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NAME: Rahul STD.: TY SEC.: CE ROLL NO.: 40 SUB.: CRE notes

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PDV sir

classmate
Date
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CHEMICAL REACTION ENGINEERING

1. Reactors:
   - → Batch & continuous
   - → Tank & Tube
   - → Homogenous & hetrogenous

Homogeneous reactions

2. $A \Rightarrow B$

Rate eq: $-r_A = K C_A^n = k_0 \exp\left(-\frac{E_a}{RT}\right) C_A^n$

3. $aA + bB \rightarrow rR + sS$

Rate: $-r_A = \frac{1}{V} \cdot \frac{dN_A}{dt}$ V: vol. of rxn mix.
N_A: moles of A

$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$ .. only for stoichiometric simple (single) rxn

i.e there shouldn't be any side rxn

4. Types of homogenous reactions:

→ Single & multiple

rxn in Point (3) in a single rxn

Multiple rxns are:

a) series: $A \rightarrow R \rightarrow S$

b) parallel:

→ competative: $A \begin{smallmatrix} \nearrow R \\ \searrow S \end{smallmatrix}$

⇒ side-by-side: $A \rightarrow R$
$B \rightarrow S$

single reaction obeys!

$$\frac{\Delta N_A}{a} = \frac{\Delta N_B}{b} = \frac{\Delta N_R}{r} = \frac{\Delta N_S}{s}$$

e) Parallel & series both

$$A + B \rightarrow R$$

$$R + B \rightarrow S$$

5. if the order of the components is ~~the~~ corresponding to the stoichiometric equation then the rxn is elementary

Molecularity : it is the no. of molecules involved in a reaction.

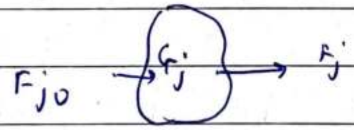
order : The power to which the conc ~~term~~ term is raised in the rate eq

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

Ideal reactor Types for Homogenous Reactions :

6. general mole bal.

Fj0 = Molar flow rate at inlet (mol/sec)
Fj = Molar flow rate at outlet (mol/sec)
rj = rate of reaction (mol/sec.m3)
Gj = Net generation of a component (mol/sec)



j: component for balance

~~In - out~~ In + generation = out + Accumulation

$$F_{j0} + G_j = F_j + \frac{dN_j}{dt}$$

$$F_{j0} - F_j + G_j = \frac{dN_j}{dt}$$

if system properties do not change with,

$$G_j = r_j \cdot V$$

$$r_j = \frac{\text{change in moles}}{\text{volume} \cdot \text{unit time}}$$

$$\therefore \quad F_{j0} - F_j + r_j \cdot V = \frac{dN_j}{dt}$$

& if r_j varies with position inside the volume,

$$g_i = \int_V r_j \cdot dV$$

$$\therefore F_{j0} - F_j + \int_V r_j \, dV = \frac{dN_j}{dt}$$

7. ## Batch reactor

$$F_{j0} = F_j = 0 \quad \ldots [\because \text{no feed \& no outstream}]$$

$$\therefore \int_V r_j \cdot dv = \frac{dN_j}{dt} \quad \ldots (i)$$

if r_j is independent of position in the volume,

$$\boxed{-r_j = \frac{1}{V} \cdot \frac{dN_j}{dt}} \quad \ldots (ii)$$

Governing equation for batch reactors

$A \rightarrow B$

if j is A,

initial moles

conversion of A

moles at time t

$$N_A = N_{A0}(1 - x_A)$$

$$\therefore \frac{dN_A}{dt} = -N_{A0} \cdot \frac{dx_A}{dt}$$

$$\therefore -r_A = \frac{N_{A0}}{V} \cdot \frac{dx_A}{dt} \quad \ldots (iii) \ldots \text{from } (ii)$$

const vol reaction systems (~~mos~~ typically liq. phase rxn)

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

$\frac{dC_A}{dt} = C_{A0} \frac{dx_A}{dt}$

positive

$\therefore$ eq (ii) becomes $r_j = \frac{dC_j}{dt}$ → conc.

Negative

eq (iii) becomes $-r_j = C_{A0} \frac{dx_A}{dt}$

$\because$ mass is const & if volume is also const the mass density of the system is also const.

$\therefore \; r_j = \frac{1}{V} \cdot \frac{dN_j}{dt}$

$$\boxed{t = \int_{N_{j0}}^{N_j} \frac{1}{V} \cdot \frac{dN_j}{r_j}}$$

8. Continuous flow Reactors :

a) CSTR - continuous flow stirred-tank reactor
mixed or Back-mixed reactors.
we assume well mixed mixture inside CSTR
∴ the effluent stream has same conc
as the reactor contents.

At steady state, Accumulation $= \frac{dN_j}{dt} = 0$

* in case of CSTR, the mixing is intense hence the rate does not change with posn inside the reactor.
(but in case of batch we can have both cases ⇒ thus integral)

$\therefore \; F_{j0} - F_j + G_j = 0$

$F_{j0} - F_j + r_j V = 0$

$$\therefore \; \boxed{-r_j = \frac{F_{j0} - F_j}{V} \quad \text{or} \quad V = \frac{F_{j0} - F_j}{-r_j}} \quad \text{— (i)}$$

Governing equation for CSTR

Design eq.

