the system.}}$$



M.B of A

Moles of A In = Moles of A out + Moles of A reacted.

$N_{A0} = N_A$ + Moles of A reacted.

Moles of A reacted $= N_{A0} - N_A$

** $\boxed{X_A = \frac{N_{A0} - N_A}{N_{A0}}}$

** $\boxed{N_A = N_{A0}(1 - X_A)}$

Valid for both constant & variable volume systems.

$$\frac{N_A}{V} = \frac{N_{A0}(1-X_A)}{V}$$

for <u>const. vol.</u> Rxn System, $V = V_0$.

$$C_A = \frac{N_{A0}(1-X_A)}{V_0} = C_{A0}(1-X_A)$$

Kinetic Equation for different order of rxn :—

⇒ for zero order rxn,

$$A \xrightarrow[n=0]{k} P$$

$$-r_A = -\frac{dC_A}{dt} = kC_A^{n=0} = k$$

$$\int_{C_{A0}}^{C_A} -dC_A = \int_0^t k\,dt$$

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

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

$$C_{A0} X_A = kt$$

$$X_A = \frac{k}{C_{A0}} \cdot t$$

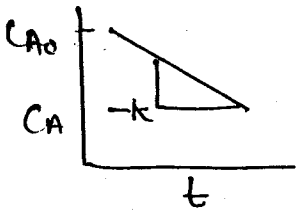
$$\frac{\partial X_A}{\partial t} = \frac{k}{C_{A0}}$$

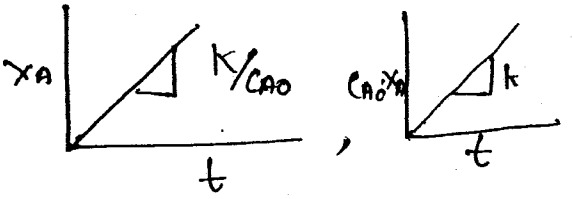
conversion depends over initial concentration

$C_A = C_{A0} - kt$

$y = c + mx$

$y = mx$





⇒ <u>for first order rxn,</u>

$$A \xrightarrow[n=1]{k} P$$

$$-r_A = -\frac{dC_A}{dt} = kC_A$$

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A} = \int_0^t k\,dt$$

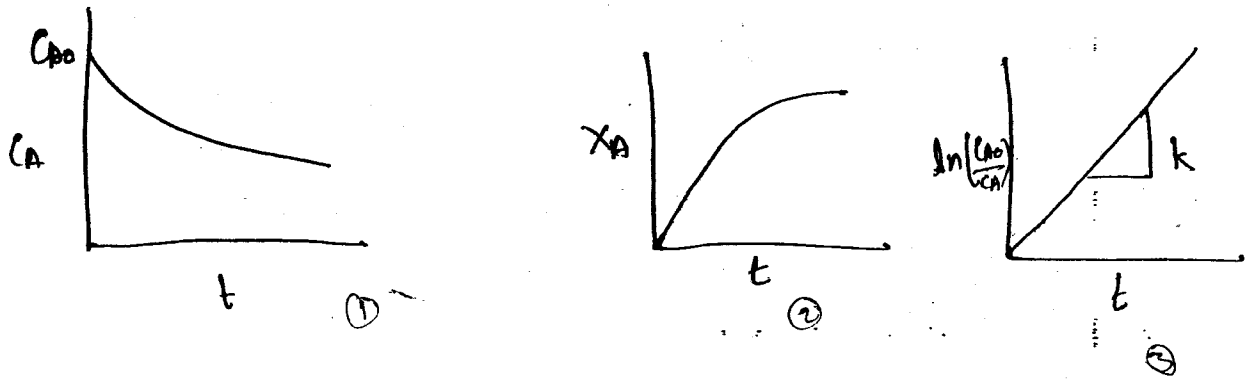
$$\ln(C_{A0}/C_A) = kt$$

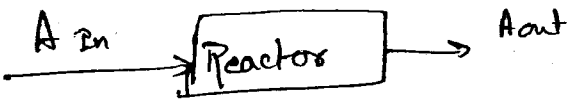
② $$\ln\left(\frac{C_{A0}}{C_A}\right) = kt$$

$$\frac{C_{A0}}{C_A} = e^{kt}$$

① $$\boxed{C_A = C_{A0}e^{-kt}}$$

② $$\boxed{X_A = 1 - e^{-kt}}$$





$$X_A = 1 - e^{-kt}$$

$$\boxed{\frac{\partial X_A}{\partial t} = (-k)e^{-kt}}$$

Conversion is independent of initial concentration.

For unimolecular second order Rxn :-

$$2A \xrightarrow[n=2]{k} B$$

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

$$\int_{C_{A0}}^{C_A} -\frac{dC_A}{C_A^2} = \int_0^t k\,dt$$

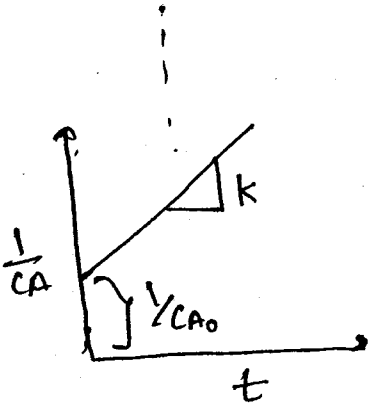
$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = kt}$$

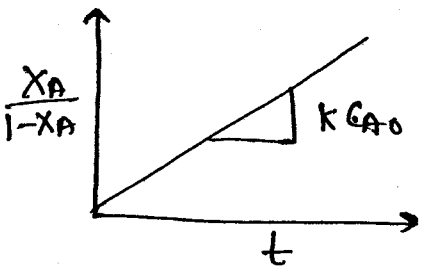
in terms of conversion.

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

$$\boxed{\frac{X_A}{1 - X_A} = C_{A0}kt}$$

$$X_A = \frac{C_{A0}kt}{1 + C_{A0}kt}$$





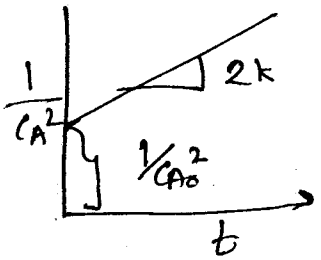
For third order rxn :—

$$A \xrightarrow[n=3]{k} B$$

$$-r_A = \frac{-dC_A}{dt} = kC_A^3$$

$$\int_{C_{A0}}^{C_A} -\frac{dC_A}{C_A^3} = \int_0^t k\,dt$$

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



for $n=2 \Rightarrow 1/C_A - 1/C_{A0} = kt$

for $n=3 \Rightarrow 1/C_A^2 - 1/C_{A0}^2 = 2kt$

for n^{th} order rxn, $\boxed{\frac{1}{C_A^{n-1}} - \frac{1}{C_{A0}^{n-1}} = (n-1)kt}$ for all order of rxns this eqn is

$$-r_A = \frac{-dC_A}{dt} = kC_A^n$$

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A^n} = \int_0^t k\,dt$$

$$-\left\{\frac{1}{(1-n)\,C_A^{n-1}}\right\}_{C_{A0}}^{C_A} = kt$$

$$\boxed{\frac{1}{C_A^{n-1}} - \frac{1}{C_{A0}^{n-1}} = (n-1)kt}$$

Q) For the rxn, $A \rightarrow P$. The rate constant is $k = 3.5$ mol/l sec. Find out the conv. after 15 sec, if C_{A0} was 10 mol/l.

$$C_{A0} X_A = kt$$

$$X_A = \frac{3.5 \times 15}{10} \frac{\text{mol}}{\text{l·sec}} \frac{\text{sec}}{\text{mol}} \cdot \text{l}$$

$$= 5.25 \text{ (}>1\text{)}$$

Value is coming but it represent that our rxn has been completed earlier.

after 15 sec $\boxed{X_A = 100\%}$

time at which rxn was complete

$$1 = \frac{3.5 \times t}{10}$$

$$t = 2.857 \text{ sec}$$

Q) for the liquid phase first order rxn, the conv. was 30% at the end of 20 min and 60% at the end of 35 mins... what will be the initial conc^n of A. and rate const A in (hr^{-1})

$$X_A = 1 - e^{-kt}$$

$$0.30 = 1 - e^{-k\,20/60}$$

$$e^{-k\,1/3} = 0.7$$

$K = 1.07 \cdot hr^{-1}$

Mole Balance

$$aA + bB \longrightarrow cC + dD$$

$$\text{Moles of B reacted} = \frac{\text{Moles of B reacted}}{\text{Moles of A reacted}} \times \text{Moles of A reacted.}$$

$$\boxed{\text{Moles of B reacted} = \frac{b}{a} \times \text{Moles of A Reacted}}$$

$$\boxed{\text{Moles of B unconverted (remaining)} = \text{Moles of B initially fed} - \text{Moles of B reacted.}}$$

$$N_B = N_{B0} - b/a \text{ Moles of A reacted}$$

$$\boxed{N_B = N_{B0} - b/a\, N_{A0} \cdot X_A}$$

$$\text{Moles of C in outlet} = \text{Moles of C initially} + \left\{\frac{c}{a} N_{A0} \cdot X_A\right\} \text{ Moles of C formed.}$$

$$\boxed{N_C = N_{C0} + \frac{c}{a} N_{A0} \cdot X_A}$$

$$\boxed{N_D = N_{D0} + \frac{d}{a} N_{A0} \cdot X_A}$$

$$\boxed{N_A = N_{A0} - N_{A0} \cdot X_A}$$

$$\frac{N_A}{V} = \frac{N_{A0} - N_{A0} \cdot X_A}{V}$$

$$\frac{N_B}{V} = \frac{N_{B0} - b/a\, N_{A0} \cdot X_A}{V}$$

$$N_C = N_{C0} + c/a\, N_{A0} \cdot X_A$$

$$\frac{N_D}{V} = \frac{N_{D0} + c/a\, N_{A0} X_A}{V}$$

for constant $V = V_0$

$$C_A = \frac{N_{A0} - N_{A0} \cdot X_A}{V} \Rightarrow C_A = C_{A0} - C_{A0} \cdot X_A$$

$$C_B = \frac{N_{B0} - \frac{b}{a} N_{A0} \cdot X_A}{V} \Rightarrow C_B = C_{B0} - b/a\, C_{A0} \cdot X_A$$

$$C_C = \frac{N_{C0} + c/a\, N_{A0} \cdot X_A}{V} \Rightarrow C_C = C_{C0} + c/a\, C_{A0} \cdot X_A$$

$$C_D = \frac{N_{D0} + d/a\, N_{A0} \cdot X_A}{V} \Rightarrow C_D = C_{D0} + d/a\, C_{A0} \cdot X_A$$

Constant Volume Rxn System:-

$$aA + bB \longrightarrow cC + dD$$
$$X_A \quad X_B$$

Moles of B reacted $= b/a$ Moles of A reacted

$$N_{B0} \cdot X_B = \frac{b}{a} N_{A0} \cdot X_A$$

$$\frac{N_{A0} \cdot X_A}{a} = \frac{N_{B0} \cdot X_B}{b}$$

Q) For the rxn $2A + 3B \longrightarrow 5C$. $C_{A0} = 100$, final Conc $C_C = 45$.
$C_{B0} = 100$,
$C_{C0} = 0$

$X_A, C_A, C_B, X_B = ?$

$$45 = C_{C0} + 5/2 \times 100\, X_A$$
$$45 = C_{C0} + 250\, X_A$$
$$C_A = 100 - 3/2 \times 100 \cdot X_A = 100 - 150 X_A$$

$45 = 0 + 250 X_A$

$X_A = 0.18$

$C_B = 100 - 250 \times X_A$

$C_B = 73$

$C_A = 100(1 - X_A)$

$= 82$

$X_B = \frac{N_{A0} \cdot X_A}{N_{B0}} \cdot \frac{b}{a}$

$= \frac{C_{A0}}{C_{B0}} \cdot X_A \cdot \frac{b}{a}$ for const vol System.

$= 0.27$

$1000 cm^3 = 1 m^3$

$1 m^3 = \frac{1}{1000}$

Sep 17, 14

Q) For a certain rxn, rate exp is given as $-r_A = 0.005 C_A^2 \frac{mol}{cm^3 min}$. If conc is to be expressed is mol/l & time in hrs, then what will be the units & value of rate constant.

$(time)^{-1}(conc)^{-n}$: $-r_A = 0.005 C_A^2$ mol/cm³ min.

$min^{-1} \left(\frac{mol}{cm^3}\right)^{-1}$ $= 0.005 \frac{mol}{cm^3} \times \frac{1 cm^3}{10^{-6} m^3} \times \frac{1 m^3}{1 l} \times \frac{60 min}{1 hr}$

$= 0.005 \frac{cm^3}{mol \cdot min}$

$= 0.005 \frac{cm^3}{mol \cdot min} \times \frac{10^6 m^3}{1 m^3} \times \frac{1 l}{10^3 cm^3} \times \frac{60 min}{1 hr}$

$= 63 \times 10^{-4} \frac{l}{mol\, hr}$

Kinetic Equation for Bimolecular second order rxn :—

$$A + B \xrightarrow[n=2]{k} P$$

$$-r_A = -\frac{dC_A}{dt} = kC_AC_B$$

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

$$C_B = C_{B0} - \frac{b}{a}C_{A0}X_A$$

$$-\frac{d}{dt}\{C_{A0}(1-X_A)\} = kC_{A0}(1-X_A)\left(C_{B0} - \frac{b}{a}C_{A0}X_A\right)$$

$$\Rightarrow C_{A0}\cdot\frac{dX_A}{dt} = kC_{A0}(1-X_A)\left(C_{B0} - \frac{b}{a}C_{A0}\cdot X_A\right)$$

$$\Rightarrow \frac{dX_A}{dt} = k(1-X_A)\left(C_{B0} - \frac{b}{a}C_{A0}\cdot X_A\right)$$

$$= k(1-X_A)C_{A0}\left(\frac{C_{B0}}{C_{A0}} - 1\cdot X_A\right) \quad \because \frac{b}{a} = \frac{1}{1} = 1$$

$$\boxed{\frac{dX_A}{dt} = kC_{A0}(1-X_A)(M-X_A)} \quad ; M = \frac{C_{B0}}{C_{A0}}$$

$$\int_0^{X_A}\frac{dX_A}{(1-X_A)(M-X_A)} = \int_0^t kC_{A0}\,dt$$

Partial fract

$$\frac{A}{(1-X_A)} + \frac{B}{(M-X_A)}$$

$$A(M-X_A) + B(1-X_A) = 1$$

$$MA + B = 1$$

$$-A - B = 0$$

$$-A = B$$

$$(M-1)A = 1$$

$$A = \frac{1}{(M-1)}$$

$$B = -\frac{1}{(M-1)}$$

$$\int_0^{X_A}\left[\frac{1}{(M-1)(1-X_A)} - \frac{1}{(M-1)(M-X_A)}\right]dX_A = \int_0^t kC_{A0}\,dt$$

$$\frac{1}{(M-1)}\left\{\int_0^{X_A}\frac{dX_A}{(1-X_A)} - \int_0^{X_A}\frac{dX_A}{(M-X_A)}\right\} = kC_{A0}t$$

$$\frac{1}{(M-1)}\left\{-\ln(1-X_A)\Big|_0^{X_A} - \left[-\ln(M-X_A)\Big|_0^{X_A}\right]\right\} = kC_{A0}t$$

$$-\left[\ln(1-X_A) - \ln(1-0)\right] + \left[\ln(M-X_A) - \ln(M-0)\right] = (M-1)kC_{A0}t$$

$$-\ln(1-X_A) + \ln(M-X_A) - \ln M = kC_{A0}t\,(M-1)$$

$$\{\ln A - \ln B = \ln(A/B)\}$$

$$\Rightarrow \boxed{\ln\left\{\frac{M-X_A}{M(1-X_A)}\right\} = (M-1)\,kC_{A0}t} \qquad M \neq 1$$

Case I It is not valid for $M=1$, $C_{A0} = C_{B0}$

$N_{A0} = N_{B0}$ equimolar A & B

Not valid for equimolar A & B,
valid only for $N_{A0} \neq N_{B0}$.

Case II Kinetic Eqn for equimolar A & B.

$$A + B \xrightarrow[n=2]{k} P$$

$$-r_A = \frac{-dC_A}{dt} = kC_AC_B = kC_A^2$$

for equimolar A&B $\boxed{C_A = C_B}$

$$N_B = N_{B0} - b/a\, N_{A0} \cdot X_A$$
$$C_B = C_{B0} - b/a\, C_{A0} X_A$$
$$= C_{B0} - C_{A0} \cdot X_A$$
$$\because N_{A0} = N_{B0}$$
$$\therefore C_{A0} = C_{B0}$$
$$C_B = C_{A0} - C_{A0} \cdot X_A$$
$$= C_{A0}(1-X_A)$$
$$C_B = C_A$$

Q1. For the rxn $A \rightarrow B$. The rate exp is given as $-r_A = kC_A^{1/2}$, $\frac{mol}{l \cdot s}$

if $C_{A0} = 100 mol/l$. find out the C_A after $t = 10$ sec, $k = 3.2 \frac{mol^{1/2}}{sec\, l^{1/2}}$

$$-r_A = kC_A^{1/2}\ mol/l \cdot sec$$

Q2. For a rxn $A \rightarrow P$, the rate const $k = 2.95 \times 10^{-3}\ sec^{-1}$. What % of A remains after 150 sec.

Soln

$$X_A = 1 - e^{-kt}$$

$\therefore$ 25.75%.

1)
Soln

$$-\frac{dC_A}{dt} = kC_A^{1/2}$$

$C_{A_0} = 25 \text{ mol/l}$.

$$\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A^{1/2}} = \int_0^t k\,dt$$

$$-\left[\frac{C_A^{1/2}}{1/2}\right]_{C_{A_0}}^{C_A} = kt$$

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

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

$$= 100^{1/2} - \frac{1 \times 10}{2} = 10.5$$

$$C_A^{1/2} = 5$$

$$C_A = 25$$

Q.) For the rxn $A \xrightarrow{k} P$, on doubling the reactant concn A. The rate eqn gets tripled. What is n?

$$-r_A = kC_A^n$$

$$-3r_A = k(2C_A)^n$$

$$\frac{1}{3} = \left(\frac{C_A}{2C_A}\right)^n$$

$$\frac{1}{3} = \left(\frac{1}{2}\right)^n$$

$$2^n = 3$$

$$n \ln 2 = \ln 3$$

$$n = 1.5849$$

$$= 1.6$$

To find out the order of rxn :-

* Initial rate of rxn :-

$$A + B \longrightarrow P$$

$$-r_A = k C_A^{\alpha} C_B^{\beta}$$

$$(-r_A)_0 = k C_{A_0}^{\alpha} C_{B_0}^{\beta}$$

Q) The decomposition of N_2O_5 is given as $2N_2O_5 \rightarrow 4NO_2 + O_2$ at initial conc^n of $N_2O_5 = 3.15\ M$, the initial rate of rxn $= 5.45 \times 10^{-5} \frac{M}{s}$

at the initial conc^n of $N_2O_5 = 1.78M$, " " " " " $= 1.35 \times 10^{-5} \frac{M}{s}$

Find out the rate const$^{\text{n}}$?

$$5.45 \times 10^{-5} = -k(C_{A_0})^n$$

$$1.35 \times 10^{-5} = -k (C_{A_0})^n$$

$$\frac{5.45 \times 10^{-5}}{1.35 \times 10^{-5}} = k \left(\frac{3.15}{1.78}\right)^n$$

$$4.0370 = (3.15/1.78)^n \qquad 2.44$$

$$n = 2.44$$

$$3.45 \times 10^{-5} = -k (C_{A_0})^n \qquad \frac{M}{s} \cdot \frac{1}{M^{2.44}}$$

$$k = 3.315 \times 10^{-6} \frac{M^{-1.44}}{s}$$

$$\boxed{k = 3.31 \times 10^{-6} \frac{1}{s M^{1.5}}}$$

* Half Lyf Method :- $(t_{1/2})$ in case of two molecule lyke $A + B \rightarrow C + D$ then $t_{1/2}$ depends upon the rate order of limiting reactant

Half lyf of the rxn

$A \rightarrow B$

$C_{A_0} \rightarrow \frac{C_{A_0}}{2}$, 50% conversion

$A + B \rightarrow C$

B → limiting reactant

50% const'

$$(n-1)kt = C_A^{1-n} - C_{A0}^{1-n}$$

at $t_{1/2}$, $C_A = C_{A0}/2$

$$(n-1)k t_{1/2} = \left(\frac{C_{A0}}{2}\right)^{1-n} - (C_{A0})^{1-n}$$

$$(n-1)k t_{1/2} = \left(\frac{2}{C_{A0}}\right)^{n-1} - \left(\frac{1}{C_{A0}}\right)^{n-1}$$

$$\boxed{t_{1/2} = \frac{2^{n-1}-1}{k(n-1)C_{A0}^{n-1}}}$$

Valid for all order of rxn except first order

$$t_{1/2} \propto \frac{1}{C_{A0}^{n-1}}$$

$$\boxed{t_{1/2} \propto C_{A0}^{1-n}}$$

for 1st order rxn,

$$\ln\left(\frac{C_{A0}}{C_A}\right) = kt$$

at $t_{1/2}$, $C_A = C_{A0}/2$

$$\ln(2) = k t_{1/2}$$

$$\boxed{t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}}$$ for 1st order

for zeroth order rxn, $n=0$

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

at $t_{1/2}$ $C_A = C_{A0}/2$

$$C_{A0} - \frac{C_{A0}}{2} = k t_{1/2}$$

$$\boxed{t_{1/2} = \frac{C_{A0}}{2k}}$$ for 0th order

$$\boxed{t_{1/2} = \frac{1}{\quad}}$$ for second order

as $n \uparrow$, $t_{1/2} \downarrow$ for increament in C_{A_0}.

Q→ The half lyf for a first order rxn is 30sec. Find out the 'K' in min^{-1}

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

$$= \frac{0.693}{30\,sec} \quad \frac{60\,sec}{min}$$

$$t_{1/2} = 1.386\ min^{-1}$$

Q.) Find the conv^n after 1 hr, in a batch reactor. for the rxn A → R and rate eqn $-r_A = 3C_A^{1/2}$ mol/l.hr., $C_{A_0} = 10$ mol/l.

$n = 1/2$

$K = 3\ \frac{mol^{1/2}}{l^{1/2}\,hr}$ $\qquad \frac{mol}{l.hr} \cdot \frac{l^{1/2}}{mol^{1/2}}$

$C_{A_0} = 1$ mol/l.

$$t = \frac{2}{3(1/2-1)\,1}\left[C_{A_0}^{1/2-1} - C_A^{1/2-1}\right]$$

$$= \frac{-0.242}{-1.5}$$

$$= 10^{1/2} - \frac{3 \times 1}{2} \times t_{1/2} = 1.662$$

$$C_A^{1/2} = 2.763$$

$$C_A = C_{A_0}(1 - X_A)$$

$$0.25 = 1 - X_A$$

$$X_A = 0.7236$$

$$= 72.36\%$$

* Fractional Lyf Method :—

$$(n-1)kt = \frac{1}{C_A^{n-1}} - \frac{1}{C_{A0}^{n-1}}$$

at t_F $\quad C_A = F \cdot C_{A0}$.

$$(n-1)kt_F = \frac{1}{(F C_{A0})^{n-1}} - \frac{1}{(C_{A0})^{n-1}}$$

$$\boxed{t_F = \frac{(F^{1-n} - 1)}{(n-1)k} C_{A0}^{1-n}}$$

Sep 19, 14

Based on no. of rate eqn

Single Rxn System

$A + B \rightarrow P$

$-r_A = kC_A C_B$

$-r_B = kC_A C_B$

$r_P = kC_A C_B$

Design variable – conc^n of reactant

Multiple Rxn System

→ Where more than 1 rxn proceeds.

→ more than one rate eqn are present (exist)

Design Variable – pdt distribution

↳ Series

↳ parallel

↳ Complex (series-parallel)

Series

$$A \xrightarrow{k_1} P \xrightarrow{k_2} U$$

$-r_A = k_1 C_A$

$r_P = k_1 C_A - k_2 C_P$

$r_U = k_2 C_P$.

Parallel

$$A \xrightarrow{k_1} B$$
$$\quad \xrightarrow{k_2} C$$

$-r_A = k_1 C_A + k_2 C_A$

$r_B = k_1 C_A$ —

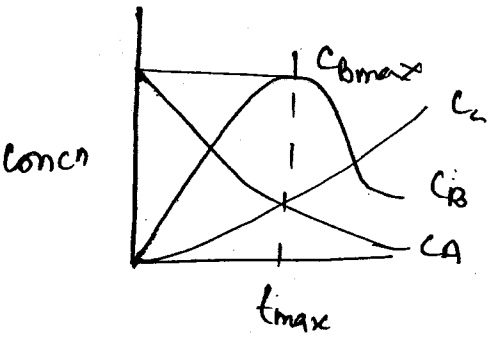
$r_C = k_2 C_A$

$$A \rightarrow P \rightarrow R$$
$$\searrow S$$

Series Rxn

$$A \xrightarrow[n_1=1]{k_1} B \xrightarrow[n_2=1]{k_2} C$$

(desired) (undesired)



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

$$C_A = C_{A_0} e^{-kt}$$

$$r_B = \frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_A$$

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

$$\frac{dy}{dx} + Py = Q(x)$$

$$y \cdot IF = \int Q \cdot IF + z$$

$$IF = e^{\int P dx}$$

$$IF = e^{\int k_2 dt} = e^{k_2 t}$$

$$C_B \cdot IF = \int Q \cdot IF + z$$

$$C_B e^{k_2 t} = \int (k_1 C_{A_0} e^{-k_1 t}) \cdot e^{k_2 t} dt + z$$

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

$$C_B e^{k_2 t} = k_1 C_{A_0} \cdot \frac{e^{(k_2 - k_1) t}}{(k_2 - k_1)} + z$$

Using B.C, $t=0, C_B=0$

$$\Rightarrow Z = \frac{-k_1 C_{A0}}{(k_2-k_1)}$$

$$C_B e^{k_2 t} = \frac{k_1 C_{A0} e^{(k_2-k_1)t}}{(k_2-k_1)} - \frac{k_1 C_{A0}}{(k_2-k_1)}$$

$$C_B \cdot e^{k_2 t} = \frac{k_1 C_{A0}}{(k_2-k_1)} \left[e^{(k_2-k_1)t} - 1 \right]$$

$$\boxed{C_B = \frac{k_1 C_{A0}}{(k_2-k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right]}$$

if $k_1 t < k_2 t$

at t_{max}, $k_1 t_{max} = k_2 t_{max}$.

after t_{max}, $k_1 t > k_2 t$

for $C_{B_{max}}$, $\frac{\partial C_B}{\partial t} = 0$

$$\frac{\partial}{\partial t} \left[\frac{k_1 C_{A0}}{(k_2-k_1)} \left\{ e^{-k_1 t} - e^{-k_2 t} \right\} \right] = 0$$

$$\frac{k_1 C_{A0}}{(k_2-k_1)} \left\{ -k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right\} = 0$$

$$k_1 e^{-k_1 t_{max}} = k_2 e^{-k_2 t_{max}} \quad ; \; t_{max} = t_{opt}.$$

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

$e^{t_{max}} \{k_1 -$

$$\ln k_1 + (-k_1 t_{max}) = \ln k_2 + (-k_2 t_{max})$$

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

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

$$\boxed{\frac{C_{Bmax}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2-k_1}}}$$

$A \longrightarrow B \longrightarrow C$

$$N_{A0} = N_A + N_B + N_C$$

$$N_C = N_{A0} - N_B - N_A$$

$$r_C = \frac{dC_C}{dt} = k_2 C_B$$

$$C_C = C_{A0} - C_B - C_A$$

$$C_C = C_{A0} - \frac{k_1 C_{A0}}{(k_2-k_1)} \left\{ e^{-k_1 t} - e^{-k_2 t} \right\} - C_{A0} e^{-k_1 t}$$

$$C_C = C_{A0} \left[1 - \frac{k_1}{(k_2-k_1)} e^{-k_1 t} + \frac{k_1 e^{-k_2 t}}{k_2-k_1} - e^{-k_1 t} \right]$$

$$\Rightarrow C_C = C_{A0} \left[1 - \left\{ \frac{k_1}{k_2-k_1} + 1 \right\} e^{-k_1 t} + \frac{k_1 e^{-k_2 t}}{k_2-k_1} \right]$$

$$\boxed{C_C = C_{A0} \left[1 - \frac{k_2}{k_2-k_1} e^{-k_1 t} + \frac{k_1}{k_2-k_1} e^{-k_2 t} \right]}$$

$$C_B = \frac{k_1 C_{A0}}{(k_2-k_1)} \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

$$C_A = C_{A0} e^{-k_1 t}$$

$$A_1 \xrightarrow[1]{k_1} B \xrightarrow[1]{k_2} C$$

$$r_B = \frac{dC_B}{dt} = \underbrace{k_1 C_A}_{\text{formation of B}} - \underbrace{k_2 C_B}_{\text{disapp. of B.}} \geq 0$$

Case-I if $k_1 \gg k_2$

$$C_c = C_{A0}\left[1 + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right]$$

$$k_2 - k_1 \simeq -k_1$$

$$\boxed{C_c = C_{A0}\left[1 - e^{-k_2 t}\right]}$$

$$A \xrightarrow[n=1]{k_2} C$$

Case-II if $k_2 \gg k_1$

$$C_c = C_{A0}\left[1 \mp \frac{k_2}{k_2} e^{-k_1 t}\right]$$

$$\boxed{C_c = C_{A0}\left[1 - e^{-k_1 t}\right]}$$

$$A \xrightarrow[n=1]{k_1} C$$

Q> In a gaseous rxn, the tym for half change for the various initial partial press. of the reactant is given by

p_{A0} (torr)	200	300	400
$t_{1/2}$ (min)	150	98.7	74.2

n_2 ?

$$t_{1/2} \propto C_{A0}^{1-n}$$

$$C_{A0} = \frac{p_{A0}}{RT}$$

$$\frac{150}{98.7} = \left(\frac{200}{300}\right)^{1-n}$$

$$\ln 1.5197 = .10666\,(1-n)$$

$$0.41855 = (1-n)(-0.405465)$$

$$n = 2.032$$

Q:) $A \xrightarrow[n_1 = 1]{k_1} B \xrightarrow[n_2 = 0]{k_2} C$

t_{max}.

$C_{A0} = 1$ mol/l.

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

$\Rightarrow C_A = C_{A0} e^{-k_1 t}$

$r_B = \frac{dC_B}{dt} = k_1 C_A - k_2$

$\frac{dC_B}{dt} = k_1 C_A - k_2$

$\frac{dC_B}{dt} = k_1 C_{A0} e^{-k_1 t} - k_2 = 0$

$k_1 C_{A0} e^{-k_1 t} = k_2$

$e^{-k_1 t} = k_2/k_1$

$-k_1 t_{max} = \ln \frac{k_2}{k_1}$

$t_{max} = -\frac{1}{k_1} \ln \frac{k_2}{k_1}$

$= \frac{1}{k_1} \ln \left(\frac{k_1}{k_2}\right)$

a) $\frac{1}{k_1} \ln \left(\frac{k_1}{k_2}\right)$

b) $\frac{1}{k_2 - k_1} \ln \frac{k_2}{k_1}$

c) $\frac{1}{k_2} \ln \left(\frac{k_2}{k_1}\right)$

d) $\frac{1}{k_2} \ln \left[\frac{k_1}{k_2}\right)$

QQ $A \rightarrow B$, $C_A = 2$ mol/l after t = 30 min, if $C_{A0} = 8$ mol/l.

$k = ?$ in $\frac{l}{Vol.s}$.

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

$$\frac{1}{2} - \frac{1}{8} = k \times 30 \times 60$$

$$\boxed{k = \frac{1}{4800} = 2.083 \times 10^{-4} \frac{l}{mol.s}}$$

Parallel Rxn

$A \xrightarrow[n=1]{k_1} R$ (desired)

$A \xrightarrow[n=1]{k_2} S$

Instantaneous Selectivity

$S = \frac{\text{rxn rate of desired}}{\text{rxn rate of undesired pdt.}}$

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

$$\int_{C_{A0}}^{C_A} -dC_A = \int_0^t (k_1 + k_2) C_A dt$$

$$\boxed{\ln\left(\frac{C_{A0}}{C_A}\right) = (k_1 + k_2)\, t}$$

$$C_A = C_{A0} e^{-(k_1 + k_2)t}$$

$\frac{\text{moles of desired pdt}}{\text{Moles of undesired pdt}}$ → Selectivity (S)

Yield (Φ)

$$S = \frac{r_R}{r_S} = \frac{k_1 C_A}{k_2 C_A}$$

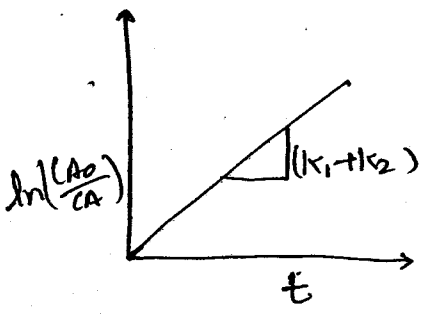
$$\frac{r_R}{r_S} = k_1 / k_2$$

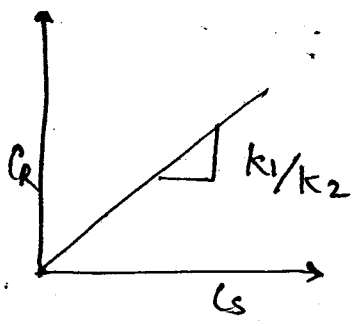
$r_R = dC_R/dt$

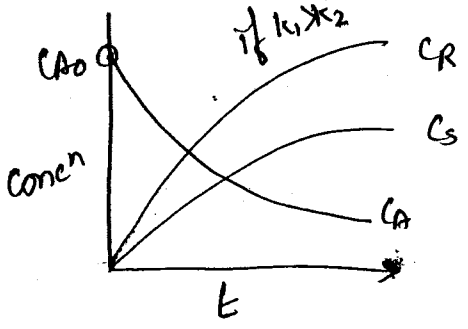
$r_S = dC_S/dt$ $\Rightarrow \frac{dC_R}{dC_S} = k_1/k_2$

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

$$\boxed{r_D = \frac{k_1}{k_2} C_S}$$







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

$$\frac{dC_R}{dt} = k_1 C_{A0} e^{-(k_1+k_2)t}$$

$$C_R = \frac{k_1 C_{A0} e^{-(k_1+k_2)t}}{-(k_1+k_2)} + C$$

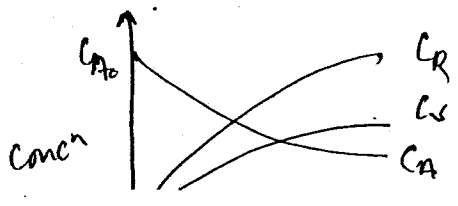
at $t=0$, $C_R=0$ $\Rightarrow$ $C = k_1 C_{A0}/k_1+k_2$

$$C_R = \frac{k_1 C_{A0} e^{-(k_1+k_2)t}}{-(k_1+k_2)} + \frac{k_1 C_{A0}}{k_1+k_2}$$

$$\boxed{C_R = \frac{k_1 C_{A0}}{(k_1+k_2)}\left[1 - e^{-(k_1+k_2)t}\right]}$$

Ily,

$$\boxed{C_S = \frac{k_2 C_{A0}}{(k_1+k_2)}\left[1 - e^{-(k_1+k_2)t}\right]}$$



* Reversible Rxn :-

$$R \rightleftharpoons P$$

Equilibrium stati achieve

$$r_{rxn} = 0$$

rxn rate = rate of forward rxn − rate of backward rxn

$$\boxed{-r_R = k_1 C_R - k_2 C_P}$$

$$\boxed{r_P = k_1 C_R - k_2 C_P}$$

- - - - - -

for Reversible Rxn

$$\boxed{X_{eq} = 1 - \frac{C_{Req}}{C_{R0}}}$$

for irreversible Rxn

$$A \longrightarrow R$$

$$C_A = 0$$

$$X_A = 1 - C_A/C_{A0}$$

$$X_A = 1$$

- - - - - - -

at equilibrium, $-r_R = 0$

$$k_1 C_{Re} - k_2 C_{Pe} = 0$$

$$k_1 C_{R0}(1 - X_e) - k_2 C_{R0} \cdot X_e = 0$$

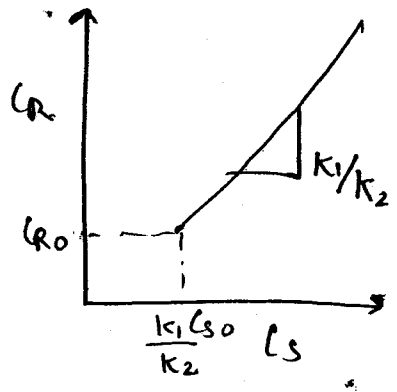
equilibrium constant $\boxed{K_e = \frac{k_1}{k_2} = \frac{X_e}{1 - X_e}}$

for parallel

$$\int_{C_{R0}}^{C_R} dC_R = \int_{C_{S0}}^{C_S} \frac{k_1}{k_2} dC_S$$

$$C_R - C_{R0} = k_1/k_2 (C_S - C_{S0})$$

$$C_R = \frac{k_1}{k_2} C_S + \left(C_{R0} - \frac{k_1}{k_2} C_{S0}\right)$$



Q.) for the liquid phase rxn, $A \xrightarrow[n_1=1]{k_1} R \xrightarrow[n_2=1]{k_2} S$. find out t_{max}?

$C_{R_{max}} = ?$ If $k_1 = k_2$.

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

$$C_A = C_{A0} e^{-k_1 t}$$

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

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} e^{-k_1 t}$$

$$\text{if} = e^{\int k_2 dt} = e^{k_1 t}$$

$$C_R e^{k_2 t} = \int k_1 C_{A0} e^{-k_1 t} e^{k_2 t} dt + C$$

$$C_R \cdot e^{k_2 t} = \int k_1 C_{A0} e^{(k_2 - k_1) t} dt + C \qquad \because k_2 = k_1$$

$$= \int k_1 C_{A0} dt + C$$

$$C_R \cdot e^{k_2 t} = k_1 C_{A0} t + C$$

at $t = 0$, $C_R = 0$

$\Rightarrow C = 0$

$$C_R \cdot e^{k_2 t} = k_1 C_{A0} \cdot t$$

$$\boxed{C_R = k_1 C_{A0} t \, e^{-k_2 t}}$$

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

$$\Rightarrow \frac{d}{dt}\left(k_1 C_{A0} t e^{-k_2 t}\right) = 0$$

$$\Rightarrow t_m(-k_2)e^{-k_2 t_m} + e^{-k_2 t_m} = 0$$

$$\Rightarrow t_m k_2 e^{-k_2 t_m} = e^{-k_2 t_m}$$

$$t_m = \frac{1}{k_2} = \frac{1}{k_1}$$

$$C_{R_{max}} = f(t_{max})$$

$$C_R = k_1 C_{A0} \cdot \frac{1}{k_1} \cdot e^{-k_2 t_m}$$

$$= C_{A0} \cdot e^{-1}.$$

2004.

Q.)

23

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

$$\frac{\frac{0.9}{1-0.9}}{\frac{0.45}{1-0.45}} = \frac{C_{A0} k t_1}{C_{A0} k t_2}$$

$$\frac{0.9}{0.1} \times \frac{0.55}{0.45} = \frac{t_1}{t_2}$$

$$t_1/t_2 = 11$$

2008

25.)

$$-\frac{r_R}{\delta} = -\frac{r_S}{\delta} = \frac{r_T}{t}$$

$$-\frac{r_R}{2} = -\frac{r_S}{1} = \frac{r_T}{1}$$

$$\frac{r_R}{2} = \frac{r_S}{1} = -\frac{r_T}{1}$$

$r_R = -2r_S = -2r_T$

26)

$$t_{1/2} \propto \frac{1}{\sqrt{C_{A_0}}}$$

$C_{A_0}^{1-n}$ $\qquad n-1 = 1/2$

$\qquad\qquad n = 1/2+1 = 3/2$

$$\frac{1}{C_{A_0}^{n-1}} = 1$$

* Variable Volume Rxn System :—

$$V = f(N)$$

$$\boxed{V = V_0 \left(\frac{P_0}{P}\right)\left(\frac{T}{T_0}\right)(1+\varepsilon_A X_A)}$$

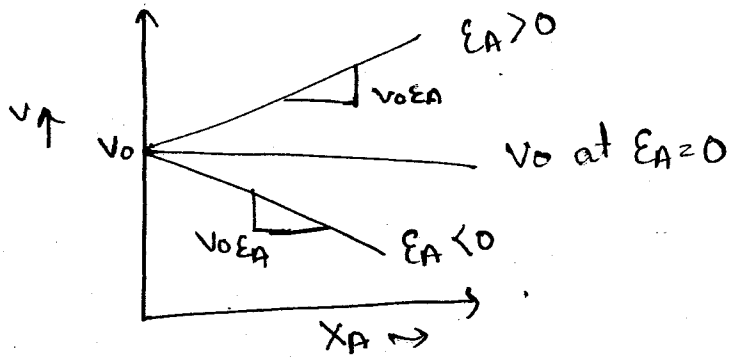
at const T & P

find out $\Rightarrow$ $\boxed{V = V_0 (1+\varepsilon_A X_A)}$

ε_A = Expansion factor

$$\boxed{\varepsilon_A = \frac{\text{Change in total moles after complete conversion}}{\text{total initial Moles of the system}}}$$

$$\boxed{\varepsilon_A = \frac{N_T|_{X_A=1} - N_T|_{X_A=0}}{N_T|_{X_A=0}}}$$



V < V₀ or V₀ < V

$\varepsilon_A > 0$ $\quad V > V_0$

$\varepsilon_A < 0$ $\quad V < V_0$

$\varepsilon_A = 0$ $\quad V = V_0$ constant vol. Rxn system.

$2A \longrightarrow 3C$

Pure feed

basis :- 1 mol feed

	$N_T\|_{x_A=0}$	$N_T\|_{x_A=1}$
A	1	0
C	0	3/2
	1	1.5

$\varepsilon_A = \frac{1.5-1}{1} = 0.5$

$\varepsilon_A = 0.5 > 0$

$N_C = N_{C0} + \frac{c}{a} N_{A0} \cdot x_A$

$= 0 + 3/2 \times 1 \times 1 =$

$3A \longrightarrow 2B$

	$N_T\|_{x_A=0}$	$N_T\|_{x_A=1}$
A	1	0
C	0	2/3
	1	2/3

$\varepsilon_A = \frac{2-3}{3} = -1/3$

$N_B = 0 + \frac{2}{3} \times 1 \times 1$

Q.) $2A + 3B \longrightarrow 4C$

$\varepsilon_A = ?$

feed contains

↳ Equimolar A & B

→ 40% A + 40% B + 20% C

→ 40% A + 40% B + 20% B

Basis = 1 mol feed

	$N_T\|_{x_A=0}$	$N_T\|_{x_A=1}$
A	0.5	0
B	0.5	−0.25
C	0	1
	1	0.75

$N_B = N_{B0} - \frac{b}{a} N_{A0} \cdot x_A$

$= 0.5 - 3/2 \times 0.5 \times 1$

$= -0.25$

$N_C = N_{C0} - \frac{c}{a} N_{A0} \cdot x_A$

$= 0 + \frac{4}{2} \times 0.5 \times 1$

$\varepsilon_A = \frac{0.75-1}{1}$

	$N_T\|_{X_A=0}$	$N_T\|_{X_A=1}$
A	0.4	0
B	0.4	−0.2
C	0.2	1
		0.8

$0.4 \mp \frac{3}{2} \cdot 0.4 \times 1$

$= 0.4 - 0.6 = -0.2$

$0.2 + \frac{4}{2} \times 0.4 \times 1$

$= 1$

$$\varepsilon_A = \frac{0.8 - 1}{1} = -0.2$$

	$N_T\|_{X_A=0}$	$N_T\|_{X_A=1}$
A	0.4	0
B	0.4	−0.2
C	0	0.8
D	0.2	0.2 inert

$$\frac{0.6 - 0.8}{0.8} = -0.25$$

$$\frac{0.8 - 1}{1} = -0.2$$

* ε_i = Conversion.
i

Sep 22, 14

Q> $2A + 3B \rightarrow 4C$ feed contains.

10 mol A | $\varepsilon_A = ?$

5 mol B | $\varepsilon_B = ?$

$$\varepsilon_A = \frac{N_T|_{X_A=1} - N_T|_{X_A=0}}{N_T|_{X_A=0}}$$

	$N_T\|_{X_A=0}$	$N_T\|_{X_A=1}$
A	10	0
B	5	−10 — 10 moles change
C	0	20
	15	10

$N_B = N_{B0} - \frac{b}{a} N_{A0} X_A$

$= -10$

$N_C = N_{C0} + \frac{c}{a} N_{A0} X_A$

$= 20$

$$\varepsilon_A = \frac{10 - 15}{15} = -\frac{5}{15} = -\frac{1}{3}$$

	$N_T\|_{X_B=0}$	$N_T\|_{X_B=1}$
A	10	20/3
B	5	0

$N_A = 10 - \frac{2a}{3} \times 8 \times 1$

$= 30 - 10 = 20$

$$\varepsilon_B = \frac{13-40}{15} = -0.11$$

$$V = V_0(1+\varepsilon_A X_A)$$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X_A)}{V_0(1+\varepsilon_A X_A)}$$

$$\boxed{C_A = \frac{C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}}$$

for const vol. system, $\varepsilon_A = 0$

$$\boxed{C_A = C_{A0}(1-X_A)}$$

$2A \rightarrow B$

$$-r_A = \left(-\frac{1}{V}\frac{dN_A}{dt}\right)$$

$$N_A = C_A \cdot V$$

$$-r_A = -\frac{1}{V}\frac{d(C_A \cdot V)}{dt}$$

$$-r_A = -\frac{1}{V}\left[C_A\frac{dV}{dt} + V\cdot\frac{dC_A}{dt}\right]$$

$$-r_A = \frac{-1}{V_0(1+\varepsilon_A X_A)} d\{N_{A0}(1-X_A)\}$$

$$-r_A = \frac{N_{A0}}{V_0(1+\varepsilon_A X_A)}\frac{dX_A}{dt}$$

$$\boxed{-r_A = \frac{C_{A0}\cdot dX_A}{(1+\varepsilon_A X_A)dt}}$$

for constant vol.

$$\varepsilon_A = 0$$

$$-r_A = -\frac{C_{A0}\cdot dX_A}{dt}$$

$$= \frac{d(C_{A0}\cdot X_A)}{dt}$$

Kinetic Eqn for different orders of rxn :—

» for zeroth order of rxn :-

$$A \xrightarrow[n=0]{k} P$$

$$-r_A = \frac{C_{A0}\, dX_A}{(1+\varepsilon_A X_A)dt} = K C_A^0 = K$$

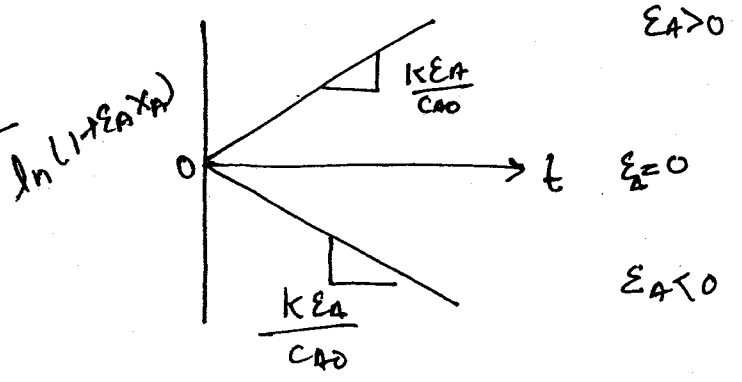
$$\int_0^{X_A} \frac{C_{A0}\, dX_A}{(1+\varepsilon_A X_A)} = \int_0^t k\, dt$$

$$C_{A0}\left[\frac{\ln(1+\varepsilon_A X_A)}{\varepsilon_A}\right]_0^{X_A} = Kt$$

$$\frac{C_{A0}}{\varepsilon_A}\cdot\left[\ln(1+\varepsilon_A X_A) - 0\right] = kt$$

$$\boxed{\ln(1+\varepsilon_A X_A) = \frac{kt\,\varepsilon_A}{C_{A0}}}$$

Levelspiel curve



» for first order rxn

$$A \xrightarrow[n=1]{K} P$$

$$-r_A = \frac{C_{A0}\, dX_A}{(1+\varepsilon_A X_A)\, dt} = K C_A$$

$$\frac{C_{A0}\cdot dX_A}{(1+\varepsilon_A X_A)dt} = \frac{k\,(C_{A0}(1-X_A))}{(1+\varepsilon_A X_A)}$$

$$C_A = \frac{C_{A0}(1-X_A)}{1+\varepsilon_A X_A}$$

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

$$\left[\frac{\ln(1-x_A)}{-1}\right]_0^{x_A} = kt$$

$$\boxed{-\ln(1-x_A) = kt}$$

for <u>const vol. system.</u>

$$\ln\left(\frac{C_{A0}}{C_A}\right) = kt$$

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

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

$$\boxed{-\ln(1-x_A) = kt}$$

» <u>for second order rxn</u>

$$A \xrightarrow[n=2]{k} P$$

$$-r_A = \frac{C_{A0}\,dx_A}{(1+\varepsilon_A x_A)\,dt} = kC_A^2$$

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

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

$$\frac{(1+\varepsilon_A)X_A}{(1-X_A)} + \varepsilon_A \ln(1-X_A) = kC_{A0}t$$

Design of Reactors:-

Q> for the rxn $A+B \rightarrow R+S$, $C_{A0}=100$, $C_{B0}=150$ and $C_A=25$ find out X_A, X_B, C_B.

$$C_A = C_{A0} - C_{A0} \cdot X_A$$

$$\frac{C_A}{C_{A0}} = (1-X_A)$$

$$0.25 = 1 - X_A$$

$$X_A = 0.75$$

$$C_B = C_{B0} - b/a\, C_{A0} \cdot X_A$$

$$= 150 - 1 \cdot 100 \cdot 0.75$$

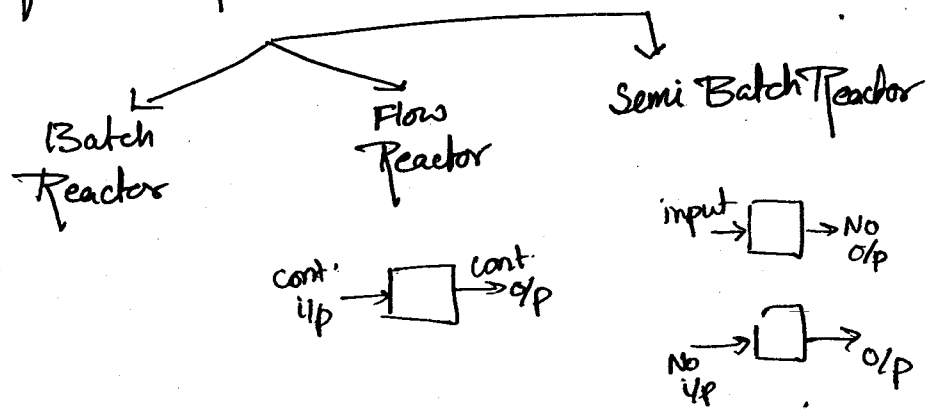
$$= 75$$

$$\frac{C_B}{C_{B0}} = (1-X_B)$$

$$\frac{75}{150} = (1-X_B)$$

$$X_B = 0.5$$

Design of Ideal Reactors :—



Design Eqn for Batch Reactor :—

Designing Parameter

→ Kinetics

→ Contacting Patterns

→ Performance Eqn / Design Eqn

* for batch Reactor, conversion is m.inp factor. is design parameter

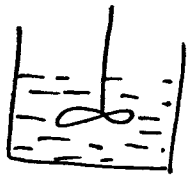
Mole Balance

Rate of Moles Accumulation = Rate of Moles Add − Rate of Moles loss.