$A \rightarrow B$

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

moles at time t ; initial moles ; conversion of A

* in case of batch we use 'N_A' ∵ moles are const & in continuous we use 'F_A' that is moles per unit time.

$$\frac{V}{F_{A0}} = \frac{F_{A0} - F_A}{F_{A0}} \cdot \frac{1}{(-r_A)}$$

from (i)

$$\star \quad V = \frac{F_{j0} - F_j}{-r_j} = \frac{F_{A0} - F_A}{-r_A}$$

$$\therefore \frac{V}{F_{A0}} = \underbrace{\frac{F_{A0} - F_A}{F_{A0}}}_{X_A} \times \frac{1}{-r_A} \quad \ldots \text{[dividing both sides by } F_{A0}\text{]}$$

$$\therefore \boxed{\frac{V}{F_{A0}} = \frac{X_A}{-r_A}} \quad \text{— (ii) design eq}^n.$$

Space time : $\star$ $\boxed{F_{A0} = Q_0 \cdot C_{A0}}$ — (iii)

$$\frac{mol}{h} \quad \frac{m^3}{h} \quad \frac{mol}{m^3}$$

τ_0 = space time at inlet conditions

what t is for batch reactor τ_0 is for flow reactors.

$1/\tau_0$: space velocity

$$\boxed{\tau_0 = \frac{V}{Q_0}} \quad \text{(time units)}$$

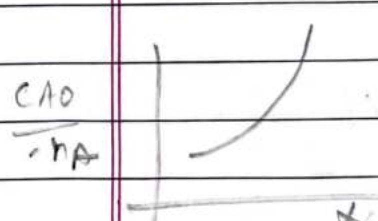
$\therefore$ for CSTR,

$$\therefore \frac{V}{F_{A0}} = \frac{X_A}{-r_A} \quad \ldots \text{from (ii)}$$

$$\therefore V = \tau_0 Q_0$$

$$\frac{\tau_0}{\frac{F_{A0}}{Q_0}} = \frac{X_A}{-r_A}$$

$$\therefore \frac{\tau_0}{C_{A0}} = \frac{X_A}{-r_A} \quad \ldots \text{[from (iii)]}$$



$$\star \therefore \boxed{\tau_0 = \frac{C_{A0} X_A}{-r_A}} \quad \text{or} \quad \boxed{\tau_0 = \frac{C_{A0} - C_A}{-r_A}}$$

if the mass density of the fluid flowing through the reactors is const throughout the subscript from τ_0 & Q_0 may be dropped.

$$\tau = \frac{V}{Q} = \frac{C_{A0} X_A}{-r_A} \quad \text{(Avg. residence time)}$$

* use Calculator where ever ~~interge~~ integration is required.

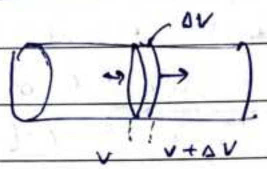
$\because$ for const fluid density,

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

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

$$\therefore \tau = \frac{V}{Q} = \frac{C_{A0} X_A}{-r_A} = \frac{C_{A0} - C_A}{-r_A}$$

6) Ideal PFR :



$$\Delta F_j = \int_{\Delta V} r_j \, dV = r_j \cdot \Delta V$$

$$F_j|_{V} - F_j|_{V+\Delta V} + r_j \Delta V = 0$$

$$\therefore \frac{F_j|_{V+\Delta V} - F_j|_V}{\Delta V} = r_j$$

For $\Delta V \to 0$, $\quad r_j = \dfrac{dF_j}{dV}$

$A \to B$, $\quad$ 4 j is A

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

$$\frac{dV}{dF_{A0}} = \frac{dX_A}{-r_A}$$

$$\boxed{\frac{V}{F_{A0}} = \int \frac{dX_A}{-r_A}}$$ design eq

Governing equation for PFR

$$\tau_0 = V / Q_0$$

$$d\tau_0 = C_{A0} \cdot \frac{dX_A}{-r_A} = \frac{-dC_A}{-r_A}$$

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

x_A : is the fraction that has been converted. / conversion of A

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

$$x_A = C_{A0} - C_A / C_{A0}$$

$$d\tau_0 = \frac{d(C_{A0} - C_A)}{-r_A}$$

$$= \frac{dC_{A0}}{-r_A} - \frac{dC_A}{-r_A}$$

$$= \frac{-dC_A}{-r_A} \quad \ldots (\because C_{A0} \text{ is const})$$

* For the same conversion volume required by ~~PFR~~ CSTR is greater than ~~CSTR~~ PFR

*

input	reactor
C_{A0},	C_{A0}'
T_0	T_0'
P_0	P_0'
k	k'

$$C_{A0} = \frac{P_0}{RT_0} y_{A0}$$

$$C_{A0}' = \frac{P_0'}{RT_0'} y_{A0}'$$

$$\frac{C_{A0}'}{C_{A0}} = \frac{P_0'}{T_0'} \frac{T_0}{P_0} \frac{y_{A0}'}{y_{A0}}$$ Same.

$$C_{A0}' = C_{A0}\left(\frac{P_0'}{P_0}\right)\left(\frac{T_0}{T_0'}\right)$$

=> for const density reaction system use 'C' (PFR & CSTR) (batch)

'N' → (Batch)

'F' → P

=> for variable volume batch reactor → 'N'

continuous → 'F'

$$\Rightarrow \quad \tau = \frac{V}{Q} \quad , \quad F = Q\,C$$

$$\therefore \frac{\cancel{\epsilon_A}\, C \cdot V}{F} = \tau$$

$$\Rightarrow \quad \tau = \frac{V}{Q_0} = \frac{V C_{A0}}{F_{A0}} = \frac{V}{F}\left(\frac{P\, y_{A0}}{RT}\right)$$

⇒ liquid phase rxns are generally const desity reactions.