Rate of Accumulation of A = Rate of Input of A + Rate of formation of A − Rate of out of A − Rate of dissp. of A

Molar Rate of Input of A = Molar Rate of output of A + Molar Rate of Accm of A + Molar rate of dissapp of A − Molar rate of formation of A

Batch Reactor



Uniform concn trough out the reactor at any time t.

$$\text{Rate of A in} = \text{Rate of A out} + \text{Rate of A accum.} + \text{Rate of A disap.} - \text{Rate of A form.}$$

$$0 = 0 + \frac{dN_A}{dt} + (-r_A)\cdot V - 0$$

$$-\frac{dN_A}{dt} = (-r_A)\cdot V$$

$$N_A = N_{A_0}(1-x_A)$$

$$dN_A = N_{A_0}\cdot dx_A$$

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

$-r_A = -\frac{1}{V}\frac{dN_A}{dt}$. $\frac{\text{mol}}{\text{m}^3\cdot\text{sec}}$

$(-r_A)\cdot V = \frac{dN_A}{dt}$. $\frac{\text{mol}}{\text{sec}}$

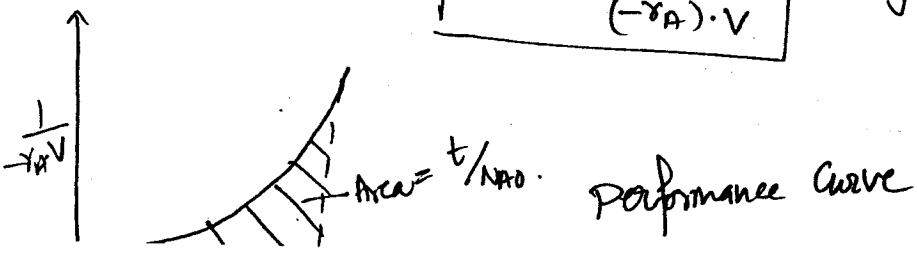
$$\int_0^t dt = \int_0^{x_A} \frac{N_{A_0}\,dx_A}{(-r_A)\cdot V}$$

$$\boxed{t = N_{A_0}\int_0^{x_A} \frac{dx_A}{(-r_A)\cdot V}}$$

Design eqn of Batch Reactor in integral form

$$\boxed{dt = \frac{N_{A_0}\cdot dx_A}{(-r_A)\cdot V}}$$

design eqn of BR in diff^{n} form.



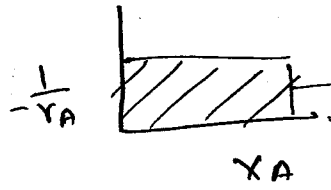
performance Curve

for 0^{th} order rxn

$n = 0$

$-r_A = k C_A^0 = k$

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{k \cdot V} = \frac{N_{A0}}{Vk} \cdot X_A = \frac{N_{A0}}{V} \cdot \frac{X_A}{-r_A}$$



$C_{A0} = \frac{N_{A0}}{V}$

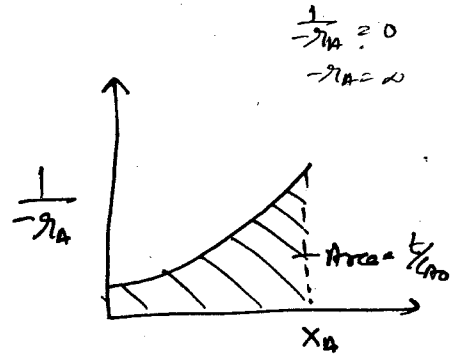
* Constant Volume System ($V = V_0$)

$$t = \int_0^{X_A} N_{A0} \frac{dX_A}{(-r_A) V}$$

$V = V_0$

$$t = \frac{N_{A0}}{V_0} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\boxed{t = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)}}$$

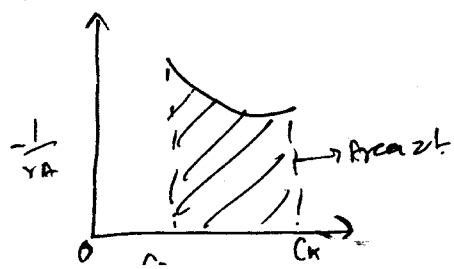


$X_A = 1 - C_A / C_{A0}$

$dX_A = -\frac{dC_A}{C_{A0}}$

$$t = C_{A0} \int_{C_{A0}}^{C_A} \frac{-\frac{dC_A}{C_{A0}}}{(-r_A)}$$

$$\boxed{t = -\int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A} = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A}}$$



$-r_A = k C_A^n$

$C_{A0} \propto -r_A$ high

$\propto \frac{1}{-r_A}$ low.

* Variable volume system :-

$$t = N_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A) \cdot V}$$

$$V = V_0 (1 + \varepsilon_A X_A)$$

$$t = \frac{N_{A0}}{V_0} \int_0^{X_A} \frac{dX_A}{(1+\varepsilon_A X_A)(-r_A)}$$

$$\boxed{t = C_{A0} \int_0^{X_A} \frac{dX_A}{(1+\varepsilon_A X_A)(-r_A)}}$$

Q) for a cetain $A \rightarrow B$, $k = 0.35$ mol/l.s, $C_{A0} = 100$ mol/l. f/o the tym reqd for 30% conv. in a batch reactor.

$$t = \int_0^{X_A} \frac{C_{A0} \cdot dX_A}{(-r_A)}$$

ln: $\frac{0.30}{0.35}$

$$= \int_0^{0.3} \frac{100 \times dX_A}{0.35}$$

$$= \frac{100}{0.35} \times 0.3$$

$$\boxed{t = 85.71} \text{ sec.}$$

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Q) for the rxn $2A \longrightarrow 3B(g)$, $C_{A0} = 10$ mol/l. find tym req for 50% conversion $-r_A = 0.05$ mol/l.s

$$\varepsilon_A = 1/2$$

$$-r_A = \frac{C_{A0}\, dX_A}{(1+\varepsilon_A X_A) dt} = k$$

$$\int_0^{0.5} \frac{C_{A0} \cdot dX_A}{(1+\varepsilon_A X_A)} = \int_0^t k\, dt$$

$$C_{A0} \cdot \ln (1+\varepsilon_A X_A) \Big|^{0.5} = kt$$

$$t = N_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)\cdot V}$$

$$V = V_0(1+\varepsilon_A X_A)$$

$$= \int_0^{X_A} \frac{C_{A0}\cdot dX_A}{(1+\varepsilon_A X_A)(-r_A)} = \frac{C_{A0}\ln(1+\varepsilon_A X_A)}{\varepsilon_A \cdot k}\Bigg|_0^{0.5}$$

For variable volume System :—

$$pV = nRT$$

$$pV = N_T RT$$

at initial condition,

$$p_0 V_0 = N_{T0} R T_0$$

at final condition,

$$pV = N_T R T$$

$$\frac{pV}{p_0 V_0} = \frac{N_T RT}{N_{T0} R T_0}$$

$$V = V_0 \left(\frac{p_0}{p}\right)\left(\frac{T}{T_0}\right)\frac{N_T}{N_{T0}}$$

; $aA + bB \rightarrow cC + dD$

; Initially $N_{A0}\ N_{B0}\ N_{C0}\ N_{D0}$

; $N_{T0} = N_{A0} + N_{B0} + N_{C0} + N_{I0}$

$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$.

$$N_A = N_{A0} - N_{A0}X_A$$

$$N_B = N_{B0} - b/a\, N_{A0}\cdot X_A$$

$$N_C = N_{C0} + c/a\, N_{A0}\cdot X_A$$

$$N_D = N_{D0} + d/a\, N_{A0} X_A$$

$$N_T = N_{I0}$$

$$N_T = N_{T0} + \left(d/a + c/a - b/a - 1\right) N_{A0}\cdot X_A$$

; $d/a + c/a - b/a - 1 = \delta$ (say)

$$N_T = N_{T0} + \delta N_{A0} X_A$$

$$\frac{N_T}{N_{T0}} = \frac{N_{T0}}{N_{T0}} + \frac{\delta N_{A0} X_A}{N_{T0}}$$

! dividing by mole fraction

$$\frac{N_T}{N_{T0}} = 1 + \underbrace{\delta y_{A0}}_{\varepsilon_A} X_A$$

y_{A0} = initial mole fract^n of A

$$\frac{N_T}{N_{T0}} = 1 + \varepsilon_A X_A$$

$$\boxed{V = V_0 \left(\frac{T}{T_0}\right)\left(\frac{P_0}{P}\right)(1+\varepsilon_A X_A)}$$

$$\frac{N_T}{N_{T0}} = 1+\varepsilon_A X_A$$

$$X_A \varepsilon_A = \frac{N_T}{N_{T0}} - 1$$

$$\varepsilon_A = \frac{N_T - N_{T0}}{N_{T0} \cdot X_A}$$

for complete conversion, $X_A = 1$

$$\boxed{\varepsilon_A = \frac{N_T|_{X_A=1} - N_{T0}}{N_{T0}}}$$

Q) same as earlier.

$$\delta = \frac{c}{a} - \frac{b}{a} - 1$$

$$= 4/2 - 3/2 - 1$$

$$\delta = -1/2$$

$$y_{A0} = \frac{10}{10+5} = 2/3$$

$$\varepsilon_A = -1/2 \times 2/3 = -1/3$$

$$\varepsilon_B = \delta \cdot y_{B0}$$

$$\delta = \frac{c}{b} - \frac{a}{b} - 1$$

$$= 4/3 - 2/3 - 1$$

$$\delta = -1/3$$

$$y_{B0} = 5/15 = 1/3$$

$$\varepsilon_B = -1/3 \times 1/3 = -1/9.$$

Q.7 $1.5H + 2.5B \rightarrow 3C$

$\varepsilon_A = ?$

↳ Equimolar A & B

↳ 40% A, 40% B, 20% C

↳ 20% A, 60% B & rest pdt.

$$\varepsilon_A = \delta_A y_{A0}$$

$$\delta_A = \frac{3}{1.5} - \frac{2.5}{1.5} - 1$$

$$= 2 - 0.666$$

$$\varepsilon_A = -0.666 \times 0.5$$

$$= 0.333 \quad (-1/3)$$

$$\varepsilon_A = -0.666 \times 0.4$$

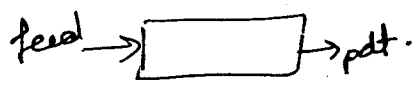
$$= -0.2664 \quad (-4/15)$$

$$\varepsilon_A = -0.666 \times 0.2$$

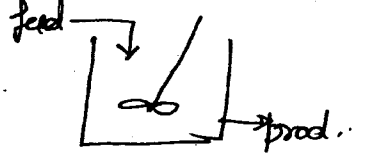
$$= -0.1332 \quad (-2/15)$$

* Design of ideal flow Reactors

Ideal Tubular Reactor



Ideal Mixed flow Reactor.
(Continuous stirred tank Reactor)



* Flow parameter

⇒ Space time(τ) (sec)

Time required to process one reactor volume

$$\tau = \frac{V}{V_0} \frac{l}{(l/s)} = \text{sec}$$

Space velocity (S)

No. of reactor volume processed per unit tym.

$$\boxed{S = 1/\tau} \quad (Sec^{-1})$$

→ Molar flow rate (mol/s) $\{F_A\}$:—

$$C_A = \frac{N_A}{V}, \quad \tau = \frac{F_A}{V_0} \qquad \frac{mol/s}{m^3/s}$$

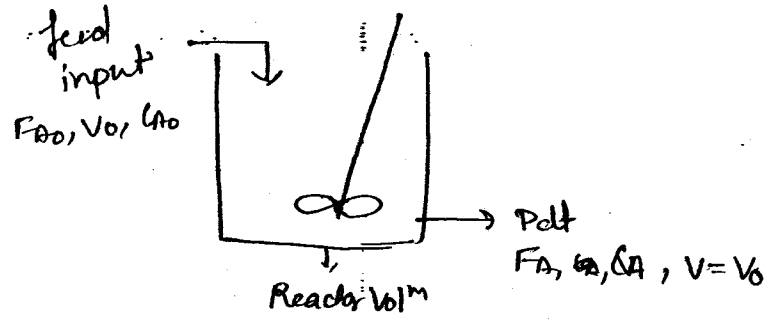
$$\boxed{C_{A_0} = \frac{F_{A_0}}{V_0}} \quad mol/m^3$$

* Design of Ideal CSTR

→ Mixed flow Reactor (MFR)

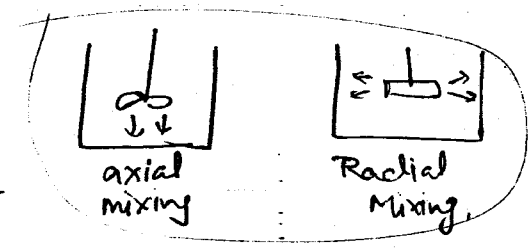
→ Back Mix Reactor (BMR)

→ Constant Flow Stirred Tank Reactor (CFSTR)



→ Uniform concentration distribution through out the reactor. at any tym t.

→ The outlet conc is same as conc within the reactor.



→ Axial mixing

Molar Rate of A Input = Molar Rate of A out + Molar rate of A accu + Molar rate of A disapp. − Molar rate of formation

$$F_{A0} = F_A + 0 + (-r_A)\cdot V \quad -0$$

$$F_{A0} - F_A = (-r_A)\cdot V$$

$$\Rightarrow F_{A0}\cdot X_A = (-r_A)\cdot V$$

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

$\because N_A = N_{A0}(1-X_A)$

and $F_A = F_{A0}(1-X_A)$

$$\boxed{\frac{V}{F_{A0}} = \frac{X_A}{-r_A}}$$ Design eqn of CSTR

$$\frac{V\cdot C_{A0}}{F_{A0}} = \frac{X_A C_{A0}}{-r_A}$$

$$\frac{V}{V_0} = \frac{C_{A0}\cdot X_A}{-r_A}$$

$C_{A0} = F_{A0}/V_0$

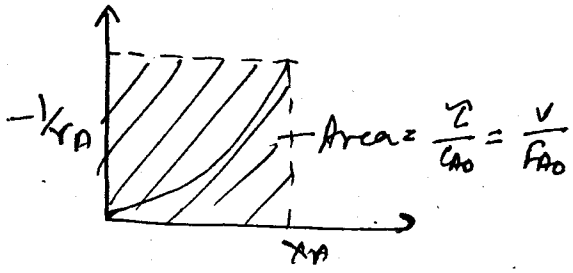
$1/V_0 = C_{A0}/F_{A0}$

$$\boxed{\tau = \frac{C_{A0}X_A}{-r_A}}$$

$$\boxed{\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{X_A}{-r_A}}$$

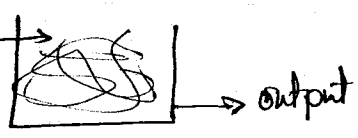
$X_A \times \left(\frac{1}{-r_A}\right)$

area



Residence Tym :—

Time taken by the molecule within the reactor from its inlet to the outlet.



for ideal reactors the residence hym is same for all molecules

for ideal flow reactors, space hym = mean residence time of molecules

Q:) for ~~non~~ non-ideal flow reactor $\boxed{\tau \lessgtr \bar{t}}$

for constant volm system

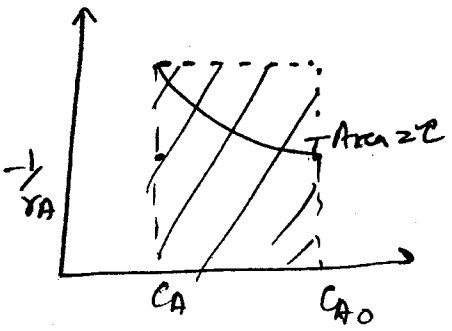
$$C_A = C_{A0}(1-X_A)$$

$$\tau = \frac{C_{A0} \cdot X_A}{-r_A}$$

$$C_{A0} \cdot X_A = C_{A0} - C_A$$

$$\boxed{\tau = \frac{C_{A0} - C_A}{-r_A}}$$

$$\boxed{\tau = \frac{V}{V_0} = \frac{VC_{A0}}{FA_0}}$$



for Variable volume System:-

$$C_A = \frac{C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$$\tau = \frac{C_{A0} \cdot X_A}{-r_A}$$

n^{th}

$$-r_A = kC_A^n = \frac{kC_{A0}^n (1-X_A)^n}{(1+\varepsilon_A X_A)^n}$$

$$\boxed{\tau = \frac{C_{A0} \cdot X_A \cdot}{\frac{kC_{A0}^n (1-X_A)^n}{(1+\varepsilon_A X_A)^n}}}$$

Sep 24, 14

Q.7 for rxn $A \rightarrow P$, $-r_A = 3C_A^2$, kmol/m³.s. If the rxn is conducting in a CSTR. & then what will be the conv. If the feed rate is 30 kmol/min, & initial concn is 10 kmol/m³. $V = 2 m^3$.

MB over A

$$\tau = \frac{C_{A0} X_A}{-r_A}$$

$$\frac{V C_{A0}}{F_{A0}} = \frac{C_{A0} X_A}{3C_A^2}$$

$$\frac{V}{F_{A0}} = \frac{X_A}{3C_{A0}^2 (1-X_A)^2}$$

$$F_{A0} = 30 \frac{\text{kmol}}{\text{min}} \times \frac{1 \text{min}}{60 \text{sec}} = 0.5 \text{ kmol/s}.$$

$$\frac{2 \text{ m}^3}{0.5 \text{ kmol/s}} = \frac{X_A}{3 \times (10 \frac{\text{kmol}}{\text{m}^3})^2 (1-X_A)^2}$$

$$\frac{300 \text{ m}^3\text{s}}{\text{kmol}} \times X$$

$$300 \frac{\text{kmol}}{\text{m}^3\text{s}} = \frac{X_A}{(1-X_A)^2}$$

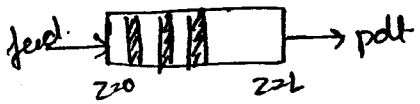
$$300(1 + X_A^2 - 2X_A) = X_A$$

$$300 X_A^2 - 599 X_A + 300 = 0$$

$$X_A = 97.16\%.$$

Design Eqn of Ideal Tubular Reactor

Slug Flow Reactor / Piston Flow Reactor / Plug Flow Reactor / Unmixed Flow R



Axial mixing = 0

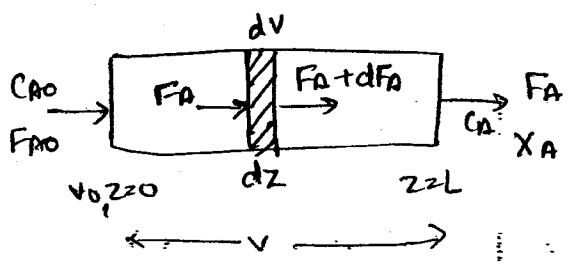
Radial mixing = ∞

→ C_A = f (time, length)

→ No axial mixing but ∞ Radial Mixing.

→ No interaction btw molecules in axial dirn

→ Residence time is same for ∀ molecules



Material balance over diff strip

Rate of A input	=	Rate of A output	+	Rate of A accumul^n	+	Rate of A dissapp	−	Rate of A form

$$F_A = (F_A + dF_A) + 0 + (-r_A).dV + 0$$

$$-dF_A = -r_A dV$$

$$F_{A0} dX_A = -r_A . dV \qquad \because F_A = F_{A0}(1-X_A)$$

$$\boxed{\frac{dV}{F_{A0}} = \frac{dX_A}{-r_A}}$$ Design eqn for PFR in diff form

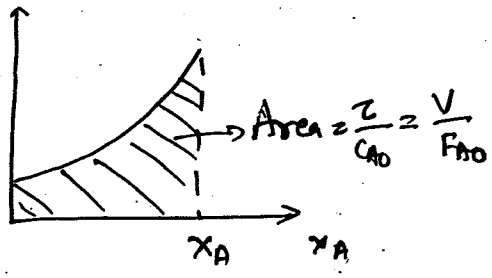
2)

$$-\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\boxed{V = F_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)}}$$ Design eqn for

$$\boxed{\tau = \frac{VC_{A0}}{F_{A0}} = \frac{V}{V_0} = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)}}$$ performance eqn.

for general case.



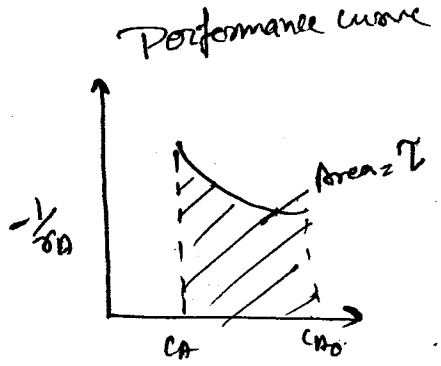
Space tym. $\tau = C_{A0}\int_0^{X_A} \frac{dX_A}{-r_A}$

$t = C_{A0}\int_0^{X_A} \frac{dX_A}{-r_A}$

t = residence tym

⇒ For constant volume Rxn System :—

$$\tau = C_{A0}\int_0^{X_A} \frac{dX_A}{-r_A}$$



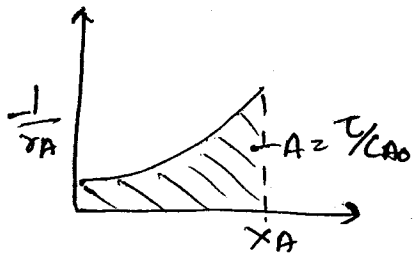
$-r_A = kC_A^n$

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

$dC_A = -C_{A0}\cdot dX_A$

$$\boxed{\tau = \int_{C_{A0}}^{C_A} \frac{-dC_A}{(-r_A)}}$$

$$\boxed{\tau = \int_{C_A}^{C_{A0}} \frac{dC_A}{(-r_A)}}$$



* For variable Vol. System

$$\tau = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$C_{A0} = \frac{C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$-r_A = kC_A^n$

- eg for Ist order

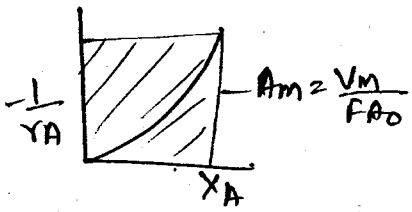
$$-r_A = kC_A = \frac{kC_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}$$

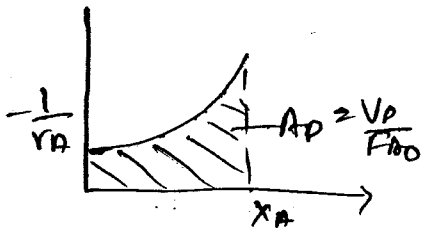
$$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{\frac{k C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}}$$

$$\boxed{\tau = \int_0^{X_A} \frac{(1+\varepsilon_A X_A)}{(1-X_A)} dX_A}$$

The volume required for CSTR is larger than that of PFR for same conversion under constant rxn condition for positive order rxns.

for CSTR





Area for CSTR > Area for PFR

$$\boxed{V_m > V_p}$$

Q) for liq phase 1st ord rxn $A \rightarrow R$, what is the size of reactor reqd required for 80% conv. of feed stream 2000 l/hr.

$C_{A0} = 10 \text{ mol/l}$, $k = 20 \text{ hr}^{-1}$

i.) for PFR ii.) for CSTR.

i.) for PFR

$$\frac{V C_{A0}}{F_{A0}} = \frac{C_{A0}}{(-r_A)} \int_0^{0.8} \frac{dX_A}{kC_A} = \frac{C_{A0}}{C_{A0}} \int_0^{0.8} \frac{dX_A}{k(1-X_A)}$$

$$\frac{V C_{A0}}{F_{A0}} = \frac{1}{k} \left| \frac{\ln(1-X_A)}{-1} \right|_0^{0.8}$$

$$V \left[\frac{10 \text{ mol/hr}}{2000 \text{ l}} \cdot \frac{1}{1} \cdot \frac{\ln 0.2}{k} \right]$$

$$\boxed{V = 160.940 \text{ l}}$$

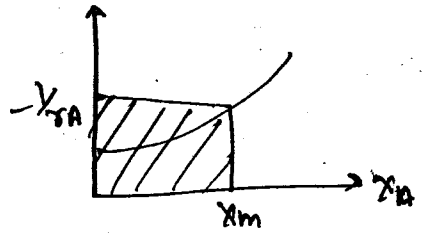
ii) for CSTR

$$\tau_c = \frac{C_{A0} \cdot X_A}{-r_A}$$

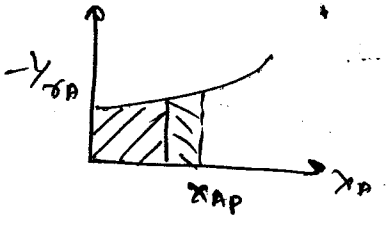
$$\frac{V_c}{V_0} = \frac{C_{A0} \cdot X_A}{k C_{A0}(1-X_A)}$$

$$\boxed{V_c = 400\ l}$$

The conversion given by PFR is more than that of given by CSTR for the same volume under constant rxn condition for (+ve) order rxn.



CSTR



PFR

Q) for a certain rxn $A \rightarrow R$, $F_{A0} = 2000$ mol/hr, $C_{A0} = 10$ mol/l

$k = 5\,hr^{-1}$. Find out the conv^n. (exit)

i) PFR of ~~200~~ 0.2 m^3 ii) CSTR of 0.2 m^3

$$\frac{V}{V_0} = \frac{C_{A0}}{k} \cdot \frac{1}{-1} \left| \ln(1-X_A) \right|_0^{X_A}$$

$$\frac{0.2}{2000} = \frac{1}{10} \left(\frac{\ln(1-X_A)}{-1} \right)$$

$$\frac{V_c}{F_{A0}} = \frac{C_{A0} \cdot X_A}{k C_{A0}(1-X_A)}$$

$$\frac{0.2}{2000} = \frac{X_A}{5(1-X_A)}$$

ii) $\frac{V_p C_{A0}}{F_{A0}} = \frac{1}{k}\left[\frac{\ln(1-X_A)}{-1}\right]_0^{X_A}$

$1\ m^3 = 10^3\ l = 10^6\ cm^3 = 10^6\ ml$

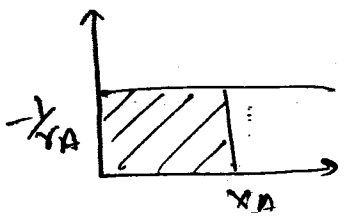
$X_A = 99.33\%$

iii) $\tau_m = \frac{C_{A0} \cdot X_A}{-r_A}$

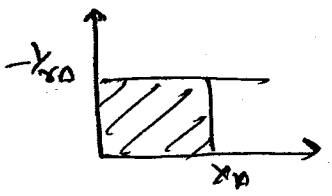
$\frac{V_m C_{A0}}{F_{A0}} = \frac{C_{A0} \cdot X_A}{k C_{A0}(1-X_A)}$

$X_A = 83.33\%$.

The volume required by CSTR is same as that of PFR for the same conversion, for 0th order rxn, under const rxn condition.



For PFR



for CSTR

<u>for 0th order rxn</u>

for CSTR

$\tau_C = \frac{C_{A0} \cdot X_A}{-r_A}$

$\frac{V_C}{V_0} = \frac{C_{A0} \cdot X_A}{k}$

$\boxed{V_C = \frac{C_{A0} \cdot X_A\ V_0}{k}}$

for PFR

$\tau_P = C_{A0} \int_0^{X_A} \frac{dx_A}{-r_A}$

$\frac{V_P}{V_0} = C_{A0} \int_0^{X_A} \frac{dx_A}{k}$

$\boxed{\frac{V_P}{V_0} = \frac{C_{A0} X_A\ V_0}{k}}$

$\boxed{V_m = V_P}$ for same X_A

Q.)5

MFR

$C_{A0} = 2\ Kmol/m^3$

$V_0 = 1\ m^3/h$ $\quad \varepsilon_A = 0.5$

$C_{A0}' = 2C_{A0}$

$V_0' = 3V_0'$ $\quad \varepsilon_A = 0.5$

A.)7

$$\frac{V}{V_0} = \frac{C_{A0} X_A}{K C_{A0}(1-X_A) C_A}$$

$$\frac{V}{1} = \frac{0.5}{K 0.5} \frac{4 X_A}{1 K 0.5}$$

$$V = \frac{8 X_A}{K}$$

$$\frac{V'}{3V_0} = \frac{0.5}{K 0.5} \frac{4 \times 2 X_A}{K \times 0.5} = \frac{16 X_A}{K}$$

$$V' = \frac{3 \times 16}{K}$$

$$\frac{V'}{V} = \frac{3/K}{1/K} \frac{3 \times 16}{8}$$

$$V' = 6k'$$

$$\frac{V}{V_0} = \frac{C_{A0} - C_A}{-r_A}$$

$$\frac{V}{1} = \frac{2 - 0.8}{K 0.5}$$

$$V = 3/K$$

$$\frac{V'}{3V_0} = \frac{4 - 0.5}{K 0.5}$$

$$V' = 21/K$$

$$\frac{V'}{V} = \frac{21}{3}$$

$$V' = 7V$$

Sep 25,14

Q.) A gaseous mixture of 20% O_3 & 80% air at 1.5 atm & 93°C is passing through a PFR at 1 l/s under these cond^n Ozone decompose as

$$2O_3 \longrightarrow 3O_2 \quad , \quad -r_{O_3} = 0.05\ C_{O_3}^2 \quad mol/l.s$$

What is the size of reactor required for 50% conv.

Sol^n

$V_0 = 1\ l/s$, $K = 0.05$

$$\frac{V}{V_0} = \int \frac{dX_A}{0.05 C_A^2} = \int \frac{dX_A}{0.05 C_{A_0}^2 \frac{(1-X_A)^2}{(1+\varepsilon_A X_A)^2}}$$

$\varepsilon_A = 0.1$, $K = 0.05$ $^{1}/_{mol\cdot s^{-1}}$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{y_{A0} P}{RT}$$

$$C_{A0} = \frac{0.2 \times 1.5}{0.0821 \frac{atm \cdot l}{mol \cdot k} \times 366 k}$$

$$C_{A0} = 0.01 \ mol/l.$$

$$\tau_p = \int_0^{X_A} \frac{C_{A0} \cdot dX_A}{-r_A}$$

$$\tau_p = \int_0^{X_A} \frac{C_{A0}\, dX_A}{\frac{k C_A^2 (1-X_A)^2}{(1+\varepsilon_A X_A)^2}}$$

$\because C_A = \frac{C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}$

$$= \int_0^{X_A} \frac{(1+\varepsilon_A X_A)^2 \, dX_A}{k C_{A0} (1-X_A)^2}$$

$$= \frac{1}{k C_{A0}} \int_0^{X_A} \left\{ \frac{1}{(1-X_A)^2} + \frac{(\varepsilon_A X_A)^2}{(1-X_A)^2} + \frac{2 \varepsilon_A X_A}{(1-X_A)^2} \right\} dX_A$$

$$= \frac{1}{k \varepsilon_{A0}} \left\{ \frac{1}{} \right.$$

$\tau_p = \frac{1}{k C_{A0}} \int_0^{X_A}$ –

$\tau_p = \frac{V_p}{V_0} \simeq 2155 l$ =

Q:) A CSTR of 20 ℓ m^3 vol^m process an aqueous feed $V_0 = 100$ l/min, $C_{A0} = 100$ m mol/l and the rxn is given as $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$, ~~$-r_A = 0.04$ min^{-1}~~

$-r_A = (0.04\ min^{-1})\ C_A - (0.01\ min^{-1}) C_R$. find the equilibrium conversion and actual conversion for the reactor. $X_{Ae} = ?$ & $X_A = ?$

$$\frac{V_P}{V_0} = \frac{C_{A0} X_A}{-r_A}$$

$$\frac{20 \times 10^3}{100} = \frac{100\ X_A}{0.04 C_A - 0.01 C_R}$$

$$6 = \frac{6 X_A}{1 + X_A}$$

$$X_A = 0.857$$

$$C_R = C_{R0} + \frac{r_R}{r_A} C_{A0} \cdot X_A$$

$$C_{Re} = 0 + 1 C_{A0} \cdot X_{Ae}.$$

for equilibrium

$$-r_A = 0$$

$$\Rightarrow 0.04 C_A - 0.01 C_R = 0$$

$$\Rightarrow 0.04 C_{Ae} = 0.01 C_{Re}$$

$$\Rightarrow 0.04 C_{A0}(1 - X_{Ae}) = 0.01 C_{A0} \cdot X_{Ae}$$

$$\boxed{X_{Ae} = 0.8}$$

$$\frac{20 \times 10^3}{100} = \frac{100\ X_A}{0.04 C_{A0}(1 - X_A) - 0.01 C_{A0} X_A}$$

$$\frac{20 \times 10^3}{100} = \frac{100\ X_A}{0.04 C_{A0} - 0.05 C_{A0} X_A}.$$

$$200 (0.04 C_{A0} - 0.05 C_{A0} X_A) = X_A$$

$$800 - 1000 X_A = X_A$$

$$X_{Ae} = 0.727$$

Q:) for the homogeneous gas decomposition of phosphene is given as

$$4PH_3 \longrightarrow P_4 + 6H_2$$

proceeds at 649°C, and the rate eqn is given as $-r_{PH_3} = (10 hr^{-1}) C_{PH_3}$

What is the vol^m of PFR required operating at 649°C & 460 KPa. for the 80% conv^n of phosphene where pure feed is entering the reactor at the rate of 40 moles/hr.

Soln :-

$$\frac{VC_{A0}}{F_{A0}} = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\frac{V}{40} = \int_0^{X_A} \frac{dX_A}{k\frac{C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}}$$

$$\frac{V}{40} = \frac{1}{kC_{A0}} \int_0^{X_A} \frac{dX_A}{\frac{(1-X_A)}{(1+\varepsilon_A X_A)}}$$

$$\frac{V}{40} = \frac{1}{kC_{A0}}$$

$$\frac{V_p C_{A0}}{F_{A0}} = \int_0^{X_A} \frac{(1+\varepsilon_A X_A)}{k(1-X_A)}\, dX_A$$

$\varepsilon_A = \delta \cdot y_{A0}$
$= \left(\frac{1+6-4}{4}\right) \times 1$
$\varepsilon_A = 3/4$

$$= 2\int_0^{0.8} \frac{1.6}{10\times 0.2}\, dX_A$$

$$\frac{V_p C_{A0}}{F_{A0}} = 0.8 \times 0.8$$

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{y_{A0}\cdot P}{RT}$$

$$R = \frac{101.325\ kPa \times 22.4\ l}{1\ mol \times 273.15\ K} = 8.314\ \frac{kPa\cdot l}{mol\cdot k}$$

$$C_{A0} = \frac{1\times 460}{8.314 \times 922}$$ } 649 + 273

$$C_{A0} = 0.06\ mol/l$$

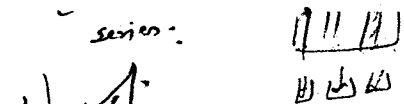
$$\frac{V_p \times 0.06}{40} = \int_0^{0.8} \frac{(1+\varepsilon_A X_A)}{k(1-X_A)}\, dX_A$$

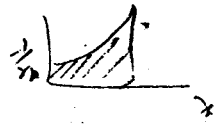
$$= \int_0^{0.8} \left[\frac{1}{1-X_A} + \frac{\varepsilon_A \cdot X_A - 1}{1-X_A} + 1\right] dX_A$$

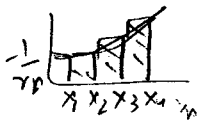
=

* Multiple Reactor System :—

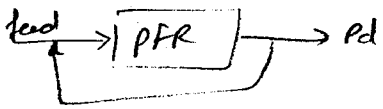
series :







PFR ≃ CSTR

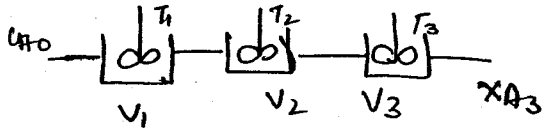


$\frac{1}{R}$ = R → ∞

recycle ratio.

$R = \frac{\text{rate of recycling stream}}{\text{rate of pdt stream}}$

* CSTR in Series



$$X_{AN} = 1 - \frac{C_{AN}}{C_{A0}}$$

} Numbers of CSTR

Design eqn for I st tank :—

$$\tau_1 = \frac{C_{Ain} - C_{Aout}}{(-r_A)_1}$$

for tank 2.

$$\tau_2 = \frac{C_{A1} - C_{A2}}{(-r_A)_2}$$

for tank 3,

$$\tau_3 = \frac{C_{A2} - C_{A3}}{(-r_A)_3}$$

$$\Rightarrow \boxed{\tau_i = \frac{V_i}{v_0}}$$

for n = 1 rxn

$$-r_A = kC_A$$

$$\tau_1 = \frac{C_{A0} - C_{A1}}{k_1 C_{A1}} = C_{A1} = \frac{C_{A0}}{(1+\tau_1 k_1)}$$

$$\tau_2 = \frac{C_{A1} - C_{A2}}{k_2 C_{A2}} = C_{A2} = \frac{C_{A1}}{(1+\tau_2 k_2)}$$

$$C_{A2} = \frac{C_{A0}}{(1+\tau_1 k_1)(1+\tau_2 k_2)}$$

for tank 3

$$C_{A3} = \frac{C_{A0}}{(1+\tau_1 k_1)(1+\tau_2 k_2)(1+\tau_3 k_3)}$$

for N-CSTR in series

$$C_{AN} = \frac{C_{A0}}{(1+\tau_1 k_1)(1+\tau_2 k_2)\ldots(1+\tau_N k_N)}$$ for 1 order rxn

$$X_{AN} = 1 - \frac{C_{AN}}{C_{A0}} = 1 - \frac{1}{(1+\tau_1 k_1)(1+\tau_2 k_2)\ldots(1+\tau_N k_N)}$$

Case 2 - if the tempr is same in all tanks:-

$k_1 = k_2 = k_3 = \ldots = k$ (say)

$$C_{AN} = \frac{C_{A0}}{(1+\tau_1 k)(1+\tau_2 k)(1+\tau_3 k)\ldots(1+\tau_N k)}$$

if V tank are equal in size

$\tau_1 = \tau_2 = \ldots = \tau_N = \tau_i$ (say), $\tau_i = \frac{V_i}{V_0}$

$$C_{AN} = \frac{C_{A0}}{(1+\tau_1 k)(1+\tau_i k)\ldots(1+\tau_i k)} = \frac{C_{A0}}{(1+\tau_i k)^N}$$

$$X_{AN} = 1 - \frac{1}{(1+\tau_i k)^N}$$

overall space tym for N CSTR in series

$= \tau_1 + \tau_2 + \tau_3 + \ldots + \tau_N$

$$\tau_{overall} = N \times \tau_i$$

for single CSTR , $N = 1$

$$C_{A1} = \frac{C_{A0}}{1+\tau k}$$

$$\tau = \frac{C_{A0} - C_{A1}}{k C_{A0}}$$

$$X_{A_1} = 1 - \frac{1}{(1+\tau K)}$$

Sec/(Sec^{-1}) $$\boxed{\tau K = \frac{X_{A1}}{1-X_{A1}}}$$

defined for reactor rest for rxn.

Damkohlen No. of I order

$$\boxed{Da_I = \tau K}$$

for n^{th} order rxn,

$$\boxed{Da_n = \tau K C_{A_0}^{n-1}}$$

for 2nd order rxn,

$$Da_{II} = \tau K C_{A_0} \Rightarrow \text{flow reactor.}$$

/ Conc^n profile along / z axis
/ Physical significance / of Da_N.

Check

$$\tau = \frac{C_{A_0} \cdot X_A}{K C_A^2} = \frac{C_{A_0} X_A}{K C_{A_0}^2 (1-X_A)^2}$$

$$\tau K C_{A_0} = \frac{X_A}{(1-X_A)^2}$$

$$\text{Sec} \cdot \frac{l}{mol} \cdot \frac{mol}{l} = \text{Nk unit}$$

Q) for the first order liq. phase rxn, the rate expression is given as $-r_A = 4 min^{-1} C_A$, $C_{A_0} = 10 mol/l$, $V_0 = 5 l/min$. Find out the conv.

for → Single CSTR of 30l.
→ Two CSTR of 15l connected in series.
→ Two CSTR in series of 10l & 20l
→ " " " " " 20l & 10l.

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

$$\frac{30}{5} = \frac{10 X_A}{4 \times 10 (1-X_A)} \Rightarrow \frac{6 \times 40}{10} = \frac{X_A}{1-X_A}$$

$$24 = 25 X_A$$

ii) $C_{A_1} = \frac{C_{A_0}}{1+\tau_1 k_1}$ $\quad \tau_1 = \frac{V_1}{v_0}$

$= \frac{10}{1+3\times4}$ $\quad = \frac{15}{305} = 3$

$= 0.7692$

$C_{A_2} = \frac{C_{A_0}}{(1+3\times4)(1+3\times4)}$

$= 0.05917$

$X_{A_2} = 1 - \frac{0.05917}{10}$

$= 0.994$

$= 99.4\%$

iii)

$C_{A_2} = \frac{C_{A_0}}{(1+2\times4)(1+4\times4)}$ $\quad \frac{10}{5} =$

$= 0.0653$

$X_{A_2} = 0.9934$

$= 99.34\%$

iv)

$C_{A_2} = \frac{C_{A_0}}{(1+4\times4)(1+2\times4)}$

$= 0.0653$

$X_{A_2} = 99.34\%$

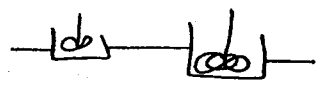
CSTR in series gives more conversion than the single CSTR of same Equivalent volume under constant rxn conditions for (+ve) order rxn.

CSTR in series required less volume than that of single CSTR for the same conversion for +ve order of rxn, under constant rxn condition.

⇒ for maximum conversion

if $n > 1$

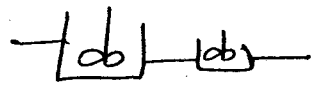
use small CSTR followed by large CSTR



late mixing required.

if $n < 1$

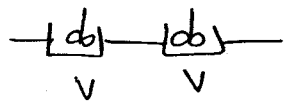
Use large CSTR followed by small CSTR.



early mixing reqd.

if $n = 1$

Use equal size CSTR in series.



Q. for a liquid ϕ second order rxn

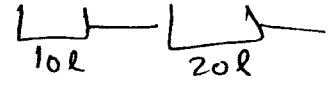
$C_{A0} = 10$ mol/l

$V_0 = 20$ l/min

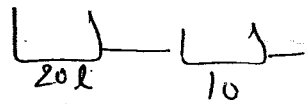
$k = 4$ l/mol.min

$-r_A = k C_A^2$. mol/l.min.

find out conv $X_A = ?$

↳ two 

$X_A = 94\%$.

→ 

$X_A = 93.5\%$

$$\tau_1 = \frac{C_{A_0} - C_{A_1}}{(-r_A)_1}$$

$$\tau_1 = \frac{C_{A_0} - C_{A_1}}{K C_{A_1}^2} \qquad \tau_1 = \frac{V_1}{V_0}$$

$$\frac{10}{20} = 0.5$$

$$0.5 = \frac{10 - C_{A_1}}{4 C_{A_1}^2}$$

$$2 C_{A_1}^2 = 10 - C_{A_1}$$

$$2C_{A_1}^2 + C_{A_1} - 10 = 0$$

$$2C_{A_1}^2 + 5C_{A_1} - 4C_{A_1} - 10 = 0$$

$$C_{A_1}(2C_{A_1} + 5) - 2(2C_{A_1} + 5) = 0$$

$$(C_{A_1} - 2)(2C_{A_1} + 5) = 0$$

$$C_{A_1} = 2, -5/2$$

for tank 2,

$$\tau_2 = \frac{C_{A_1} - C_{A_2}}{K C_{A_2}^2}$$

$$1 = \frac{2 - C_{A_2}}{4 C_{A_2}^2}$$

$$\frac{20}{20} = 1$$

$$-b \pm \frac{\sqrt{b^2 - 4ac}}{2a}$$

$$4 C_{A_2}^2 = 2 - C_{A_2}$$

$$4C_{A_2}^2 + C_{A_2} - 2 = 0$$

$$\frac{-b \pm \sqrt{4ac}}{2a}$$

$$\frac{-1 \pm \sqrt{-8}}{2}$$

$$C_{A_2} = 0.59 \text{ mol/l}$$

$$2i\sqrt{2}$$

$$X_{A_2} = 1 - \frac{0.59}{16}$$

$$= 94.1\%$$

Q.) CSTR in series $V_1 = 5l$, $V_2 = 10l$, $V_3 = 15l$, for max = conver
which combination is best
↳ if $n < 1$
↳ if $n > 1$

centres
$1_0/^n$ for ~~Rank~~ (1),

$$\tau_i = \frac{C_{A0} - C_{A1}}{k C_{A1}^2}$$

Sep 26, 14

Q.) A CSTR is used for a second order rxn gives 45% conv. if the CSTR is replaced by 7 times larger CSTR then what will be the conv^n for same rxn cond^n

$$\frac{V}{V_0} = \frac{C_{A0} X_A}{-r_A = k C_A^2}$$

$$\frac{V}{V_0} = \frac{C_{A0} X_A}{C_{A0}^2 (1 - X_A)^2}$$

$$\frac{V}{V_0} = \frac{0.45}{(1-0.45)} \quad \frac{0.45}{C_{A0}(0.55)^2}$$

$$V = 0.818 V_0 \quad 1.4876 \frac{V_0}{C_{A0}}$$

$$\frac{7V}{V_0} = \frac{X_A}{(1 - X_A)^2 C_{A0}}$$

$$7 \times \frac{0.818 V_0}{V_0} = \frac{X_A}{1 - X_A}$$

$$7 (0.818 - 0.818 X_A) = X_A$$

$$\frac{7 \times 1.4871 V_0}{C_{A0} \times V_0} = \frac{X_A}{C_{A0}(1 - X_A)^2}$$

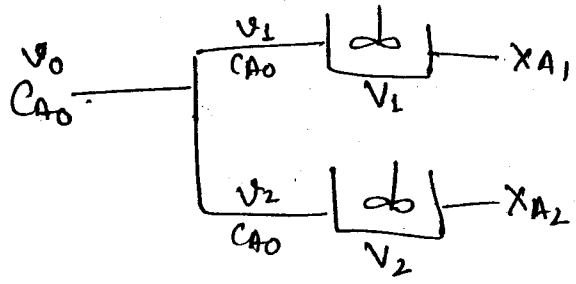
$$10.41 (1 + X_A^2 - 2X_A) = X_A$$

$$10.41 + 10.41 X^2 - 21.826 X_A = 0$$

$$21.82 \pm \sqrt{476.34}$$

shutdown of plant.