⇒ more conversion ($\uparrow x_A$) more reactor volome.

⇒ $C_A = C_{A0}(1 - x_A)$ valid only for const density reactions

⇒ $k = k_0\, e^{-E_a/RT}$

9. Systems of continuous reactors

a) Reactors in Series

CSTRs in series

conv. in the stream leaving reactor $(N+1)$ is always higher than conv. in stream leaving reactor N

Rate in - Rate out + Gen = 0 (steady state)

$$F_{A_1} - F_{A_2} + V \cdot r_A |_{x_{A_2}} = 0$$

$$F_{A_0}(1 - x_{A_1}) - F_{A_0}(1 - x_{A_2}) + V \cdot r_A|_{x_{A_2}} = 0 \quad (x_{A_2} > x_{A_1})$$

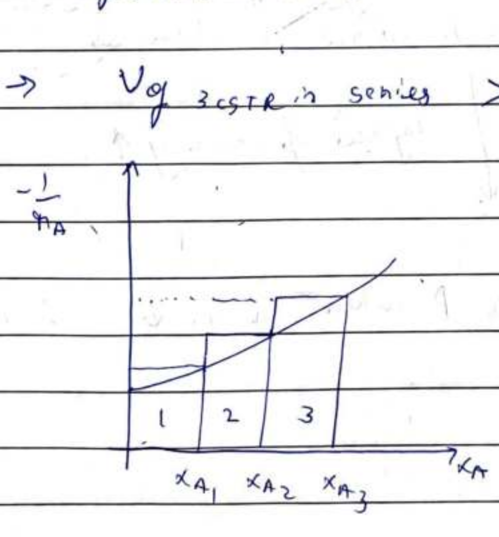
$$\cancel{\frac{V_2}{V_f}} \quad \frac{V_2}{F_{A_0}} = \frac{x_{A_2} - x_{A_1}}{-r_A|_{x_{A_2}}}$$

$$\frac{V_N}{F_{A_0}} = \frac{x_N - x_{N-1}}{-r_A|_{x_N}} \quad \text{design eq.}$$

For 1st order kinetics usually 10 CSTRs in series approach the performance of a PFR

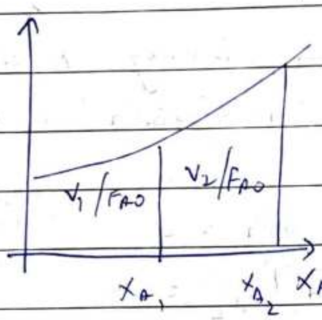
→ $V_{of\ 3\ CSTR\ in\ series} < V_{of\ single\ CSTR}$ (for same overall conv.)

→ $V_{of\ 3\ CSTR\ in\ series} > V_{of\ single\ PFR}$



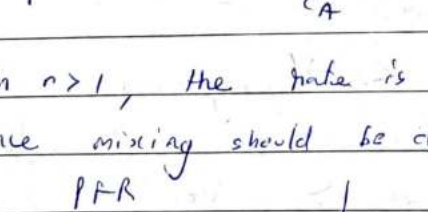
PFRs in series

$$\frac{V_1}{F_{A0}} = \int_0^{X_{Ae_1}} \frac{dX_A}{-r_A} \qquad \frac{V_2}{F_{A0}} = \int_{X_{Ae_1}}^{X_{Ae_2}} \frac{dX_A}{-r_A}$$



V of 2 PFR in series = V of single PFR (for same Σ ~~c~~)

10. PFR & CSTR in series



when $n>1$, the rate is higher when C_A is more hence mixing should be done as later as possible

PFR
Small CSTR
Big CSTR
↓ degree of mixing ↑

when $n<1$, rate is ↑ when C_A is ↓ ∴ the order is ~~res~~ reversed.

11. Reactors in parallel

CSTRs in Parallel

$V_{2\,CSTR\ in\ parallel}$ < single V_2 CSTR in parallel.
with same feed to both reactors with same volume | diff. feeds to both reactor with diff. volume

* same with the PFRs in parallel

$V_1 + V_2 > 2V$

Series is better than parallel

12 * For CSTR $\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{X_A}{kC_A} = \frac{C_{A0} - C_A}{C_{A0}\, k C_A}$

for 1st order $\frac{V}{Q_0 C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}\, k C_A} = \tau$ | $\tau = \frac{C_{A0} - C_A}{-r_A}$

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

& $X_A = 1 - \frac{C_A}{C_{A0}} = 1 - \frac{1}{1+k\tau} = \frac{k\tau}{1+k\tau}$

* $C_n = (1 - X_A)^n C_0$

$X_n = 1 - \frac{C_n}{C_0} = 1 - \frac{1}{(1+k\tau)^n}$

12. relationship btw τ & x for CSTR & PFR (for 1st order)

CSTR :
$$\frac{V_S}{F_{A0}} = \frac{X_A}{-r_A} = \frac{X_A}{kC_A} = \frac{C_{A0}-C}{C_{A0}\,kC_A}$$

$$\therefore \frac{V_s}{Q_0 \cancel{C_{A0}}} = \frac{C_{A0}-C}{\cancel{C_{A0}}\,kC_A}$$

$$\therefore \frac{V_S}{Q_0} = \frac{C_{A0}-C}{kC_A}$$

$$C = \frac{C_{A0}}{1+k(V_s/Q)}$$

$$X = 1 - \frac{C}{C_{A0}} = 1 - \frac{1}{1+k(V_s/Q)} = \frac{k(V_s/Q)}{1+k(V_s/Q)}$$

PFR :
$$\frac{V_P}{Q} = C_0\int_0^x \frac{dx}{-r} = C_0\int_0^x \frac{dx}{kC_0(1-x)}$$

$$= -\frac{1}{k}\ln(1-x)$$

$$X = 1 - e^{-k(V_P/Q)}$$

if conv. is same in both reactors

$$\frac{k(V_s/Q)}{1+k\left(\frac{V_s}{Q}\right)} = 1 - e^{-k(V_p/Q)}$$

Let $\alpha = \frac{V_s}{V_P}$ $\Rightarrow$ $V_s = \alpha V_P$

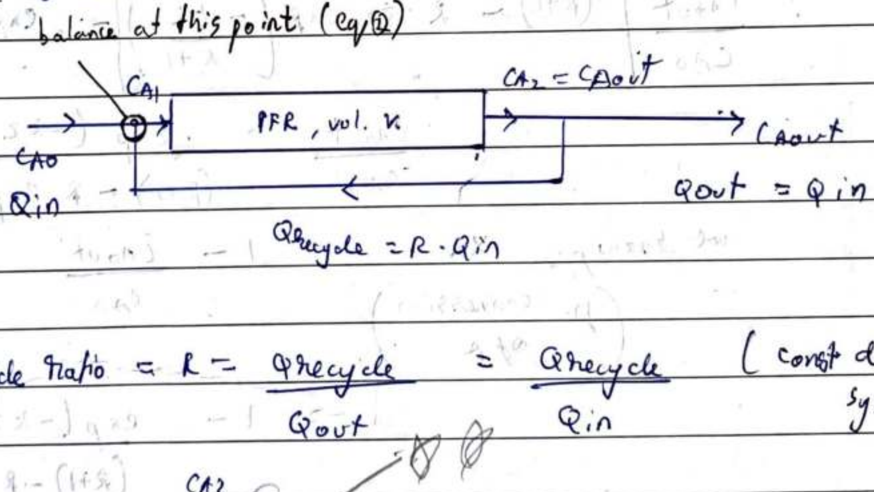
$$\therefore \frac{\cancel{k/\alpha}\ \frac{k\alpha V_p}{Q}}{1 + \frac{k\alpha V_p}{Q}} = 1 - e^{-k(V_p \varphi)}$$

Let $\frac{k V_p}{Q} = y$

$$\frac{\alpha y}{1+\alpha y} = 1 - e^{-y}$$

$$\boxed{\alpha = \frac{y}{(y-1)\ln(1-y)}}$$

13. * Recycle Reactors



Recycle ratio $= R = \frac{Q_{recycle}}{Q_{out}} = \frac{Q_{recycle}}{Q_{in}}$ (const density system)

For PFR, $$\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{-r_A} = \frac{V}{Q_{in} + Q_{recycle}}$$

$$\therefore -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{kC_A} = \frac{V}{Q_{in}(R+1)} = -\frac{\tau}{R+1}$$

considering 1st order $\therefore$ $$\ln\left(\frac{C_{A2}}{C_{A1}}\right) = \ln\left(\frac{C_{Aout}}{C_{A1}}\right) = \frac{-k\tau}{(R+1)} \quad \text{— ①}$$

$$C_{A0}\, Q_{in} + C_{Aout}\, R \cdot Q_{in} = C_{A1}\, Q_{in} (R+1) \quad \text{--- (2)}$$

$$\therefore \quad C_{A0} + C_{Aout} \cdot R = C_{A1} (R+1)$$

$$\therefore \quad C_{A1} = \frac{C_{A0} + R C_{Aout}}{R+1} \quad \ldots$$

substituting this in (1)

$$\ln\left(\frac{C_{Aout}(R+1)}{C_{A0} + R C_{Aout}}\right) = -\frac{k\tau}{R+1}$$

$$\frac{C_{Aout}(R+1)}{C_{A0} + R C_{Aout}} = \exp\left(\frac{-k\tau}{R+1}\right)$$

$$\therefore \quad C_{Aout}(R+1) = C_{A0} \exp\left(-\frac{k\tau}{R+1}\right) + R \cdot C_{Aout} \cdot \exp\left(\frac{-k\tau}{R+1}\right)$$

$$\therefore \quad \frac{C_{Aout}}{C_{A0}}\left[(R+1) - R \cdot \exp\left(-\frac{k\tau}{R+1}\right)\right] = \exp\left(\frac{-k\tau}{R+1}\right)$$

$$\therefore \quad \frac{C_{Aout}}{C_{A0}} = \frac{\exp(-k\tau/R+1)}{(R+1) - R\exp(-k\tau/R+1)}$$