* CSTR in Parallel :—



$$V_0 = V_1 + V_2$$

$$\tau_1 = \frac{V_1}{v_1}$$

$$\tau_2 = \frac{V_2}{v_2}$$

$\Rightarrow$ **if $\tau_1 = \tau_2$**
$X_{A_1} = X_{A_2}$

$\tau_1 \neq \tau_2$
$X_{A_1} \neq X_{A_2}$

$$\tau_1 = \frac{C_{A0} \cdot X_{A_1}}{k C_{A0}^n (1 - X_{A_1})^n}$$

$$\tau_2 = \frac{C_{A0} \cdot X_{A_2}}{k C_{A0}^n (1 - X_{A_2})^n}$$

if $\tau_1 = \tau_2$

$$\frac{C_{A0} X_{A_1}}{k C_{A0}^n (1 - X_{A_1})^n} = \frac{C_{A0} X_{A_2}}{k C_{A0}^n (1 - X_{A_2})^n}$$

$\Rightarrow$ if $X_{A_1} = X_{A_2}$ (given)

$$\tau_1 = \tau_2$$

$$\boxed{\frac{V_1}{v_1} = \frac{V_2}{v_2}} \Rightarrow \boxed{\frac{V_1}{F_{A_1}} = \frac{V_2}{F_{A_2}}}$$

~~* PFR in Series :-~~

* Damkohler no:-

$$Da_n = \tau k C_{A0}^{n-1}$$

$$\frac{V}{V_0} C_A^{(n-1)}$$

$$Da_n = \frac{\text{Chemical Reaction Rate}}{\text{Convective Mass Transfer Rate}}$$

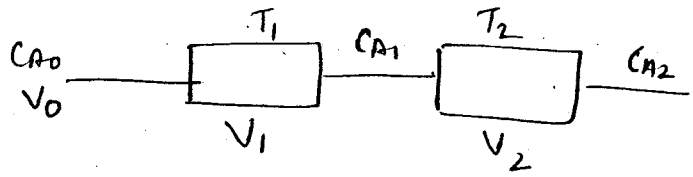
$\Rightarrow Da_n > 10$ (high)

Conversion is high.

$\Rightarrow Da_n < 0.1$ (low)

Conversion is low.

* PFR in Series:-



$$X_{AN} = 1 - \frac{C_{AN}}{C_{A0}}$$

$$X_{A2} = 1 - \frac{C_{A2}}{C_{A0}}$$

MB over (1) Reactor

$$\tau_1 = -\int_{C_{A0}}^{C_{A1}} \frac{dC_A}{(-r_{A1})}$$

Reactor (2)

$$\tau_2 = -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{(-r_{A2})}$$

Case-I for isothermal condition

$$T_1 = T_2 = T_3 = \cdots = T_n$$

$$\tau_1 = -\int^{C_{A1}} \frac{dC_A}{\tilde{r}} = -\int^{C_{A1}} \frac{dC_A}{r}$$

$$\tau_2 = -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{(-r_A)} = -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{kC_A^n}$$

overall space tym

$$\tau = \Sigma \tau_i = \tau_1 + \tau_2$$

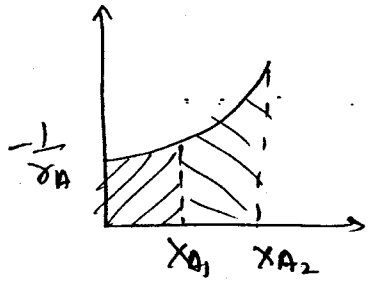
$$\tau = \tau_1 + \tau_2 = -\int_{C_{A0}}^{C_{A1}} \frac{dC_A}{(-r_A)} - \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{(-r_A)}$$

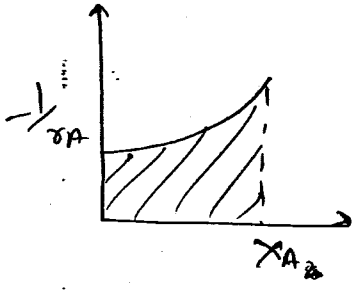
$$\boxed{\tau = -\int_{C_{A0}}^{C_{A2}} \frac{dC_A}{(-r_A)}}$$

$$\tau_t = \tau_1 + \tau_2$$

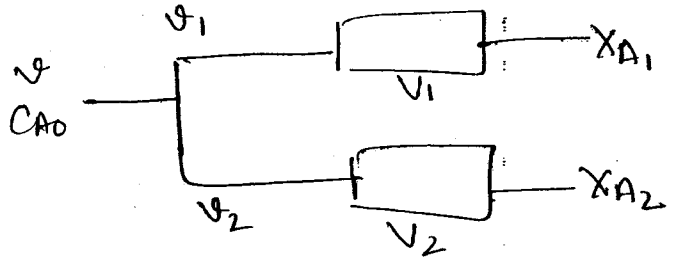
$$\frac{V}{V_0} = \frac{V_1 + V_2}{V_0}$$

PFR in series gives same conversion as single PFR of same equivalent volume.





* PFR in parallel :—



If $X_{A_1} = X_{A_2}$

$$\frac{V_1}{v_1} = \frac{V_2}{v_2}$$

$$\boxed{V_1 \propto V}$$

Q.) A liquid reactant with C_{A0} = [illegible] processed in a PFR in series the conen of A in the exit stream from the first reactor is 0.5 mol/l. Find C_{A2}. & $A \xrightarrow{k} R$, $-r_A = kC_A^2$, $V_2 = 2V_1$

$C_{A0} = 1$ mol/l

$C_{A1} = 0.5$ mol/l

$-r_A = kC_A^2$

$V_2 = 2V_1$

$C_{A2} = ?$

$$\tau_1 = \frac{C_{A0} - C_{A1}}{(-r_A)_1} \qquad \tau_1 = \frac{V_1}{V_0}$$

$$\frac{V_1}{V_0} = \frac{1 - 0.5}{kC_A^2}$$

$$\frac{V_1}{V_0} = \frac{0.5}{kC_{A0}^2(1-X_A)^2} \qquad \frac{0.5}{k\,0.25}$$

$$\frac{V_1}{V_0} = \frac{0.5}{k(1-X_{A_1})^2} \qquad \tau_1 = 2/k$$

$$\tau_2 = \frac{C_{A1} - C_{A2}}{kC_{A1}(1-X_A)} \qquad \tau_2 = \frac{C_{A1} - C_{A2}}{kC_{A2}^2}$$

$$=$$

$\therefore V_2 = 2V_i$

$$\frac{V_2}{V_0} = \frac{0.5 - C_{A2}}{0.25k(1-X_{A_2})^2}$$

$$2\tau_1 = \frac{C_{A1} - C_{A2}}{kC_{A2}^2}$$

$$\frac{V_2}{V_0} = \frac{2V_i}{V_0}$$

$$\tau_2 = 2\tau_1$$

$$\frac{2V_1}{V_0}$$

$$2 \times \frac{2}{k} = \frac{1 - C_{A2}}{kC_{A2}^2}$$

$$\frac{0.5}{k(1-X_{A_1})^2} = \frac{0.5 - C_{A2}}{2(0.25k(1-X_{A_2})^2)}$$

$$4C_{A2}^2 + C_{A2} - 1 = 0$$

$$C_{A2} = 0.25$$

$$C_{A2} = 0.265$$

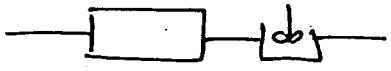
$$=$$

$-2 - 17$

18

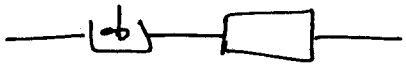
$$\frac{-b \pm \sqrt{1+16}}{2a}$$

for $n>1$,



late mixing is reqd

for $n<1$,



Early mixing is reqd.

for $n=1$,

we can use any combination.

Q.) For elementary irreversible liq phase rxn $A+B \longrightarrow R+S$ takes place in a PFR using equimolar cmt of A & B as 1 mol/lit. Conv^n 96%. (PFR)

If a CSTR, 10 times as large as PFR is connect in the series wid existing PFR which reactor should come first

$C_{A0} = C_{B0} = 1$ mol/l

& $X_A = 96\%$. PFR

$-r_A = k C_A C_B$ (elementary)

$= k C_A^2$ (equimolar)

$$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$= C_{A0} \int_0^{C_A} \frac{dX_A}{k C_{A0}^2 (1-X_A)^2 / (1+\varepsilon_A X_A)^2}$$

$\tau_1 = \frac{0.316}{k C_{A0}}$

$\tau_p = \frac{1}{k \cdot} \left(\frac{X_A}{1-X_A} \right)_0^{0.96}$

$\varepsilon_A = \frac{V_{f0} - V_{i0}}{V_{i0}}$

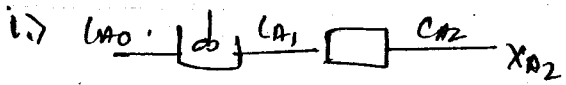
$1 - X_A = 2t$

$-dX_A = dt$

$\frac{dt}{t_0}$

$\tau = \frac{C_{A0} X_A}{-r_A}$

$$\tau_m = 10\,\tau_p = \frac{240}{K}$$

i) 

$$\tau_m = \frac{C_{A0} - C_{A1}}{K C_{A_1}^2}$$

$$\frac{240}{K} = \frac{C_{A0} \cdot 1 - C_{A1}}{K C_{A_1}^2}$$

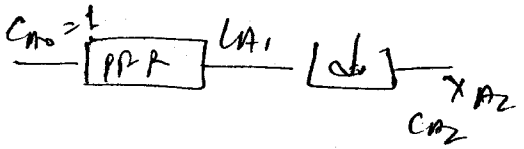
$$240\,C_{A_1}^2 + C_{A1} - 1 = 0$$

$$\tau_p = \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{K C_A^2}$$

$$\frac{24}{K} = \frac{1}{K}\left(\frac{1}{C_{A_2}} - \frac{1}{C_{A_1}}\right)$$

$$C_{A_2} = 0.025 \text{ mol/l}$$

$$X_{A_2} = 97.5\%$$



$$C_{A_1} = C_{A_0}(1 - X_A)$$

$$= 1\,(1 - 0.96)$$

$$= 0.04$$

$$\frac{240}{K} = \frac{C_{A_1} - C_{A_2}}{K C_{A_2}^2} \quad \text{2)}$$

$$C_{A_2} = 0.003$$

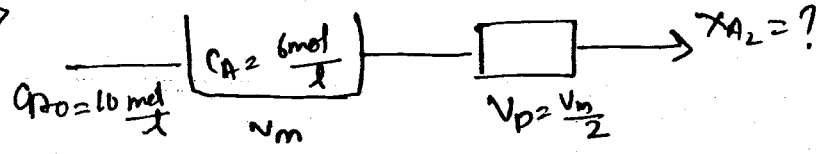
$$X_{A_2} = 99.7$$

—

-1 ± √1+
30.983
0.06.
0.062

Sept 14

Q.7



$V_0 = 1 \, l/sec$

If $-r_A = kC_A^2 \; \frac{mol}{l\,s}$

$\tau_m = \frac{C_{A_0} X_A}{-r_A}$

$\frac{V_m}{V_0} = \frac{C_{A_0} X_A}{C_{A_0}^2 (1-X_A)^2}$ | $\frac{C_{A_0} X_A}{kC_A^2} = \frac{C_{A_0} - C_A}{kC_A^2} = \frac{V_m}{V_0}$

$\frac{V_m}{1} = \frac{10 X_A}{k 6^2}$ | $V_m = \frac{10-6}{k \cdot 36} = \frac{4}{36} k$

$3.6 V_m k = X_A$ | $k = \frac{X_A}{3.6 V_m}$

$\tau_p = C_{A_0} \int_0^{X_{A_2}} \frac{dX_A}{kC_A^2}$

$= \int_0^{X_{A_2}} \frac{dX_A}{\frac{X_A}{3.6 V_m} C_{A_0}^2 (1-X_{A_2})^2}$

$= \frac{\Delta X V_m}{\Delta X} = 0.6 \, V_m$

$\tau_p = \frac{V_p}{V_0} = \frac{1}{k} \int_{C_{A_2}}^{C_{A_1}} \frac{dC_A}{-r_A = kC_A^2}$

$\frac{V_p}{V_0} = \frac{1}{k} \left[\frac{1}{C_{A_2}} - \frac{1}{6} \right]$

$\frac{V_m}{2} = \frac{1}{k} \left(\frac{1}{C_{A_2}} - \frac{1}{6} \right)$

$\frac{4k}{36 \times 2} = \frac{1}{k} \left[\frac{1}{C_{A_2}} - \frac{1}{6} \right]$

$C_{A_2} = 4.5 \; mol/l$

$X_{A_2} = 1 - C_{A_2}$

$= 55\%.$

Multiple Rxn System :—

↓ Series rxn ⇒ $A \xrightarrow[n_1]{k_1} R \xrightarrow[n_2]{k_2} S$ (R: desired, S: undesired)

$-r_A = k_1 C_A^{n_1}$

$r_R = k_1 C_A^{n_1} - k_2 C_R^{n_2}$

↳ Parallel rxn ⇒ $A \xrightarrow[n_1]{k_1} R$, $A \xrightarrow[n_2]{k_2} S$

$-r_A = k_1 C_A^{n_1} + k_2 C_A^{n_2}$

$r_R = k_1 C_A^{n_1}$

↳ Complex rxn ⇒ $A \to R \to S$, $R \to T$ or $A + B \to R \xrightarrow{+B} S$

↳ Independent rxn ⇒ $A + B \to C + D$, $R + S \to P + Q$

Parallel Rxn :—

$A \xrightarrow[n_1]{k_1} R$ (desired), $r_R = k_1 C_A^{n_1}$

$A \xrightarrow[n_2]{k_2} S$ (undesired), $r_S = k_2 C_A^{n_2}$

Selectivity

↳ overall selectivity = $\frac{\text{Moles of desired pdt formed}}{\text{Moles of undesired pdt formed.}}$

↳ Instantaneous Selectivity $S = \frac{\text{rxn rate of desired pdt}}{\text{rxn rate of undesired pdt.}}$

$$S_{R/S} = S = \frac{r_R}{r_S}$$

$$\boxed{S_{R/S} = k_1/k_2 \, C_A^{n_1 - n_2}}$$

Case-I if $n_1 > n_2$,

$$S_{R/S} = k_1/k_2 \, C_A^{\Delta n > 0}$$

∴ Keep high C_A for S_{max}

Case-II if $n_1 < n_2$,

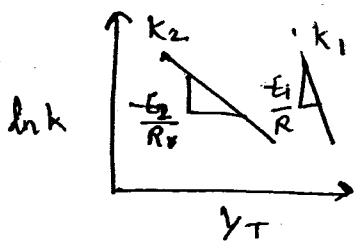
$$S_{R/S} = k_1/k_2 \, C_A^{\Delta n < 0}$$

Case III - if $n_1 = n_2$

$S = k_1/k_2$

↳ if $E_1 > E_2$ $\left\{ \begin{matrix} T\uparrow, k\uparrow \\ T\downarrow, k\downarrow \end{matrix} \right\}$ $k \propto e^{-E/RT}$

$\ln k = -E/RT + \ln k_0$



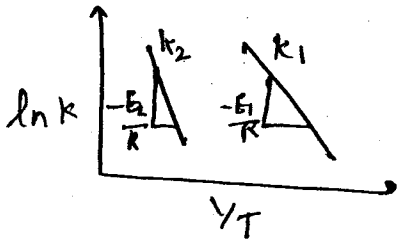
→ keep temp high

$T\uparrow, 1/T\downarrow, \ln k\uparrow$

↳ if $E_1 < E_2$

→ keep temp low.

$T\downarrow, 1/T\uparrow, \ln k\downarrow$



* $A + B \xrightarrow{k_1} R$, $r_R = k_1 C_A^{n_1} C_B^{m_1}$

$\xrightarrow{k_2} S$, $r_S = k_2 C_A^{n_2} C_B^{m_2}$

$$S_{R/S} = \frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^{n_1 - n_2} C_B^{m_1 - m_2}$$

Case I if $n_1 > n_2$, & $m_1 > m_2$

Keep C_A high & C_B high.

Case II if $n_1 > n_2$ & $m_1 < m_2$

Keep C_A high & C_B low

Case III if $n_1 < n_2$ & $m_1 < m_2$

Keep C_A low & C_B low.

Case IV if $n_1 < n_2$ & $m_1 > m_2$

Keep C_A low & C_B high

Case V If $n_1 = n_2$ & $m_1 = m_2$

$$\boxed{S_{R/S} = \frac{r_R}{r_S} = \frac{k_1}{k_2}}$$

⇒ if $E_1 > E_2$

keep temp high.

⇒ $E_1 < E_2$

keep temp low

How to maintain C_A high :—

↳ Use PFR

↳ keeping low conversion.

↳ Removing inerts from the system.

↳ for gas phase rxn increase the pressure.

How to keep C_A Low :—

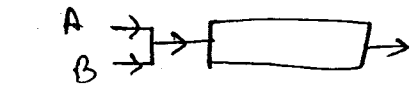
↳ Use CSTR

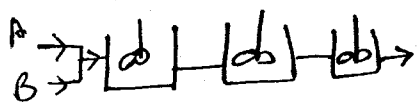
↳ keeping high conversion

↳ Adding inerts to the system

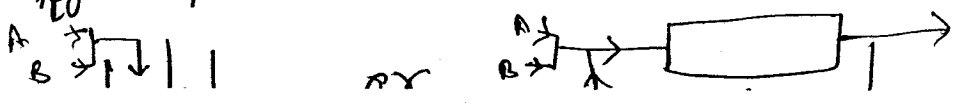
↳ for gaseous rxn decrease the pressure.

I.) If keep C_A high & C_B low :—

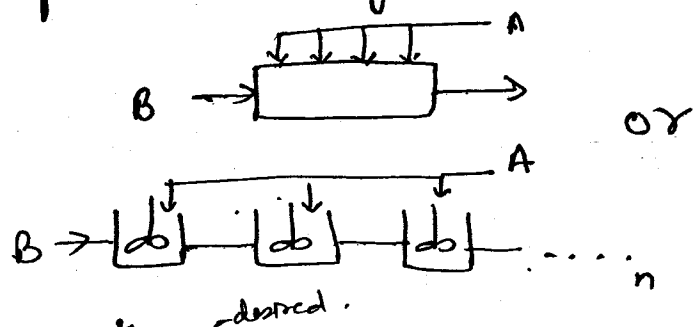




II.) If to keep C_A low & C_B low



iii) If C_A low & C_B high



Q) $A + B \xrightarrow{k_1} R + T$ (desired)

$A + B \xrightarrow{k_2} S + Q$

$r_R = k_1 C_A^{0.5} C_B^{1.3}$ $\quad E_1 = 80$ J/mol

$r_S = k_2 C_A^{0.8} C_B^{1}$ $\quad E_2 = 800$ J/mol

What should be the condition for this case.

Soln $\quad S_{R/S} = \frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^{0.5-0.8} C_B^{1.3-1}$

$= \frac{k_1}{k_2} C_A^{-0.3} C_B^{0.3}$

C_A low, C_B high, T low.

We will use CSTR for C_A, PFR for C_B.

Q) Reactant A decomposes by 3 simultaneous rxns $A \xrightarrow{k_1} X$, $A \xrightarrow{k_2} Y$, $A \xrightarrow{k_3} Z$

$r_X = 0.0001$ mol/l.s, $r_Y = 0.0015 C_A$ mol/l.s (desired), $r_Z = 0.008 C_A^2$ mol/l.s. If this rxn is conducted in a CSTR operating at 300 k and the activation energy for $E_1 = 10$ kcal/mol, $E_2 = 15$ kcal/mol, $E_3 = 20$ kcal/mol, $C_{A0} = 0.4$M, $V_0 = 2$ l/s.

i) What will be the optimum concentration of A for max selectivity

ii) " " " " max selectivity for the desired pdt.

$S = \frac{r_Y}{r_X + r_Z}$

$= \frac{k_2 C_A}{}$

$= C_{A0} \frac{dx}{k C_{A0}}$

$\frac{2}{V_m} = \frac{0.4}{0.001} \times A$

S_{max}

$$\frac{\partial S}{\partial C_A} = 0$$

$$\Rightarrow \frac{(k_1 + k_3 C_A^2) k_2 - k_2 C_A (2k_3 C_A)}{(k_1 + k_3 C_A^2)^2} = 0$$

$$k_1k_2 + k_2k_3C_A^2 - 2k_2k_3C_A^2 = 0$$

$$k_1k_2 - k_2k_3 C_{A_{opt}}^2 = 0$$

$$k_1 k_2 = k_2 k_3 C_{A_{opt}}^2$$

$$C_{A_{opt}} = (k_1/k_3)^{1/2}$$

$$C_{A_{opt}} = ~~0.268~~\ 0.1118 \text{ mol}/l.$$

$$S_{max} = \frac{k_2 C_{A_{opt}}}{k_1 + k_3 C_{A_{opt}}^2} = 0.838$$

Q) Physical significance of selectivity & yield.

Q) $A \rightarrow P$, PFR $V_m = 5l$ $F_{A_0} = 1$ lit/min $C_{A_0} = 2$ mol/lit

1) $C_A = 0.5$ mol/lit $k = ?$ min^{-1}

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

$$\frac{V}{F_{A_0}} = \frac{C_{A_0} - C_A}{kC_A}$$

$$\frac{5 l}{1 \text{ lit/min}} = \frac{2 - 0.5 \text{ mol/lit}}{k\ 0.5 \text{ mol/lit}}$$

$$\frac{5 \times 0.5}{1.5}$$

$$\frac{V}{F_{A_0}} = C_{A_0} \int_0^{X_A} \frac{dX_A}{kC_A}$$

$$\frac{5}{1} = \frac{1}{k} \int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A}$$

$$\frac{5 \times 2}{1} = \frac{1}{k} \ln \frac{C_{A_0}}{C_A}$$

$$\frac{5}{1} = k = 0.28 \text{ min}^{-1}$$

08/03/11

2011

32.

$P \to Q$, $n = 1$, $v_0 = 500\,cm^3/min$, $C_{P0} = 1.5\times10^{-4}\,mol/cm^3$, $V_m = 5\,l$, $X_A = 60\%$, CSTR

$k\,(in\,min^{-1}) = ?$

$$\frac{V_m}{v_0} = \frac{C_{A0}X_A}{kC_{A0}(1-X_A)}$$

$$\frac{5}{500\times10^{-3}} = \frac{\cancel{1.5\times10^{-4}}\times0.6}{k\,(0.4)}$$

$$k = 0.15\,min^{-1}$$

$1\times10^3\,cm^3$

53.

$$X_{AN} = 1 - \frac{1}{(1+\tau_i k)^N}$$

$$\tau_i = \frac{V_i}{V_0} = \frac{10^3\,cm^3}{500\,cm^3/min} = 2\,min$$

(3)73

2010

54.

$A \to B$ CSTR

$\tau = 2s$ $C_{A0} = 2\,mol/l$ $C_A = 1\,mol/l$

$$-r_A = \frac{kC_A}{K+C_A} \qquad k = 5\,mol/lit\,s^{-1}$$

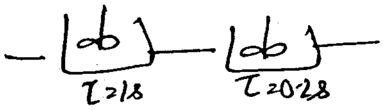
Value of K in mol/lit.

$$2 = \frac{2-1}{\frac{5\times1}{K+(1)}} = \frac{1}{5}(K+1)$$

$$10 = K+1$$

$$K = 9$$

55.