we know, X_A (fr. conversion of A) $= 1 - \dfrac{C_{Aout}}{C_{A0}}$

$$= 1 - \frac{\exp(-k\tau/R+1)}{(R+1) - R\exp(-k\tau/R+1)}$$

$$= \frac{(R+1) - R\exp(-k\tau/R+1) - \exp(-k\tau/R+1)}{R+1 - R\exp(-k\tau/R+1)}$$

$$= \frac{R+1 - \exp(-k\tau/R+1)\cdot(R+1)}{R\left[1 - \exp(-k\tau/R+1)\right] + 1}$$

$$= \frac{R+1 - \exp(-k\tau/R+1)\cdot(R+1)}{R\left(1 - \dfrac{1}{\exp(k\tau/R+1)}\right) + 1}$$

$$X_A = \frac{R+1 - \exp(-k\tau/R+1)(R+1)}{R\left(\exp(k\tau/R+1) - 1\right) + \exp(k\tau/R+1)}$$

$$\exp(k\tau/R+1)$$

$$= \frac{R\cdot\exp(k\tau/R+1) + \exp(k\tau/R+1) - 1\cdot(R+1)}{R\exp(k\tau/(R+1)) - R + \exp(k\tau/R+1)}$$

$$= \frac{\exp(k\tau/R+1)(R+1) - (R+1)}{\exp(k\tau/R+1)(R+1) - R}$$

$$\boxed{X_A = \frac{R+1 - e^{k\tau/R+1}(R+1)}{R - e^{k\tau/R+1}(R+1)}}$$

when, $R \to 0$

$X_A = 1 - e^{-k\tau}$

behaves as an ideal PFR

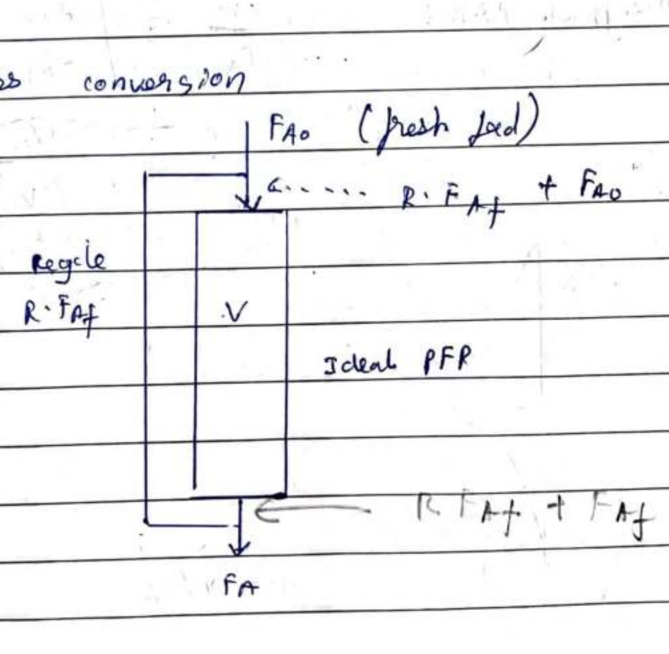
$R \to \infty$.

$X_A = \frac{k\tau}{1+k\tau}$ $\left[\text{as } a \to 0 \quad e^a \to 1 + a \right]$

(taylor expansion)

behaves as ideal CSTR.

14. per pass conversion



$\therefore$ ~~for~~ $\because$ PFR

$$\frac{V}{F_{A0} + R \cdot F_{Af}} = \int_0^{X_{out}} \frac{dX_A}{-r_A} \quad \text{... design eq}$$

$$X_{out} = 1 - \frac{(R+1) F_{Af}}{F_{A0} + R F_{Af}} \quad \ldots$$

$$X_{out} = \frac{F_{A0} - F_{Af}}{F_{A0} - R F_{Af}} \quad \text{(by definition of } X_{out})$$

fn. of total feed converted in a single pass

we can still write, $F_{Af} = F_{A0} \cdot (1 - X_{Af})$

$$\therefore X_{out} = \frac{F_{A0} - F_{Af}}{F_{A0} - R \cdot F_{Af}} = \frac{F_{A0} - F_{A0}(1 - X_{Af})}{F_{A0} - F_{A0}(1 - X_{Af})R}$$

$$= \frac{1 - (1 - X_{Af})}{1 - (1 - X_{Af})R}$$

$$\boxed{X_{out} = \frac{X_{Af}}{1 - R(1 - X_{Af})}}$$

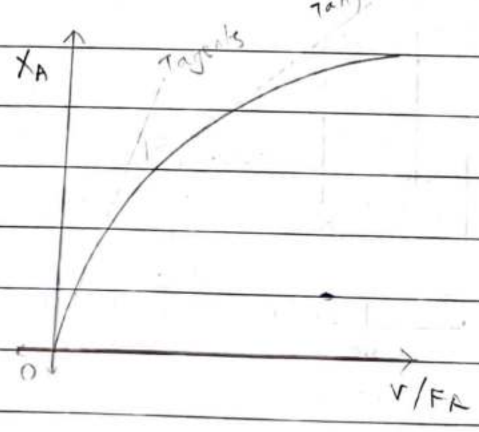
15. chemical kinetics

integral PFR :

$$\frac{V}{F_{A0}} = \int \frac{dX_A}{-r_A}$$

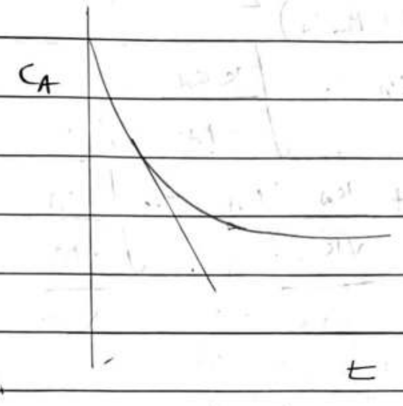
$$-r_A = \frac{dX_A}{d\left(\frac{V}{F_{A0}}\right)}$$

Tangents



& Sums from pg 67-72

Batch reaction:



slope $= -\underbrace{(-r_A)}_{\text{this is +ve}}$

16 analyze data

(i) Differential method of analysis (usually used when rate data are obtained at different conc.)

steps
→ linearize the rate eq
→ plot a graph (regress on calc → statistics (6))

eg: (1) $-r_A = k C_A^{\,n}$

$$\underbrace{\log(-r_A)}_{y} = \underbrace{\ln k}_{c} + \underbrace{n \ln C_A}_{mx}$$

(2) $-r_A = \dfrac{k C_A}{1 + k_A C_A}$

$$\frac{1}{-r_A} = \frac{1 + k_A C_A}{k C_A}$$

$$\frac{1}{-r_A} = \frac{1}{k C_A} + \frac{k_A}{k}$$

$$\underbrace{(1/-r_A)}_{y} = \underbrace{\frac{(1/C_A)^{x}}{k \leftarrow m}}_{mx} + \underbrace{\frac{k_A}{k}}_{c}$$ or $$\underbrace{\frac{C_A}{-r_A}}_{y} = \underbrace{\frac{1}{k}}_{c} + \underbrace{\frac{k_A C_A}{k}}_{mx}$$

evaluate this seperately in table

(3) $$-r_A = \frac{kC_A}{(1+K_A C_A)^2}$$

$$\therefore 1 + K_A C_A = \sqrt{\frac{kC_A}{-r_A}}$$

$$\therefore \underbrace{\frac{1}{\sqrt{k}}}_{c} + \underbrace{\frac{K_A}{\sqrt{k}}}_{m} \underbrace{C_A}_{x} = \underbrace{\sqrt{\frac{C_A}{-r_A}}}_{y}$$

(4) $$-r_A = k\, C_A^{\alpha} C_B^{\beta}$$

$$\rightarrow \underbrace{\ln(-r_A)}_{y} = \underbrace{\ln[k\, C_B^{\beta}]}_{c} + \underbrace{\alpha}_{m} \underbrace{\ln C_A}_{x}$$

we get, α

$$\rightarrow \underbrace{\ln\left(\frac{-r_A}{C_A^{\alpha}}\right)}_{y} = \underbrace{\ln k}_{c} + \underbrace{\beta}_{m} \underbrace{\ln C_B}_{x}$$

we get, β & k

(ii) integral method of analysis: (use this if data is of c v/s t or x v/s t
or τ or τ)

steps

→ Assume rate equation

→ integrate design eq & find relation b/w conc. v/s t or x v/s t

→ linearize the relation

→ make a plot

→ If the relation fits the data, find unknown parameters

eg! $$-r_A = \frac{kC_A}{1+K_A C_A}$$, Batch reactor

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

$$\frac{-dC_A}{dt} = \frac{k C_A}{1 + k_A C_A}$$

$$\int_{C_{A0}}^{C_A} \frac{dC_A (1 + k_A C_A)}{C_A \cdot \cancel{dt}} = -\int_0^t k\,dt$$

$$\int \frac{dC_A}{C_A} + k_A \int dC_A = -\int k\,dt$$

$$\ln \frac{C_A}{C_{A0}} + k_A (C_A - C_{A0}) = -kt$$

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

$$\underset{y}{} \qquad \underset{mx}{} \qquad \underset{c}{}$$

$$\frac{t}{C_A - C_{A0}} = x$$

17. Batch reactor (All the following derivations are for const vol. batch reactor)

(i) First order.

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

$$\therefore \int \frac{dC_A}{dC_A} = -k \int dt$$

$$\boxed{\begin{aligned} C_A &= C_{A0}(1 - X_A) \\ \frac{dC_A}{dt} &= -C_{A0} \frac{dX_A}{dt} \end{aligned}}$$

$$C_{A0} \cdot \frac{dX_A}{dt} = k C_A$$

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

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

$D_a = k t C_{A0}^{n-1}$

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$\therefore x_A = 1 - e^{-kt} = \underline{1 - e^{-D_a}}$