$C_A = 1\,mol/l$ $C_{A0} = ?$

$$0.2s = \frac{C_{A0}-C_A}{\frac{5\times1}{9+1}}$$

$$0.2 = \frac{C_{A0}-1}{}$$

$$1 < \frac{C_{A0} - 1.1}{0.5}$$

$$0.5 = C_{A0} - 1.1$$

$$C_{A0} = 1.6 \text{ mol/l}$$

Q:) $A \longrightarrow R$, $r_R = k_1 C_A^2$, $E_1 = 20$ cal/mol

$A \longrightarrow S$ (desired) , $r_S = k_2 C_A^2$, $E_2 = 30$ cal/mol

$S_{max} = ?$ for S,

$$S = \frac{k_2 C_A^2}{k_1 C_A^2}$$

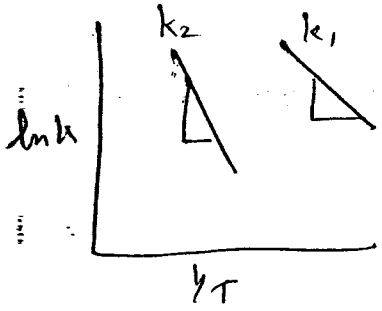
$$S = \frac{k_2}{k_1}$$

$$\frac{\partial S}{\partial C_A} = 0$$

$S_{max} = ?$

$E_2 > E_1$

$T \uparrow$



* Yield

↳ fractional yield

↳ Overall yield at outlet

$$\phi = \frac{\text{Moles of desired pdt formed}}{\text{Total moles of A reacted.}}$$

$$-r_A = k_1 C_A^{n_1} + k_2 C_A^{n_2} = r_R + r_S$$

$A \rightarrow R$ (desired), $A \rightarrow S$

$$\phi = \frac{d\frac{n_R}{V}}{dC_A} = -\frac{dC_R}{dC_A} = \frac{C_R - C_{R0}}{C_{A0} - C_A}$$

$$\Rightarrow \boxed{C_R = C_{R0} + \phi (C_{A0} - C_A)}$$

⇒ ϕ depends on type of Reactor

Fractional Yield :— ψ

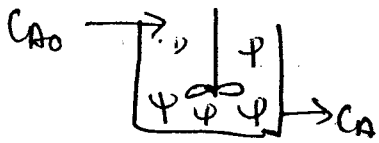
within the reactor

$$\psi = \frac{\text{rxn rate of desired product}}{\text{rxn rate of A}}$$

$$\psi = \frac{r_R}{-r_A} = \frac{k_1 C_A^{n_1}}{k_1 C_A^{n_1} + k_2 C_A^{n_2}}$$

$\phi = \overline{\psi}$ Average fractional yield.

for CSTR

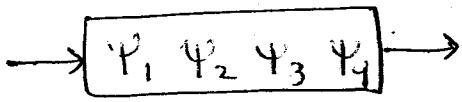


$$\overline{\psi} = \psi|_{C_A}$$

$$\phi_m = \overline{\psi} = \psi|_{C_A}$$

$C_A \rightarrow$ exit conc^n of A

for PFR



$$\overline{\psi} = \frac{\int_{C_{A0}}^{C_A} \psi \, dC_A}{\int_{C_{A0}}^{C_A} dC_A}$$

$$\overline{\psi} = \frac{\int_{C_{A0}}^{C_A} \psi \, dC_A}{C_A - C_{A0}}$$

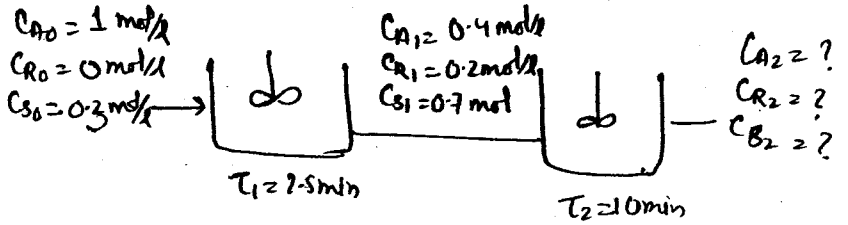
$$\overline{\psi} = \frac{\int_{C_A}^{C_{A0}} \psi \, dC_A}{(C_{A0} - C_A)}$$

$$\phi_p = \overline{\psi} = \frac{1}{(C_{A0} - C_A)} \int_{C_A}^{C_{A0}} \psi \, dC_A$$

$$C_R = C_{R0} + \phi_p (C_{A0} - C_A)$$

$$C_R = C_{R0} + \int_{C_A}^{C_{A0}} \psi\, dC_A$$

Q:> for a liq. phase rxn $A \rightarrow R$, $r_R = k_1 C_A^2$; $A \rightarrow S$, $r_S = k_2 C_A$ } $\frac{mol}{l\,min^{-1}}$, $C_{A0} = 1\ mol/l$, $C_{R0} = 0\ mol/l$, $C_{S0} = 0.2\ mol/l$. The feed contain these condition is enter to MFR in series $\tau_1 = 2.5$ min, $\tau_2 = 10$ min. Comp $C_{A1} = 0.4\ mol/l$, $C_{R1} = 0.2\ mol/l$, $C_{S1} = 0.7\ mol/l$. Find composition at the exit



$$2.5 = \frac{-0.2}{k_1 (0.4)}$$

$$C_R = C_{R0} + \Phi_m (C_{A0} - C_A)$$

$$\Psi_{R/A}$$

$$C_S = C_{S0} + \Phi_m (C_{A0} - C_A)$$

$$\Psi_{S/A}$$

$$\Phi = \frac{dC_R}{dC_A}$$

$$\Phi = \frac{dC_S}{dC_A}$$

Yield method

$$C_{R1} = C_{R0} + \Phi_{m_1}^{R} (C_{A0} - C_{A1})$$

$$\Psi_{R/A} = \frac{r_R}{-r_A} = \frac{k_1 C_A^2}{k_1 C_A^2 + k_2 C_A} = \frac{k_1 C_A}{k_1 C_A + k_2}$$

$$\Phi_{m_1}^{R} = \Psi_{R/A}\big|_{C_{A1}} = k_1 C_{A1} / k_1 C_{A1} + k_2$$

$$\boxed{C_{R1} = C_{R0} + \left(\frac{k_1 C_{A1}}{k_1 C_{A1} + k_2}\right)(C_{A0} - C_{A1})} \quad (1)$$

$$C_{S1} = C_{S0} + \Phi_{m_1}^{S} (C_{A0} - C_{A1})$$

$$\Phi_{m_1}^{S} = \Psi_{S/A}\big|_{C_{A1}} = \frac{r_S}{-r_A}\Big|_{C_{A1}} = \frac{k_2 C_A}{k_1 C_A^2 + k_2 C_A}\Big|_{C_{A1}}$$

$$\Phi_{m_1}^{S} = \frac{k_2}{k_1 C_{A1} + k_2}$$

$$\boxed{C_{S1} = C_{R0} + \frac{k_2}{k_1 C_{A1} + k_2} (C_{A0} - C_{A1})} \quad (2)$$

$$0.2 = 0 + \frac{0.4k_1}{0.4k_1 + k_2}(1-0.4)$$ First eqn

$$(0.4k_1 + k_2)0.2 = 0.4k_1(1-0.4)$$

$$0.08k_1 + 0.2k_2 = 0.24k_1$$

$$0.2k_2 = 0.16k_1$$

$$k_1 = 1.25k_2$$

$$0.7 = 0.2 + \frac{k_2}{k_1 \times 0.4 + k_2}(1-0.4)$$ Second eqn

$$(0.4k_1 + k_2)0.5 = 0.6k_2$$

$$0.2k_1 + 0.5k_2 = 0.6k_2$$

$$0.2k_1 = 0.1k_2$$

$$k_1 =$$

$$0.2 \times 1.25k_2 = 0.1k_2$$

Mole Balance Method

M.B over R tank 1

Rate of R in = Rate of R out + Rate of R over − Rate of R form^n

$$V_0 \cdot C_{R0} = V_0 C_{R1} + (0 - r_R) \cdot V_1$$

$$\tau_1 = \frac{V_1}{v_0} = \frac{C_{R1} - C_{R0}}{r_R} = \frac{C_{S1} - C_{S0}}{r_S}$$

$$2.5 = \frac{0.2-0}{k_1 C_{A1}^2}$$

$$2.5 \times (0.16)k_1 = 0.2$$

$$k_1 = 0.5 \text{ l/mol.min}$$

$$2.5 = \frac{0.7-0.2}{k_2 C_{A1}}$$

$$2.5 \times 0.4 k_2 = 0.5$$

$$k_2 = 0.5 \text{ min}^{-1}$$

$$10 = \frac{C_R - 0.2}{0.5 \times 6A_1^2}$$

$$C_{R_2} \; 5C_{A_1}^2 = C_{R_2} - 0.2$$

$$C_{R_2} = 0.227.$$

or

$$\tau_2 = \frac{C_{A_1} - C_{A_2}}{-r_A}$$

$$10 = \frac{C_{A_1} - C_{A_2}}{k_1 C_{A_2}^2 + k_2 C_{A_2}}$$

$$10 = \frac{0.4 - C_{A_2}}{0.5 C_{A_2}^2 + 0.4 C_A}$$

$$5C_A^2 + 4C_A + C_{A_2} - 0.4 = 0$$

$$5C_{A_2}^2 + 5C_{A_2} - 0.4 = 0$$

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\frac{-5 \pm \sqrt{25 - 8}}{10}$$

$$C_{A_2} = 0.074$$

$$\tau_2 = \frac{C_{S_2} - C_{S_1}}{r_S = k_2 C_{A_2}}$$

$$C_{S_2} = 0.998$$

Q.) $A \longrightarrow R$, $r_R = k_1 C_A^2$; $A \longrightarrow S$, $r_S = k_2 C_A$ } mol/l.s

$k_1 = 0.4$ l/mol.s

$k_2 = 2$ Sec^{-1}

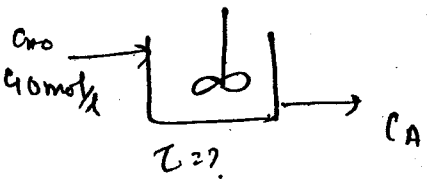
$C_{A_0} = 40$ mol/l

Calculate C_R, C_S, τ, & C_A

i) In MFR for $X_A = 0.9$

ii) In PFR for $X_A = 0.9$

1)



$k_1 = 0.4$

$k_2 = 2$

$C_{R_0} =$

$$\phi_{m_1} = \psi_{R/A}\big|_{C_A} = \frac{k_1 C_A^2}{k_1 C_A^2 + k_2 C_A} = \frac{k_1 C_A}{k_1 C_A + k_2}$$

$$C_R = C_{R_0} + \frac{k_1 C_A}{k_1 C_A + k_2}(C_{A_0} - C_{A_1})$$

$$C_S = C_{S_0} + \frac{k_2}{k_1 C_A + k_2}(C_{A_0} - C_{A_1})$$

$$C_R = C_{R_0} +$$

$$\tau_2 = \frac{C_{A_0} - C_{A_6}}{k_1 C_A^2 + k_2 C_A} = \frac{C_{A_0} X_A}{k_1 (1 - X_A)^2 C_{A_0}^2 + k_2 (1 - X_A) C_{A_0}}$$

$$\tau = \frac{40 - C_A}{0.4 C_A^2 + 2 C_A} = \frac{40 \times 0.9}{0.4 \times 0.01 \times 40^2 + 2 \times 0.1 \times 40}$$

$$= 40$$

$\tau =$ ~~17649~~ 2.5 sec.

i)

$C_R = 16$

$C_S = 20$

$\tau = 2.5$ sec

ii)

$C_R =$

$C_S = 28$

$\tau = 0.347$ sec

PFR

$$C_R = C_{R0} + \phi_p \cdot (C_{A0} - C_A)$$

$$\phi_p = \frac{\int_{C_A}^{C_{A0}} \psi dC_A}{(C_{A0} - C_A)}$$

$$\psi_{R/A} = \frac{r_R}{-r_A} = \frac{k_1 C_A}{k_1 C_A + k_2}$$

$$C_R = \int_{C_A}^{C_{A0}} \psi dC_A = \int_{C_{A2}}^{40} \left(\frac{0.4 C_A}{0.1 C_A + 2}\right) dC_A$$

$$C_S = C_{A0} - C_A - C_R$$

Oct-06,14

* Non Ideal Reactor

Fogler

RT (Residence tym)

- Ideal Reactor ⇓ → ∀ molecules have same RT
- Non-Ideal Reactors ⇓ → Different molecules have different RT.

Non-Ideal

- RTD
- model
- Mixing

Causes for non-idealities :—

⇒ Dead zone

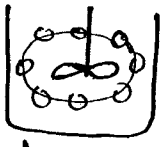
unbit unutilize or corner part of reactor.

infinite residence tym

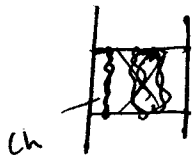
- By Tunning :-

small residence tym

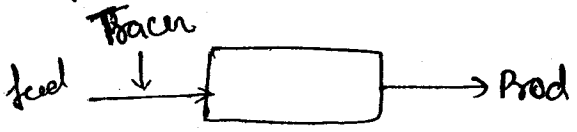
» Turbulence :-



» Channeling :- kind of by passing.



Residence Tym distribution



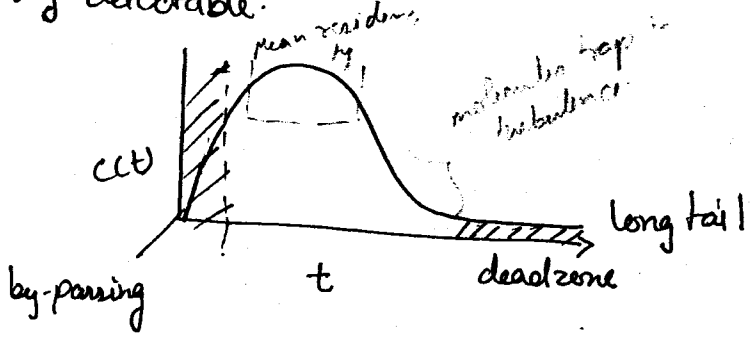
read.

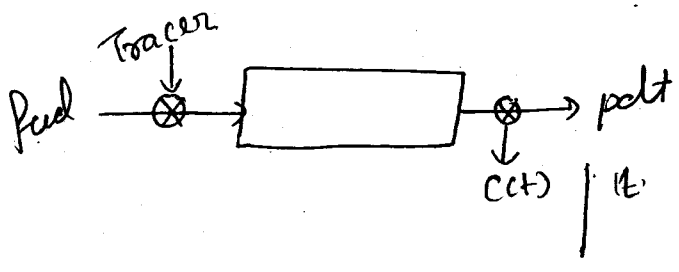
Tracer's property

→ Chemically Inert

→ Soluble in the feed Mixture

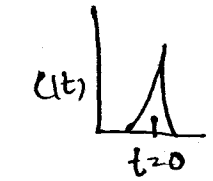
→ Easily detectable.





Tracer Input experiments

Pulse Input Step Input.



tracer input one shot

Q(8) $A \rightarrow P$, $n=1$,

P:) $1m^3$ CSTR followed by a $1m^3$ PFR

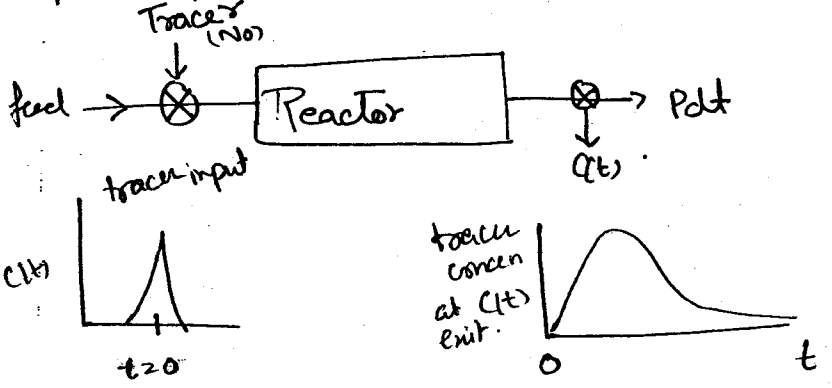
Q:) $2m^3$ CSTR

R:) $1m^3$ PFR followed by a $1m^3$ CSTR

S:) $1m^3$ CSTR followed by $1m^3$ CSTR

Ans b.) $X_P = X_R > X_S > X_Q$.

Pulse Input Experiment



Let 'No' amount of tracer is injected at one shot in the feedstream. the amt of tracer leaving the reactor b/w time t & t+dt,

$$dN = V_0 \cdot C(t)\, dt \quad \text{---(1)}$$

dividing 'No',

$$\frac{dN}{N_0} = \frac{V_0 \cdot C(t)\, dt}{N_0}$$

$\frac{dN}{N_0}$ → fraction of reactor leaving the reactor [illegible]

exit Age funct^n $\boxed{E(t) = \frac{V_0 \cdot C(t)}{N_0}}$

⇒ time taken by the molecule to leave the reactor.

$$\boxed{\frac{dN}{N_0} = E(t)\,dt}$$

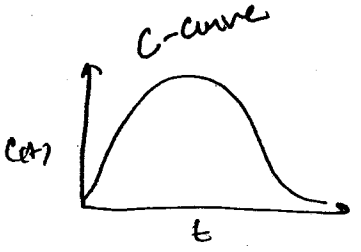
↳ fract^n of material leaving the reactor b/w time t & t+dt.

$$\int_0^{N_0} \frac{dN}{N_0} = \int_0^{\infty} E(t)\,dt$$

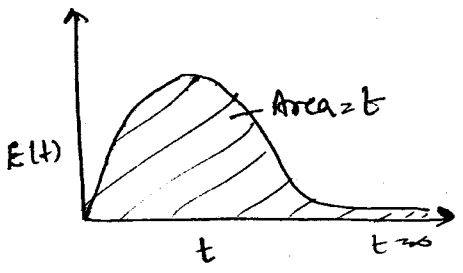
$$\frac{1}{N_0}(N)_0^{N_0} = \int_0^{\infty} E(t)\,dt$$

$$\frac{N_0}{N_0} = \int_0^{\infty} E(t)\,dt$$

$$\boxed{\int_0^{\infty} E(t)\,dt = 1}$$



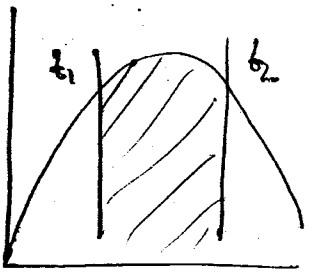
E-curve



Area of E-Curve represents the fracn of material leaving the reactor.

fract^n of material leaving the reactor b/w t_1 & t_2

$$= \int_{t_1}^{t_2} E(t)\,dt$$



$$\int_0 dN = \int_0 V_0 C(t)\,dt$$

$$\Rightarrow \quad N_0 = V_0 \int_0^\infty C(t)\,dt \qquad \because E(t) = \frac{V_0 \cdot C(t)}{N_0}$$

$$\frac{C(t)}{E(t)} = \int_0^\infty C(t)\,dt$$

$$\boxed{E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}}$$

* Moments of RTD

→ **nth moment RTD,**

$$\mu_n = \int_0^\infty t^n \cdot E(t)\,dt.$$

→ **Zeroth moment of RTD,**

$$\mu_0 = \int_0^\infty t^0 \cdot E(t)\,dt = \int_0^\infty E(t)\,dt = 1$$

* First Moment of RTD

$$\boxed{\bar{t} = \mu_1 = \int_0^\infty t \cdot E(t)\,dt}$$

$$\bar{t} = \int_0^\infty t \cdot \left[\frac{C(t)}{\int_0^\infty C(t)\,dt}\right] dt$$

$$\boxed{\bar{t} = \frac{\int_0^\infty t \cdot C(t)\,dt}{\int_0^\infty C(t)\,dt}}$$

* Second moment of RTD:-

$$\mu_2 = \int_0^\infty t^2 \cdot E(t)\,dt$$

Variance

$$\sigma^2 = \mu_2 - \mu_1^2$$

$$\boxed{\sigma^2 = \int_0^\infty t^2 \cdot E(t)\,dt - \bar{t}^2}$$

Variance (Central Moment of ...)

$$\boxed{\sigma^2 = \int_0^\infty (t-\bar{t})^2 \cdot E(t)\,dt}$$

$$\sigma^2 = \int_0^\infty (t-\bar{t})^2 E(t)\,dt$$

$$= \int_0^\infty t^2 \cdot E(t)\,dt + \int_0^\infty \bar{t}^2 E(t)\,dt - \int_0^\infty 2t \cdot \bar{t}\, E(t)\,dt$$

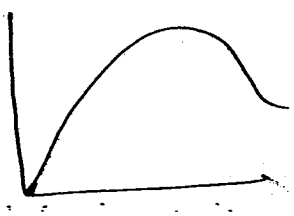
$$\sigma^2 = \mu_2 + \bar{t}^2 \int_0^\infty E(t)\,dt - 2\bar{t}\int_0^\infty t \cdot E(t)\,dt$$

$$= \mu_2 + \bar{t}^2 - 2\bar{t}\,\bar{t}$$

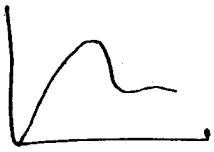
$$= \mu_2 - \bar{t}^2$$

σ^2 = Spreadness of curve.

σ^2 high



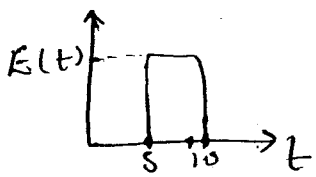
σ^2 small



Gate 2004

40)

t	C(t)	$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C(t)}{50}$
0	0	0
5	10	1/5
10	10	1/5



$y = mx + c$

$E = 0 \cdot t + 1/5 \Rightarrow$

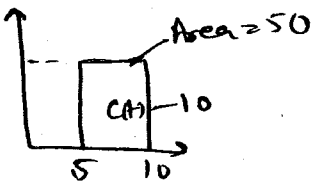
$E(t) = 1/5$ for $5 < t < 10$

$$\bar{t} = \int_0 t \cdot E(t)\,dt$$

$$\bar{t} = \int_5^{10} t \cdot \tfrac{1}{5}\,dt$$

$$= \frac{1}{5}\left(\frac{t^2}{2}\right)_5^{10}$$

$$\bar{t} = 7.5 \text{ min}$$



$$\bar{t} = \frac{\int_0^\infty t \cdot C(t)\,dt}{\int_0^\infty C(t)\,dt}$$

$$= \frac{\int_5^{10} t\,dt}{\int_5^{10} dt} = 7.5$$

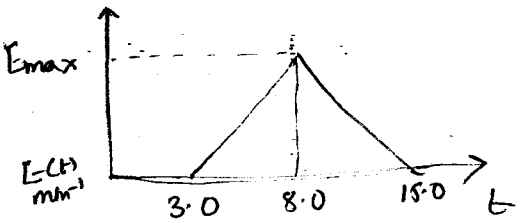
2005

8(a)

Area of E curve = 1

$$\frac{1}{2} \times (15-3) \times E_{max} = 1$$

$$E_{max} = \frac{1}{6}$$



8(b)

$$\bar{t} = \int_0^{15} t\,E(t)\,dt$$

$$(y - y_1) = \frac{y_2 - y_1}{x_2 - x_1}(x - x_1)$$

(x_2, y_2)

(x_1, y_1)

$$E_1(t) - 0 = \frac{1/6 - 0}{8 - 3}(t - 3)$$

$$= \frac{1}{30}(t-3) \quad 3 < t < 8$$

1/6, 8

$$E_2(t) = -\frac{1}{\cdots}(t - 15)$$

$$\bar{t} = \int_3^{15} t \left(\frac{1}{30}(t-3) + \left(-\frac{1}{42}(t-15)\right) dt \right.$$

$$= \int_3^{15} \left(\frac{t^2}{30} - \frac{3t}{10} - \frac{t^2}{42} + \frac{t}{2} \right) dt$$

$$= \int_3^{15} \frac{8 t^2}{1260} + \frac{28t}{20} \, dt$$

$$\frac{8t^3}{3 \times 1260} + \frac{28 t^2}{5 \times 2} \Big|_3^{15}$$

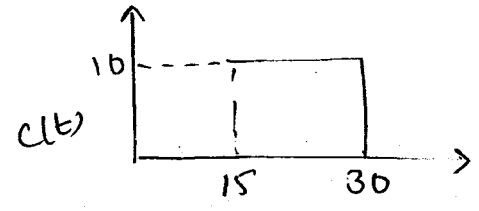
$$\therefore \left| \frac{15^3 \times 8}{3 \times 1260} + \frac{15^2}{5} - \frac{3^3 \times 8}{3 \times 1260} + \frac{3^2}{5} \right|$$

$$= 52.142 -$$

$$=$$

final ans =

Q.)



find $\bar{t} = ?$

$$\bar{t} = \frac{\int_0^\infty t\, C(t)\, dt}{\int_0^\infty t\, C(t)\, dt}$$

$y = mx + c$

$C(t) = 10$

$$= \frac{\int_0^\infty t \cdot 10\, dt}{\int_0^\infty 10\, dt}$$

$$\bar{t} = \frac{\int_{15}^{30} t\, C(t)\, dt}{\int_{15}^{30} C(t)\, dt}$$

$$= \frac{t^2/2 \Big|_{15}^{30}}{t \Big|_{15}^{30}} = \frac{\frac{30^2}{2} - \frac{15^2}{2}}{30 - 15}$$

$$= \frac{450 - 112.5}{30 - 15} =$$

$$= 22.5$$

OR

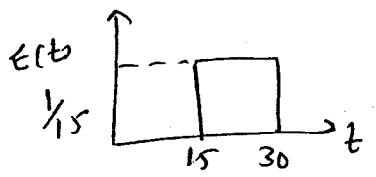
$$t = \int_0 t \cdot E(t)\,dt$$

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t)\,dt}$$

$$= \frac{C(t)}{\int_{15}^{30} 10 \cdot dt}$$

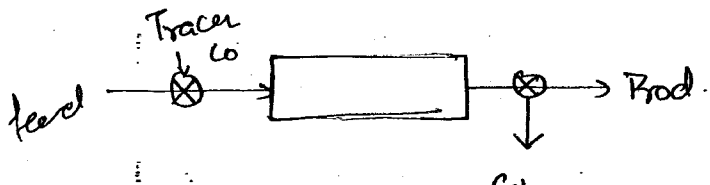
$$E(t) = \frac{C(t)}{150}$$

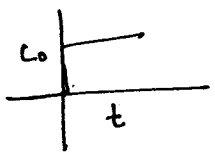
t	C(t)	E(t)
0	0	0
15	10	$10/150 = 1/15$
30	10	$10/150 = 1/15$

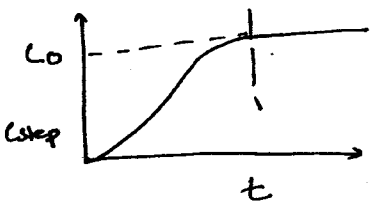


$E(t) = \frac{1}{15}$

⇒ Step Input Experiment:—







MB over tracer

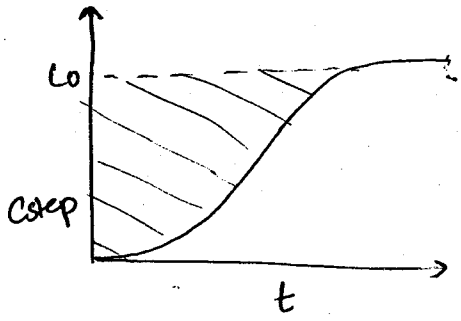
Rate of tracer input = Rate of tracer out + Rate of tracer Accumulated.

$$V_0 C_0 = V_0 \cdot C_{step} + V \cdot dC/dt$$

$$\frac{dC}{dt} + \frac{V_0}{V} C_{step} = \frac{V_0}{V} \cdot C_0$$

$$\frac{dC}{dt} + \frac{1}{\tau} C_{step} = 1/\tau\, C_0$$

On solving,



$\int_0^y x\,dy$.