(ii) 2 nd order

a) $2A \rightarrow P$

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

imp step

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

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

$$-\frac{1(-1)}{1-x_A} - \frac{1(-1)}{1-0} = k C_{A0} t$$

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

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

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

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

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

$$x_A = \frac{k C_{A0} t}{k C_{A0} t + 1} = \underline{\frac{D_a}{D_a + 1}}$$

b) $A + B \rightarrow P$

if $C_{A0} = C_{B0}$

* same as above *

c) $A + B \rightarrow P$

$* \; C_B = C_{B_0} - C_{A_0} X_A$

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

$$-C_{A_0} \frac{dX_A}{dt} = k C_{A_0} (1 - X_A) (C_{B_0} - C_{A_0} X_A)$$

$$\int_0^{X_A} \frac{-dX_A}{(C_{B_0} - C_{A_0} X_A)(1 - X_A)} = \int_0^t k \, dt$$

splitting numerator, (Partial fractions)

$$\frac{A}{C_{B_0} - C_{A_0} X_A} + \frac{B}{1 - X_A}$$

$$= \frac{A(1 - X_A) + B(C_{B_0} - C_{A_0} X_A)}{(C_{B_0} - C_{A_0} X_A)(1 - X_A)}$$

$$= \frac{A - A X_A + B C_{B_0} - B C_{A_0} X_A}{(1 - X_A)(C_{B_0} - C_{A_0} X_A)}$$

$$\therefore A - A X_A + B C_{B_0} - B C_{A_0} X_A = 1$$

$$A + B C_{B_0} - X_A (A + B C_{A_0}) = 1$$

$A + B C_{B_0} = 1$ & $A + B C_{A_0} = 0$

$-B C_{A_0} + B C_{B_0} = 1$ $\quad$ $A = -B C_{A_0}$

$B (C_{B_0} - C_{A_0}) = 1$ $\quad$ $A = \dfrac{-C_{A_0}}{C_{B_0} - C_{A_0}}$

$B = \dfrac{1}{C_{B_0} - C_{A_0}}$

$$\therefore \int_0^{X_A} \left[\frac{C_{A_0} \, dX_A}{(C_{B_0} - C_{A_0})(C_{B_0} - C_{A_0} X_A)} - \frac{1 \, dX_A}{(C_{B_0} - C_{A_0})(1 - X_A)} \right] = \int k \, dt$$

$$\int_0^{X_A} \frac{1}{C_{B_0} - C_{A_0}} \left[\frac{C_{A_0}}{C_{B_0} - C_{A_0} X_A} \cdot dX_A - \frac{dX_A}{(1 - X_A)} \right] = \int k \, dt$$

$$\frac{1}{C_{B_0} - C_{A_0}} \left[\frac{C_{A_0}}{(-C_{A_0})} \ln\left(\frac{C_{B_0} - C_{A_0} X_A}{C_{B_0}}\right) - \ln(1 - X_A) \right] = \int k \, dt$$

$$\boxed{x_A = \frac{C_{A0} - C_A}{C_{A0}}}$$

$$1 - x_A = C_{A0} - \frac{C_{A0} + C_A}{C_{A0}}$$

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

$$\therefore \ln\left(\frac{C_{B0} - C_{A0}x_A}{C_{B0}(1 - x_A)}\right) = (C_{B0} - C_{A0})kt$$

$$\therefore \frac{C_{B0} - C_{A0}x_A}{C_{B0}(1 - x_A)} = e^{(C_{B0} - C_{A0})kt}$$

$$C_{B0} - C_{A0}x_A = e^{(C_{B0} - C_{A0})kt} C_{B0} - x_A e^{(C_{B0} - C_{A0})kt} C_{B0}.$$

$$x_A = 1 - \frac{C_{A0} - C_{B0}}{C_{A0} - C_{B0}e^{(C_{B0} - C_{A0})kt}}$$

(iii) general n^{th} order

$$-\frac{dC_A}{dt} = kC_A^n \qquad n \neq 1$$

$$\therefore C_{A0} \cdot \frac{dx_A}{dt} = kC_{A0}^n (1 - x_A)^n$$

no -ve sign here

$\because \frac{dC_A}{dt} = \frac{C_{A0}\,dx_A}{dt}$

$$\int_0^{x_A} \frac{dx_A}{(1 - x_A)^n} = \int_0^t kC_{A0}^{n-1} \cdot dt$$

$$\left[\frac{(1 - x_A)^{1-n}}{n-1}\right]_0^{x_A} = kC_{A0}^{n-1}t$$

$$\frac{(1 - x_A)^{1-n}}{n-1} - \frac{1}{n-1} = kC_{A0}^{n-1}t$$

$$\frac{(1 - x_A)^{1-n} - 1}{n-1} = kC_{A0}^{n-1}t$$

$$1 - x_A = \left[(kC_{A0}^{n-1}t)(n-1) + 1\right]^{1/1-n}$$

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

$$= \left[Da\,(n-1) + 1\right]^{1/1-n}$$

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18. Damkoelher no. (Da)

let, $Da = Kt\, C_{A0}^{n-1}$

$\therefore$ for: 1^{st} order $\rightarrow$ $X_A = 1 - e^{-Da}$

2^{nd} order $\rightarrow$ $X_A = \frac{Da}{1+Da}$

n^{th} order $\rightarrow$ $X_A = 1 - [Da(n-1)+1]^{1/1-n}$ $n \neq 1$

19 Half - life Period

when $C_A = C_{A0}/2$; $t = t_{1/2}$

for n^{th} order, $\left(\frac{C_A}{C_{A0}}\right)^{1-n} = (k\, C_{A0}^{n-1}\, t)(n-1)+1$

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

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

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

let, $\frac{C_A}{C_{A0}} = F$ ... (Fraction of A)

$$\boxed{t = \frac{F^{1-n} - 1}{K\, C_{A0}^{n-1}(n-1)}}$$, when, $F = 1/2$ we get $t_{1/2}$