$\int_0^x y\,dx$

$$\text{Area} = \int_0^{C_0} t \cdot dC_{step}$$

$$dC_{step} = C_0 \left(0 + \frac{1}{\tau} \cdot e^{-t/\tau} \cdot dt\right)$$

$$\int_0^{C_0} t \cdot dC_{step} = \int_0^{\infty} \frac{C_0}{\tau} \cdot t \cdot e^{-t/\tau}\, dt$$

$$= \frac{C_0}{\tau}\left[t \cdot \frac{e^{-t/\tau}}{-1/\tau} - \int\left\{1 \cdot \frac{e^{-t/\tau}}{-1/\tau}\right\}\right]_0^{\infty}$$

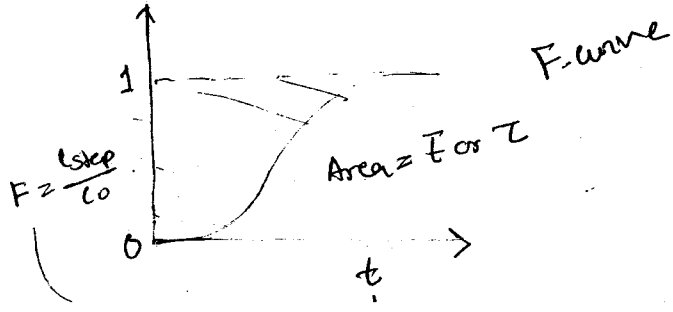
$$= \frac{C_0}{\tau}\left[-t \cdot \tau \cdot e^{-t/\tau} - \tau^2 \cdot e^{-t/\tau}\right]_0^{\infty}$$

$$\int_0^{C_0} t\, dC_{step} = \frac{C_0}{\tau}\left[(\infty \cdot e^{-\infty} - 0 \cdot e^{-0}) - \tau^2(e^{-\infty} - e^{0})\right]$$

$$= \frac{C_0}{\tau}\left[-\tau^2(0-1)\right]$$

$$\boxed{\int_0^{C_0} t \cdot dC_{step} = C_0 \times \tau}$$

$$\boxed{\bar{t} = \tau = \frac{1}{C_0}\int_0^{C_0} t \cdot dC_{step}}$$



E(t) & F(t)

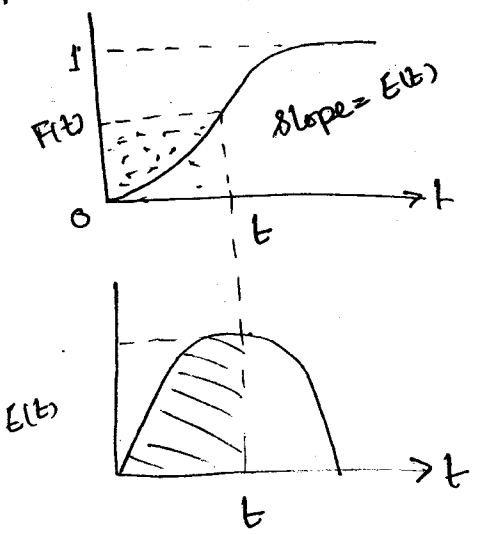
↙ fraction of material leaving the reactor at time 't'

at time kitna fraction bhar aa rha h.

↘ fracth of material left the reactor till time t,

at time kitna fraction bhr aa chuka h.

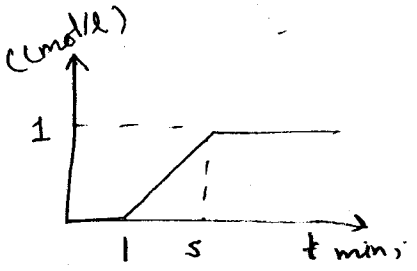
* Relationship btw E & F Curve



$$F(t) = \int_0^t E(t)\,dt$$

$$\boxed{E(t) = \frac{d}{dt} F(t)}$$

Gate 2008 Q 74)



$$V_0 = F_0 / C_0$$

$$V_0 = \frac{1 \text{ mol/min}}{1 \text{ mol/l}}$$

$$V_0 = 1 \text{ l/min}$$

15.) $E = \frac{1}{C_0}\int_0^{\infty} t \cdot dC_{step}$

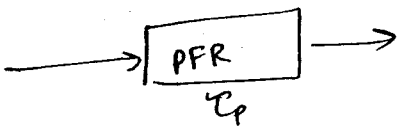
$= \frac{1}{1}\left[5\times 1 - \frac{1}{2}\times(5-1)\times 1\right]$

$= 3$

* RTD in PFR :—

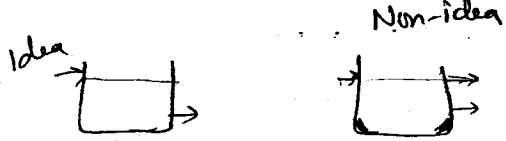
delay τ_p

Train → Japan

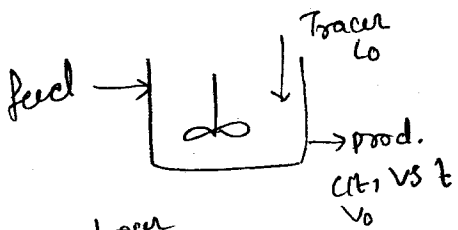


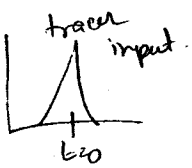
$$E(t) = \delta(t-\tau_p)$$

* RTD in CSTR :—



$X_{A_1} > X_{A_2}$





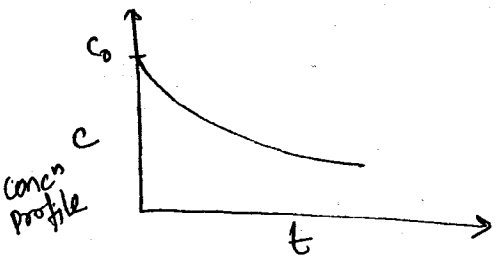
MB over tracer

Rate of tracer in = Rate of tracer out + Rate of tracer acc.

$0 = V_0 \cdot C + V\frac{dC}{dt}$ / Conc^n accumulation = conc^n with in the reactor

$\Rightarrow -\frac{dC}{C} = \frac{V_0}{V}dt$

$$C = C_0 e^{-t/\tau_m}$$

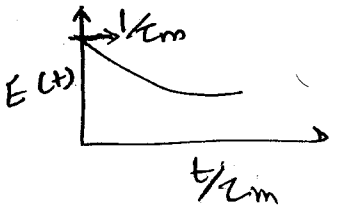


$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}$$

$$E(t) = \frac{C_0 e^{-t/\tau_m}}{\int_0^\infty C_0 \cdot e^{-t/\tau_m}\,dt}$$

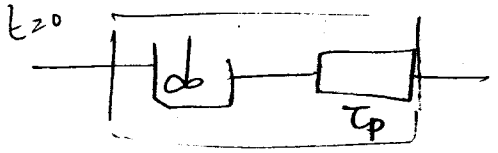
$$= \frac{C_0 e^{-t/\tau_m}}{\frac{C_0 e^{-t/\tau_m}}{-1/\tau_m}\Big|_0^\infty}$$

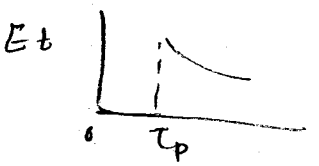
$$\boxed{E(t) = \frac{e^{-t/\tau_m}}{\tau_m}}$$



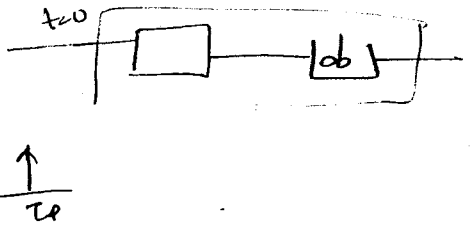
CSTR = decay
PFR = delay

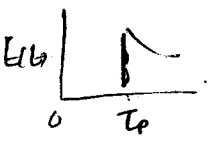
* TPTD in CSTR & PFR Series



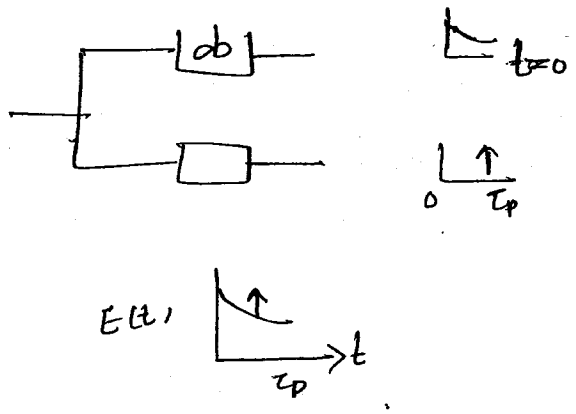


$$E(t) = \begin{cases} 0, & t < \tau_p \\ \frac{e^{-(t-\tau_p)/\tau_m}}{\tau_m}, & t > \tau_p \end{cases}$$





* RTD for CSTR ..... .



Oct 08,14

Q.) C-Curve, E-Curve, F-Curve,

$\bar{t}$ = ?, σ^2 = ?, fract^n leaving b/w 20-25 sec.

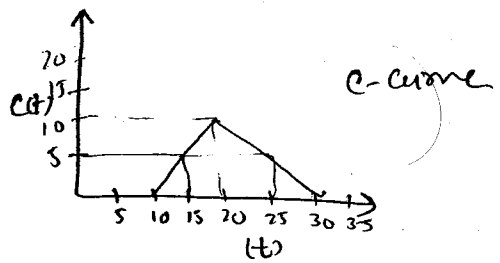
fract^n that spent 20 sec time less than 20 sec.

t	C(t)	$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} = \frac{C(t)}{100}$
0	0	0
5	0	0
10	0	0
15	5	1/20
20	10	1/10
25	5	1/20
30	0	0

C-curve

$$\bar{t} = \frac{\frac{30^2}{2} - \frac{10^2}{2}}{\frac{30}{2} - \frac{10}{2}}$$

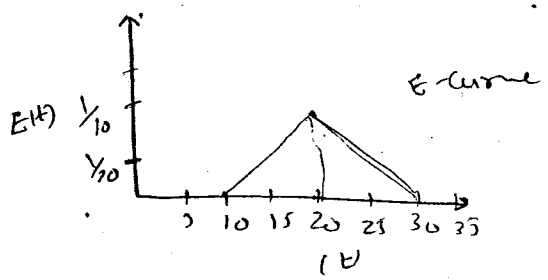
$$= 40$$



E-curve

$$E_1(t) = \frac{1}{100}(t-10) \quad \text{for } 10<t<20$$

$$E_2(t) = -\frac{1}{100}(t-30) \quad \text{for } 20<t<30.$$



$$\bar{t} = \int_{10}^{30} t \cdot E(t)\,dt$$

$$= \int_{10}^{20} \frac{1}{100}(t-10)\,t\,dt + \int_{20}^{30} -\frac{1}{100}(t-30)\,t\,dt$$

$$\frac{1}{100}\left[\frac{t^3}{3} - 10\frac{t^2}{2}\right]_{10}^{20} + -\frac{1}{100}\left[\frac{t^3}{3} - 30\frac{t^2}{2}\right]_{20}^{30}$$

$$= \frac{1}{100}\left[\frac{20^3}{3} - \frac{10\times 20^2}{2} - \frac{20^3}{3} + \frac{10\times 10^2}{2} - \frac{30^3}{3} + \frac{30\times 30^2}{2} + \frac{20^3}{3} - \frac{30\times 20}{2}\right]$$

$\bar{t} = 20$ sec.

$$\sigma^2 = \int_{10}^{30} t^2 \cdot E(t)\,dt - \bar{t}^2$$

Ans: 16.67 sec.

$=$

$$F(t) = \int_0^t E(t)\,dt$$

$E(t) = 0$ for $t < 10$.

$$F(15) = \int_{10}^{15} E_1(t)\,dt$$

$$= 0.125$$

$$f(20) = \int_{10}^{20} E_1(t)\,dt$$

$$= 0.5$$

$$f(25) = \int_{10}^{25} E(t)\,dt \Rightarrow \int_{10}^{20} E_1(t)\,dt + \int_{20}^{25} E_2(t)\,dt$$

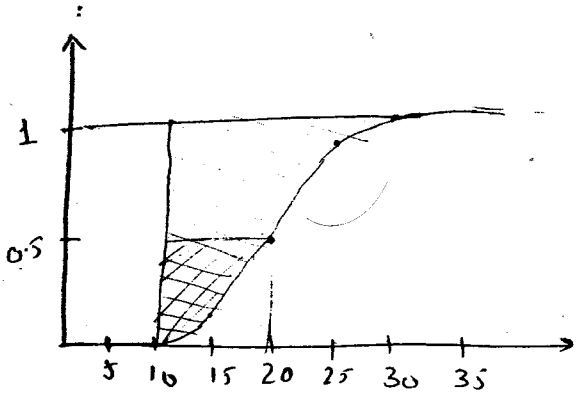
$$= 0.5 + 0.375$$

$$= 0.875$$

$$f(30) = \int_{10}^{30} E(t)\,dt \Rightarrow \int_{10}^{20} E_1(t)\,dt + \int_{20}^{30} E_2(t)\,dt$$

$$= 0.5 + 0.5$$

$$= 1.$$



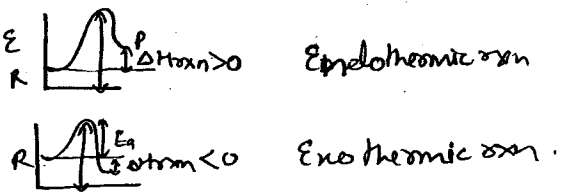
fraction leaving btw 20-25 $\int_{20}^{25} E_2(t)\,dt$

$F(25) - F(20)$

* Non-isothermal Reactor or Temp & Pressure Effect :—

→ Endo absorb

→ Exo release



~~for Reversible Rxns~~

for Endothermic Rxns

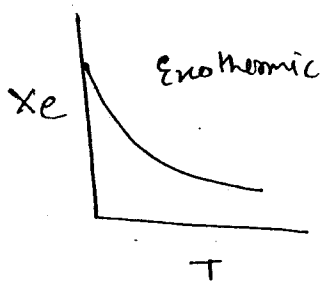
the Equilibrium K & Equilibrium Xe

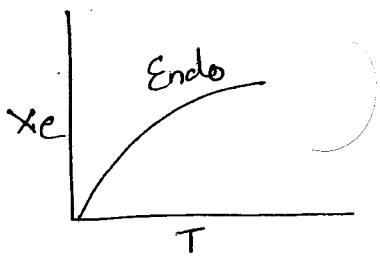
both ↑ with ↑ in temp^r.

for Exothermic Rxns

the Ke & Xe both ↓

with ↑ in temp^r.





Eg $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

$$-r_A = k_1 C_A - k_2 C_B$$

at Equilibrium

$$-r_A = 0$$

$$\Rightarrow k_1 C_{Ae} - k_2 C_{Be} = 0$$

$$\boxed{K_e = \frac{k_1}{k_2} = \frac{C_{Be}}{C_{Ae}}}$$

$$K_e = \frac{C_{A0} \cdot X_e}{C_{A0}(1-X_e)}$$

$$\boxed{K_e = \frac{X_e}{1-X_e}} \quad \text{or} \quad \boxed{X_e = \frac{K_e}{1+K_e}}$$

⇒ $K_e = f(T)$ only

$$\boxed{\Delta G^\circ = -RT \ln K_e}$$

$$\boxed{\frac{\partial \ln K_e}{\partial T} = \frac{\Delta H_{rxn}}{RT^2}}$$ Vant hoff Eqn

$$\int_{K_{e_1}}^{K_{e_2}} \partial \ln K_e = \int_{T_1}^{T_2} \frac{\Delta H_{rxn}}{RT^2} \cdot \partial T$$

$$\boxed{\ln\left(\frac{K_{e_2}}{K_{e_1}}\right) = \frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$K_{e_2} = K_{e_1} \exp\left\{\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right\}$$

$$X_e = f(T)$$

$$K_e = K_1/K_2 \longrightarrow \infty ,$$

$$K_1 \longrightarrow \infty$$

Irreversible

$$X_e = \frac{\infty}{1+\infty} \longrightarrow 1$$

for ~~Irreversible~~ Spontaneous rxns

$$\boxed{\Delta G^\circ = -\infty}$$

Spontaneous = naturally start + Irreversible rxn.

$\Delta G^\circ < 0$ Spontaneous in fwd dirn

$\Delta G^\circ = 0$ rxn is in Equilibrium

$\Delta G^\circ > 0$ Spontaneous in backward dirn

$\Delta G^\circ > 0$, $K_e << 1 \Rightarrow \frac{K_1}{K_2} X < 1 \Rightarrow k_1 << k_2$

⇒ $X_e = f(T, P, \text{inerts})$ or CHe

$$aA + bB \longrightarrow cC + dD$$

$$\nu = c + d - a - b$$

$$k = \frac{C_C^c C_D^d}{C_A^a C_B^b} = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$k = \frac{y_C^c y_D^d}{y_A^a y_B^b} = P^{\nu}$$

$$\frac{y_C^c y_D^d}{y_A^a y_B^b} = k \cdot P^{-\nu}$$

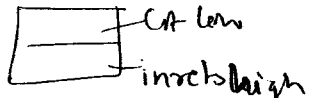
if $\nu > 0$, $A \rightarrow 2B$

P ↑ , x_e ↓ for Max. x_e, keep low pr.
Add inerts to the feed.

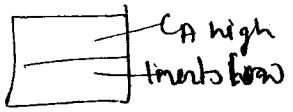
if $\nu < 0$, $2A \rightarrow B$

P ↑ , x_e ↑ , keep high pr for Max x_e.
Remove inerts from feed

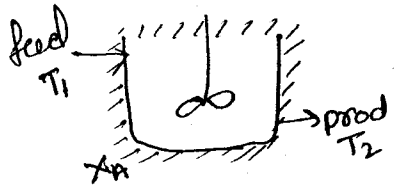
$P_A = C_A RT$



P_A high



* Adiabatic Reactors



Energy in − Energy out = Energy absorbed/released

$A \longrightarrow R$, ΔH_{rxn}

$$nC_pT_1 - nC_pT_2 = \Delta H_{rxn} \times n X_A$$

Assumption

C_p is constant for rxn mix.

$$\boxed{X_A = \frac{C_p(T_2 - T_1)}{-\Delta H_{rxn}}}$$

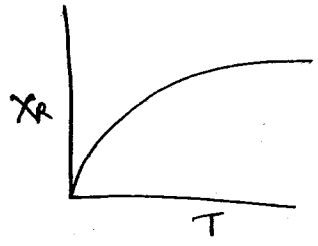
* Non Adiabatic Reactors :—

Energy In − Energy out = Energy absorb or released + Energy less.

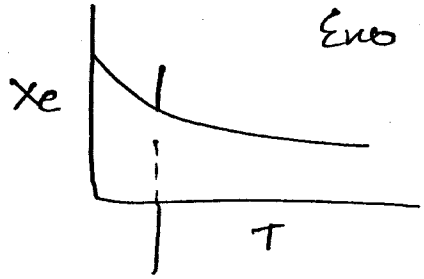
$$C_p T_1 - C_p T_2 = \Delta H_{rxn} X_A + Q.$$

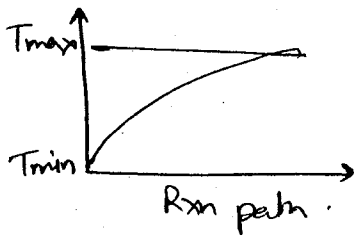
$$X_A = \frac{C_p(T_2 - T_1) + Q}{-\Delta H_{rxn}}$$

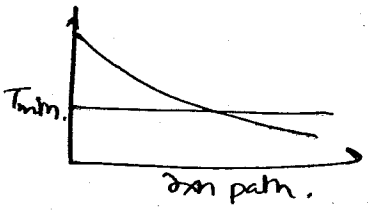
Endo



Exo







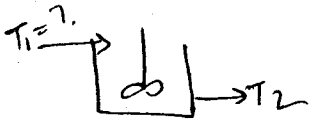
Gate -2004

Q-> 76.)

b.)

Q77.)

$A + B \longrightarrow P$



$C_{A0} = 4\ k\ mol/m^3$

$V_0 = 8\ m^3/h$

$T_2 = 390\ K.$

$\Delta H_{rxn} = -50\ kJ/mol$

$\rho_{rm} = 1000\ kg/m^3,$

C_p Sp. heat$_{mix}$ = 2 kJ/kg·k.

∵ Since acc- to Input temp cannot be greater than outlet temp.

Endothm
minm temp
$X_A = 1$

$$X_A = \frac{C_p (T_2 - T_1)}{-\Delta H_{rxn}}$$

For max^n temp $X_A = 1$

$$1 = \frac{C_p (390 - T_1)}{+50}$$

$$250 = 390 - T_1$$

$$C_p = 2\,kJ/kgK \times 1000\,kg/m^3 \times \frac{1\ m^3}{4\ kmol} \times \frac{1\ kmol}{10^3\ mol}$$

$$= \frac{2}{4}\ kJ/mol\,k$$

Gate
2008 → 58
2009 → 39
2012 → 41

$$1 = \frac{2/4\ (390 - T_1)}{50}$$

$$50 \times 2 = 390 - T_1$$

$$T_1 = 290\ K$$

Oct 09, 14

* Heterogeneous Rxn System

More than one phase exist.

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt}$$

This method is not used as we r not able to calculate the volume of rxn mix which consist of diff phases.

→ Unit Surface area of two Immiscible fluid Systems

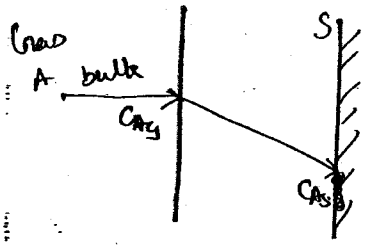
$$-r_A'' = -\frac{1}{S}\frac{dN_A}{dt}, \quad \frac{mol}{m^2 s}$$

→ Unit weight of Solid present in fluid - Solid System;

$$-r_A' = -\frac{1}{W}\frac{dN_A}{dt}, \quad \frac{mol}{kg \cdot s}$$

If catalyst or any solid phase is present

* Rate Controlling Step :—



rate of MT, $r_1'' = k_g (C_{Ag} - C_{As})$

rate of rxn, $r_2'' = k'' C_{As}$

$$r'' = r_1'' = r_2''$$

$$r'' = k_g (C_{Ag} - C_{As}) = k'' C_{As}$$

$$C_{As} = \frac{k_g C_{Ag}}{(k_g + k'')}$$

$$r'' = k'' \cdot \frac{k_g C_{Ag}}{k_g + k''}$$

$$\boxed{r'' = \frac{C_{Ag}}{\frac{1}{k_g} + \frac{1}{k''}}}$$

Case I If $k_g >> k''$,

$$\frac{1}{k_g} << \frac{1}{k''}$$

$$r'' = \frac{C_{Ag}}{1/k''}$$

$$\boxed{r'' \simeq k'' C_{Ag}}$$

rate controlling will be rxn rate.

Case-II If $k'' >> k_g$

$$\frac{1}{k''} << \frac{1}{k_g}$$

$$\boxed{r'' = k_g C_{Ag}}$$

rate controlling step will be M.T.

Heterogeneous Rxns

- ↳ catalytic Rxns
- ↳ Non-catalytic Rxns.

Steps of Catalytic Rxns :—

1.) Diffusion / convective M.T from bulk phase to solid surface (surface Diffusion Step).

*2.) Diffusion of molecules from solid surface to inside the pores (pore diffusion step)

3.) Adsorption of molecules on the pore walls.

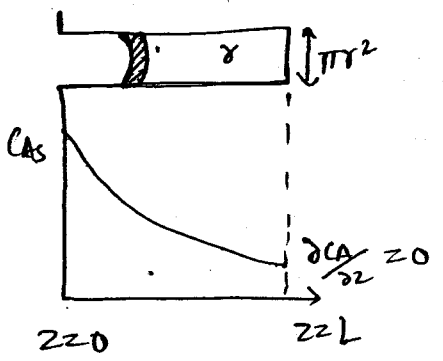
*4.) Chemical Rxn

5.) Desorption of product molecules.

6.) Diffusion of product molecules from inside the pores to solid surface. (Reverse pore diffusion)

7.) Diffusion of prdt molecules from solid surface to bulk phase (reverse surface diffusion step)

* Surface Rxn + Pore diffusion :—



Rate of A Input = Rate of A out + Rate of A disapp.

$$-D\frac{\partial C_A}{\partial z}\Big|_z \times \pi r^2 = -D\frac{\partial C_A}{\partial z}\Big|_{z+dz} \times \pi r^2 + (-r_A'').S$$

$$\Rightarrow D\cdot\left[-\frac{\partial C_A}{\partial z}\Big|_z + \frac{\partial C_A}{\partial z}\Big|_{z+dz}\right]\pi r^2 = (-r_A'').2\pi r\,dz.$$

$$\Rightarrow \frac{-\frac{\partial C_A}{\partial z}\Big|_z + \frac{\partial C_A}{\partial z}\Big|_{z+dz}}{dz} = (-r_A'')\cdot\frac{2}{rD}$$

$$\frac{\partial^2 C_A}{\partial z^2} = (-r_A'')\cdot\frac{2}{rD}$$

for 1st order rxn

$$-r_A'' = k''C_A$$

$$\Rightarrow \frac{\partial^2 C_A}{\partial z^2} = \frac{k''C_A\cdot 2}{rD}$$

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

$$-r_A'' = -\frac{1}{S}\frac{dN_A}{dt} = k''C_A$$

$$\frac{S}{V} = \frac{k}{k''}$$

$$\frac{2\pi rL}{\pi r^2 L} = k/k''$$

$$\frac{\partial^2 C_A}{\partial z^2} = \frac{kC_A}{D}$$

$$\frac{\partial^2 C_A}{\partial z^2} - \frac{k}{D} C_A = 0$$

Say $k/D = m^2$

$$\frac{\partial^2 C_A}{\partial z^2} - m^2 C_A = 0$$

$$D^2 - m^2 = 0$$

$$D = \pm m$$

$$C_A = C_1 e^{mz} + C_2 e^{-mz}$$

Using Boundary condition 1 :-

at $z = 0$, $C_A = C_{AS}$

B.C 2

at $z = L$, $\frac{\partial C_A}{\partial z} = 0$

$$C_A = C_1 + C_2 \quad -(1)$$

$$\frac{\partial C_A}{\partial z} = C_1 m e^{mz} - C_2 m e^{-mz}$$

$$0 = C_1 m e^{mL} - C_2 m e^{-mL}$$

$$C_1 m e^{mL} = C_2 m e^{-mL}$$

$$C_1 = C_2 \frac{e^{-mL}}{e^{mL}} \quad -(2)$$

from (1) & (2),

$$C_2 + C_2 \frac{e^{-mL}}{e^{mL}} = C_{AS}$$

$$C_2 (e^{mL} + e^{-mL}) = C_{AS} e^{mL}$$

$$C_2 = \frac{C_{AS} e^{mL}}{e^{mL} + e^{-mL}}$$

$$C_1 = \frac{C_{AS} e^{-mL}}{e^{mL} + e^{-mL}}$$

$$C_A = \frac{C_{AS} \cdot e^{mL}}{e^{mL}+e^{-mL}} + \frac{C_{AS} \cdot e^{-m(2-L)}}{e^{mL}+e^{mL}}$$

$$\boxed{C_A = \frac{C_{AS}}{e^{mL}+e^{-mL}} \left[e^{m(2-L)} + e^{-m(2-L)} \right]}$$

$$\cosh\theta = \frac{e^{\theta}+e^{-\theta}}{2}$$

$$C_A = \frac{C_{AS}}{2\cosh mL} \left[2\cosh m(2-L) \right]$$

$$\boxed{C_A = \frac{C_{AS} \cdot \cosh m(2-L)}{\cosh mL}}$$

$mL \rightarrow \sqrt{k/D} \cdot L$

$$\sqrt{\frac{Sec^{-1}}{m^2 sec^{-1}}} \cdot x\,m$$

$\Rightarrow \frac{1}{m} x\,m$ = Dimensionless quantity.

* $\boxed{mL \longrightarrow \text{Thiele Modulus } (\phi)}$

$$\boxed{\phi = \sqrt{k/D} \cdot L}$$

$L \Rightarrow$ characteristic length

$D \Rightarrow$ Diffusivity coeff.

$$\phi \propto \sqrt{\frac{\text{Surface rxn rate}}{\text{Diffusion rate}}}$$

$$\propto \sqrt{\frac{\text{Diffusion resistance}}{\text{Surf. Rxn resistance}}}$$

\# $\underline{\phi \uparrow}$ $\rightarrow$ rate controlling step will be pore diffusion.
Strong pore diffusion resistance.

If Φ is low :— rate controlling step will be surface rxn, & low pore diffusion resistance.

* Effectiveness factor (η)

$$\eta = \frac{\text{rxn rate wid diffusion resistance}}{\text{diffusion rate wid/out diffusion resistance}}$$

for first order rxn.

$$\eta = \frac{-\bar{r}_A'' = k'' \bar{C}_A}{-r_A'' = k'' C_{As}}$$

$$\bar{C}_A = \frac{\int_0^L C_A \cdot dz}{\int_0^L dz}$$

$$C_A = \frac{C_{As} \cdot \cosh m(z-L)}{\cosh mL}$$

$$\bar{C}_A = \frac{\int_0^L \frac{C_{As} \cdot \cosh m(z-L)}{\cosh mL} dz}{\int_0^L dz}$$

$$\bar{C}_A = \frac{\frac{C_{As}}{\cosh mL} \left[\frac{\sinh m(z-L)}{m}\right]_0^L}{z\Big|_0^L}$$

$$= \frac{\frac{C_{As}}{m \cosh mL} [\sinh m(0) - \sinh m(-L)]}{L}$$

$$= \frac{C_{As}}{mL \cosh mL} [0 - (-\sinh mL)]$$

$$\boxed{\bar{C}_A = \frac{C_{As} \tanh mL}{mL}}$$

$$\eta = \frac{k'' C_{As} \cdot \frac{\tanh mL}{mL}}{k'' C_{As}}$$

$$\boxed{\eta = \frac{\tanh mL}{mL} \approx \frac{\tanh \phi}{\phi}}$$

$$-r_A'' = k'' C_A^n \cdot \eta$$

⇒ If $\phi > 4$,

Strong pore diffusion resistance,

$\tanh \phi = 1$, $\eta = 1/\phi$

$$\boxed{-r_A'' = k'' C_A^n \cdot 1/\phi}$$

$$-r_A'' \propto 1/\phi$$

$$\boxed{-r_A'' \propto 1/\phi \propto 1/L \mid \propto 1/R}$$

Characteristic Length = $\frac{\text{Volume}}{\text{Surface area}}$

for Cylindrical, $L = R/2$
for Sphere, $L = R/3$
flat plate, $L = \frac{\text{thickness}}{2}$

ϕ will be high

→ for fast rxn
→ for slow diffusion rate
→ largest pore

⇒ if $\phi < 0.4$

$\tan \phi \approx \phi$

$\eta = 1$

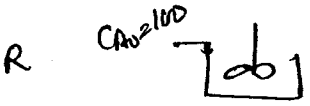
→ slow rxn rate
→ fast diffusion rate
→ shortest pore

⇒ If $0.4 < \phi < 4$

Surface rxn resistance & pore diffusion resistance are approximately same.

Oct 10, 14

late 2007 Q.S6)

$A \rightarrow R$ $C_{A0} = 100$  W fixed.

$$\phi = \sqrt{k/D} \cdot L$$

d_p	F_{A0}	X_A
4	2	0.8
6	4	0.4

$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A}$$

for MFR $\frac{W}{F_{A0}} = \frac{X_A}{-r_A''}$

for PFR $\frac{W}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A''}$

for strong pore diffusion

$$\phi > 4$$

$$\eta = 1/\phi$$

$$-r_A'' \propto \frac{1}{\phi} \propto \frac{1}{d_p}$$

$$W(-r_A)'' = X_A F_{A0}$$

$$W(-r_A)_1'' = 0.8 \times 2 = 1.6$$

$$W(-r_A)_2'' = 0.4 \times 4 = 1.6$$

$$\frac{(-r_A'')_2}{(-r_A'')_1} = \frac{d_{p1}}{d_{p2}} = 4/6$$

∴ It is diffusion free resistance.

for n^{th} order rxn,

$$\phi = \frac{(-r_{As}'').L}{\left|2De\int_0^{C_{As}}(-r_A'').dC_A\right|^{1/2}}$$

Effective diffusivity

$$-r_A'' = k''C_A^n$$

$$= \frac{k''C_{As}^n.L}{\left[2De\int_0^{C_{As}} k''C_A^n.dC_A\right]^{1/2}}$$

$$= \frac{k''C_{As}^n.L}{\left[2.De\frac{k''C_{As}^{n+1}}{(n+1)}\right]^{1/2}}$$

$$\phi = \sqrt{\frac{(n+1)k''}{2De}C_{As}^{n-1}}.L$$

Effective Diffusivity :—

$$De = \frac{D_{AB}\,\delta_c.\phi_p}{\tau}$$

$\delta_c \Rightarrow$ Constriction factor.
ϕ = porosity
τ = tortuosity factor.

$$\tau = \frac{\text{Actual distance travelled by molecules}}{\text{Shortest distance b/w two pts.}}$$

* Catalyst Henry :-

* Catalyst deactivation :-

the decrement in the available active sites of the catalyst.

$$\boxed{-r_A'' = k'' C_A^n a}$$

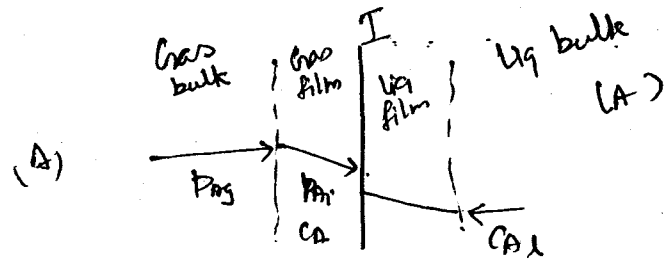
$$a = \frac{\text{rxn rate at any time } t \text{ in the presence of catalyst}}{\text{rxn rate at } t=0 \text{ in the presence of fresh catalyst}}$$

Factors

- ↳ Ageing — rxn progression
- ↳ Fouling — deposition of impurities
- ↳ Poisoning — any component forming a chemically inert on the surface of catalyst.

* Non Catalytic Rxn :-

Rate of absorption w/o chem rxn :-



rate of MTr

gas film, $r_g'' = k_g (P_{Ag} - P_{Ai})$

$$\Rightarrow P_{Ag} - P_{Ai} = r_g''/k_g \quad \text{—(1)}$$

rate of MTr

liq film, $r_l'' = k_l (C_{Ai} - C_{Al})$

$$C_{Ai} - C_{Al} = \frac{r_l''}{k_l} \quad \text{—(2)}$$

from Henry's law,

$$P_{Ai} = H \cdot C_{Ai}$$

$$\frac{p_{Ag}}{H} - \frac{p_{Ai}}{H} = \frac{\gamma_g''}{H \cdot k_g}$$

$$\frac{p_{Ai}}{H} - C_{Al} = \frac{\gamma_l''}{k_l}$$

$$\frac{p_{Ag}}{H} - C_{Al} = \frac{\gamma_g''}{H k_g} + \frac{\gamma_l''}{k_l}$$

$\gamma_g'' = \gamma_l'' = \gamma''$ Rate of absorptn

$$\rightarrow \boxed{\frac{\frac{p_{Ag}}{H} - C_{Al}}{\frac{1}{H k_g} + \frac{1}{k_l}} = \gamma''}$$

$p_{Ag} = H \times C_{Al}^*$

$$\boxed{\frac{C_{Al}^* - C_{Al}}{\frac{1}{H \cdot k_g} + \frac{1}{k_l}} = \gamma''}$$

$$\gamma'' = K_{Al} \cdot (C_{Al}^* - C_{Al})$$

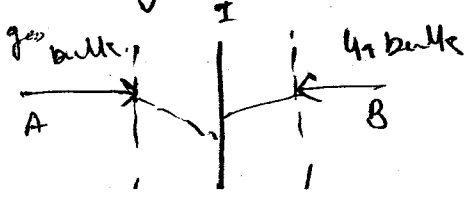
$$\boxed{\frac{1}{K_{Al}} = \frac{1}{H \cdot k_g} + \frac{1}{k_l}}$$

overall gas mass transfer coeff.

$$\boxed{\frac{1}{K_{Ag}} = \frac{1}{k_g} + \frac{H}{k_l}}$$

* Rate of absorption wid chemical rxn :—

$A(g) + B(l) \longrightarrow P$



$$-r_A'' = \frac{\Delta P_A}{\frac{1}{k_g \cdot a} + \frac{H_A}{k_l \cdot a \cdot E} + \frac{H_A}{K C_{Bb} f_l}}$$

a → interfacial area per unit vol.

$f_l \Rightarrow$ fractional liq hold up.

$E \Rightarrow$ liquid film enhancement factor. $f(E_i, M_H)$

E_i → Liq film enhancement factor for extremely fast rxn.

M_H → Hatta No. or Hatta Modulus.

$$E = \frac{\text{rate of absorption with chem rxn}}{\text{rate of absorption w/o chem rxn}}$$

Hatta Modulus (M_H^2) :—

$$M_H^2 = \frac{\text{Maxm possible conversion through liq film}}{\text{Maxm possible diffusion through liq film}}$$

↳ Wheather rxn will take place in liq film or liq bulk.

↳ wheather we require large liquid hold up.

↳ or large interfacial area.

if $M_H > 2$

↳ rxn will takes place in liquid film.

↳ ↳ large interfacial area

↳ ↳ small liquid hold up.

use packed bed reactors.

if $M_H < 0.02$

↳ rxn will occur in liquid bulk.

↳ large liquid hold up

↳ small interfacial area.

use — bubble column Reactor.

III

$0.02 < M_H < 2$

rxn will take place in liq film & liq bulk.

Use Agitated vessels.

Oct 13, 14

$A \rightarrow R$

* Autocatalytic Rxn

$A \rightarrow R$

$A + R \longrightarrow R + R$

2) Constant Volume System & Homogeneous

$$-r_A = -\frac{dC_A}{dt} = kC_AC_R$$

$$\frac{N_{A0}+N_{R0}}{V} = \frac{N_A+N_R}{V} = \frac{N_0}{V}$$

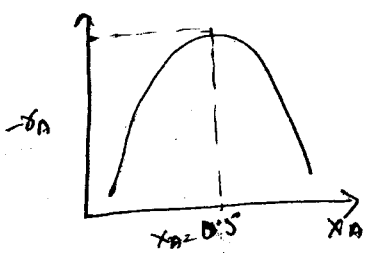
$$\boxed{C_{A0}+C_{R0} = C_A+C_R = C_0}$$

Initially $N_{A0}=11$, $N_{R0}=1$

	A	+ R	→ R	+ R
	11	1	1	1
	10	2	2	2
	8	4	4	4
	4	8	4	4
	0	4		
	0	12		

rate of rxn is maxm

When $\boxed{C_A = C_R}$



$$-\frac{dC_A}{dt} = kC_A(C_0-C_A)$$

$$-\frac{dC_A}{C_A(C_0-C_A)} = k\,dt$$

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A(C_0-C_A)} = \int_0^t k\,dt$$

$$kt = \int_{C_A}^{C_{A0}} \frac{dC_A}{C_A(C_0-C_A)}$$

$$= \int_{C_A}^{C_{A0}} \left[\frac{1}{C_0-C_A} + \frac{1}{C_0(C_0-C_A)}\right]$$

$$\frac{A}{C_A} + \frac{B}{(C_0-C_A)}$$

$$A(C_0-C_A) + B(A)$$

$A = 1$

$B - A = 0$

$B = 1$

$$C_0kt = \ln C_A + \frac{\ln(C_0 - C_A)}{-1} \Big|_{C_{A0}}^{C_A}$$

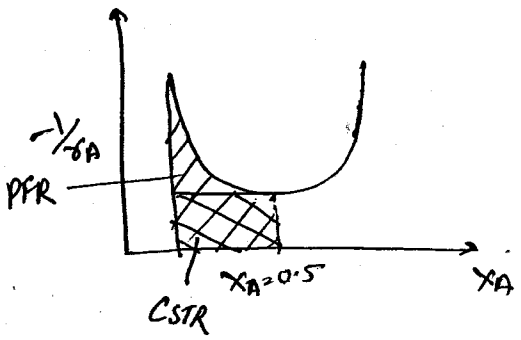
$$\boxed{C_0kt = \ln\left[\frac{C_{A0}\cdot(C_0 - C_A)}{C_A(C_0 - C_{A0})}\right]}$$

$$A + R \longrightarrow R + R$$

$\boxed{N_{A0} = N_{R0}}$

$$(M-1)kt = \ln\left(\frac{M - X_A}{M(1 - X_A)}\right)$$

$$\boxed{M = \frac{C_{A0}}{C_{A0}}}$$



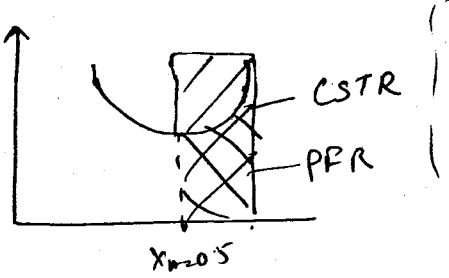
for conversion $X_A < 0.5$

use CSTR

for conversion $X_A > 0.5$

use PFR

As minimum area required.



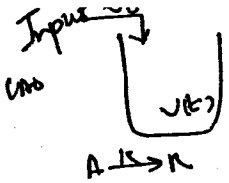
Overall arrangement of reactor:

$\boxed{\text{CSTR} \longrightarrow \text{PFR}}$

* Semi-batch Reactor

Purpose

» To maximise the selectivity.



Rate of A In = Rate of A out + Rate of A accum + Rate of A disapp

$$V_0 \cdot C_{A0} = 0 + \frac{d}{dt}(C_A \cdot V) + (-r_A) \cdot V$$

$$V_0 \cdot C_{A0} = V \cdot \frac{dC_A}{dt} + C_A \cdot \frac{dV}{dt} + (-r_A) \cdot V$$

$$V \cdot \frac{dC_A}{dt} + C_A \cdot \frac{dV}{dt} + (-r_A) \cdot V = V_0 \cdot C_{A0}.$$

Mass Balance

Mass flow in = Mass flow out + mass accum.

$$\rho V_0 = 0 + \frac{d}{dt}(\rho V)$$

assuming density is constant

$$\boxed{V_0 = \frac{dV}{dt}}$$

$$= \boxed{V = V_0 t}$$

$$\Rightarrow V \cdot \frac{dC_A}{dt} + C_A \cdot V_0 + (-r_A) \cdot V = V_0 C_{A0}$$

$$\frac{dC_A}{dt} + C_A \cdot \frac{V_0}{V} + (-r_A) \cdot \frac{V}{V} = \frac{V_0 C_{A0}}{V}$$

$$\boxed{\frac{dC_A}{dt} + \frac{C_A}{t} + (-r_A) = \frac{C_{A0}}{t}}$$

For first order rxn $n = 1, \quad -r_A = kC_A$

$$\frac{dC_A}{dt} + \frac{C_A}{t} + kC_A = \frac{1}{t} C_{A0}$$

$$\boxed{\frac{dC_A}{dt} + \left(\frac{1}{t} + k\right) C_A = \frac{1}{t} C_{A0}}$$

$$\text{I.F.} = e^{\int (\frac{1}{t} + k)\, dt} = t \cdot e^{kt}$$

$$C_A \cdot t \cdot e^{kt} = \int \frac{1}{t} C_{A0} \times t \cdot e^{-kt}\, dt + C$$

$$C_A \cdot e^{kt} \cdot t = \frac{C_{A0}}{k} e^{kt} + C$$

at $t = 0$, $C_A = C_{A0}$,

$$C = -C_{A0}/k$$

$$\boxed{C_A = \frac{C_{A0}}{kt}(1 - e^{-kt})}$$

$$X_A = 1 - C_A/C_{A0}$$

Gate 2007 Q.52)

$k = 1\ min^{-1}$

$C_{A0} = 1\ mol/l$

$V_0 = 1\ l/min$

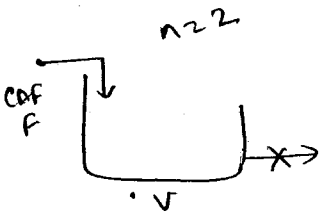
, $t = 2\ min$ $\quad X_A = ?$

$$C_A = \frac{1}{1 \times 2}(1 - e^{-2})$$

$$C_A = 0.432$$

$$X_A = 0.567$$

Gate 2004 Q.72)



ρ liq mass = (cons.)

$$\rho F = 0 + \frac{d}{dt}(\rho V)$$

$$\boxed{Ft = V}$$

$$\frac{dC_A}{dt} + \frac{C_A \cdot F}{V} + (-r_A) \cdot \frac{V}{V} = \frac{F C_{A0}}{V}$$

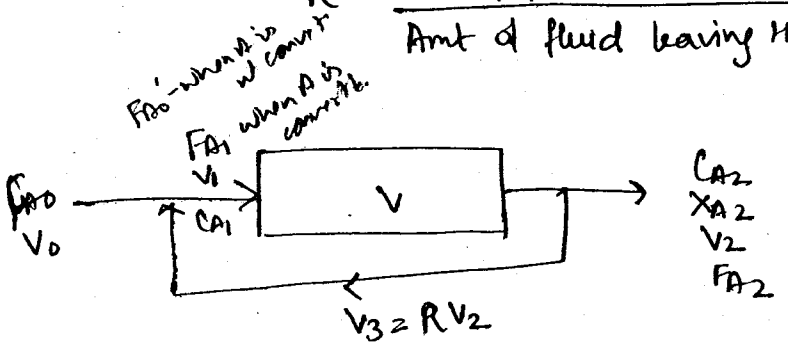
$$\frac{dC_A}{dt} + \frac{C_A}{t} + kC_A^2 = \frac{C_A}{t}$$

$$F_{AF} = 0 + \frac{d(C_A \cdot V}{dt} + kC_A^2 V$$

$$\frac{d(VC_A)}{dt} = FC_{AF} - kC_A^2 V$$

Recycle Reactor :—

$$R = \frac{\text{Amt of fluid sent back to the reactor inlet}}{\text{Amt of fluid leaving the system.}}$$



$$F_{A3} = RF_{A2}$$

$$\frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

F'_{A0} = Molar flow of A in fresh feed + Molar rate of recycle when A is completely unconverted

$$F'_{A0} = F_{A0} + RF_{A0}$$

$$\frac{V}{F'_{A0}} = \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{-r_A}$$

$$C_{A1} = \frac{C_{A0}(1-X_{A1})}{(1+\varepsilon_A X_{A1})} \Rightarrow X_{A1} = \frac{1 - C_{A1}/C_{A0}}{1 + \varepsilon_A C_{A1}/C_{A0}}$$

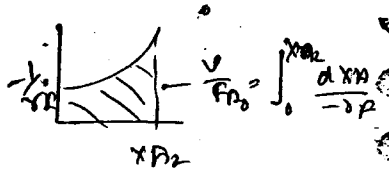
$$C_{A1} = \frac{F_{A1}}{V_1} = \frac{F_{A0} + F_{A3}}{V_0 + V_3} = \frac{F_{A0} + RF_{A2}}{V_0 + RV_2} = \frac{F_{A0} + RF_{A0}(1-X_{A2})}{V_0 + RV_0(1+\varepsilon_A X_{A2})}$$

$$C_{A1} = C_{A0}\left[\frac{1 + R(1-X_{A2})}{1 + R(1+\varepsilon_A X_{A2})}\right]$$

$\frac{F_{A0}}{V_0} = C_{A0}$.

$$\boxed{X_{A1} = \left(\frac{R}{R+1}\right) X_{A2}}$$

$$\frac{V}{(R+1)F_{A0}} = \int_{\frac{R}{R+1}X_{A2}}^{X_{A2}} \frac{dX_A}{-r_A}$$



to enhance the degree of Mixing.