Fractional life method

20. Reversible rxn (1st order)

#

$$A \rightleftharpoons B$$

$$-\frac{dC_A}{dt} = k_1 C_A - k_1' C_B$$

At const vol. $\boxed{C_{B0} + C_{A0} = C_A + C_B}$

$$\therefore C_B = C_{A0} + C_{B0} - C_A \quad \text{--- (1)}$$

$$\therefore -\frac{dC_A}{dt} = k_1 C_A - k_1'(C_{A0} + C_{B0} - C_A)$$

$$= (k_1 + k_1') C_A - k_1'(C_{A0} + C_{B0}) \quad \text{--- (2)}$$

At eq^{bm}, $r_{forward} = r_{reverse}$

$$\therefore k_1 C_{Aeq} = k_1' C_{Beq}$$

$$\frac{C_{Beq}}{C_{Aeq}} = \frac{k_1}{k_1'} = K \quad \text{--- (3)}$$

$$\therefore -\frac{dC_A}{dt} = \left(k_1 + \frac{k_1}{K}\right) C_A - \frac{k_1}{K}(C_{A0} + C_{B0})$$

$$= k_1 \left[\frac{(K+1)}{K} C_A - \frac{1}{K}(C_{A0} + C_{B0})\right] \quad \text{--- (4)}$$

At eq^{bm}, $C_{Beq} = C_{A0} + C_{B0} - C_{Aeq}$

$$K = \frac{C_{Beq}}{C_{Aeq}} = \frac{C_{A0} + C_{B0} - C_{Aeq}}{C_{Aeq}}$$

$$K = \frac{C_{A0} + C_{B0}}{C_{Aeq}} - 1$$

$$\left.\begin{aligned} (K+1) C_{Aeq} &= C_{A0} + C_{B0} \\ C_{Aeq} &= \frac{C_{A0} + C_{B0}}{K+1} \end{aligned}\right\} \quad \text{--- (5)}$$

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substituting (5) in (4)

$$\therefore -\frac{dC_A}{dt} = k_1 \left[\frac{(k+1)\,C_A}{k} - \frac{(k+1)\,C_{Aeq}}{k} \right]$$

$$\therefore \frac{-dC_A}{dt} = k_1 \left[\left(\frac{k+1}{k}\right) \left(C_A - C_{Aeq}\right) \right]$$

$$= \underbrace{\frac{k_1(k+1)}{k}}_{k_R} \left(C_A - C_{Aeq} \right) = k_R\, C_A'$$

$$\therefore -\frac{dC_A}{dt} = k_R \left(C_A - C_{Aeq} \right)$$

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

$$-\ln\left(\frac{C_A - C_{Aeq}}{C_{A0} - C_{Aeq}} \right) = k_R t$$

$$\frac{C_A - C_{Aeq}}{C_{A0} - C_{Aeq}} = e^{-k_R t} \quad \dots (6)$$

from (5), $$C_{Aeq} = \frac{C_{A0} + C_{B0}}{k+1}$$

if $C_{B0} = 0$

$$\therefore C_{Aeq} = \frac{C_{A0}}{k+1} \quad \dots (7)$$

putting in (6)

$$\frac{C_A - \frac{C_{A0}}{k+1}}{C_{A0} - \frac{C_{A0}}{k+1}} = e^{-k_R t}$$

$$\frac{C_A\left(1-\frac{C_{A0}}{C_A(K+1)}\right)}{C_{A0}\left(1-\frac{1}{K+1}\right)} = e^{-k_R t}$$

$$\frac{C_A}{C_{A0}}\left[1-\frac{C_{A0}}{C_A(K+1)}\right] = \left(1-\frac{1}{K+1}\right) e^{-k_R t}$$

$$\frac{C_A}{C_{A0}} - \frac{1}{K+1} = \frac{K+\cancel{1}-\cancel{1}}{K+1} e^{-k_R t}$$

$$\frac{C_A}{C_{A0}} = \frac{1}{K+1} + \frac{K}{K+1} e^{-k_R t}$$

$$\therefore \quad X_A = 1 - \frac{C_A}{C_{A0}}$$

$$= 1 - \frac{1}{K+1} - \frac{K}{K+1} e^{-k_R t}$$

$$= \frac{K}{K+1}\left[\frac{K+1}{K} - \frac{1}{K} - e^{-k_R t}\right]$$

$$= \frac{K}{K+1}\left[1 - e^{-k_R t}\right]$$

$$X_{Aeq} = 1 - \frac{C_{Aeq}}{C_{A0}} = \frac{K}{K+1} \quad \ldots \text{from } (7)$$

$$\therefore \quad X_A = X_{Aeq}\left[1 - e^{-k_R t}\right]$$

$$* \quad X_A = X_{Aeq}\left[1 - e^{-k_1\left(\frac{K+1}{K}\right)t}\right]$$

$$X_A = X_{Aeq}\left[1 - e^{-k_1 t / X_{Aeq}}\right]$$

Assumptions: → const vol system

→ initial conc of $B = 0$

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21. variable vol. Batch reactor

$$\epsilon = \frac{V_{x_A=1} - V_0}{V_0}$$

to characterize the volume change during a rxn

$$\epsilon = \frac{V_{x_A=1}}{V_0} - 1$$

$$V_{x_A=1} = (\epsilon+1) V_0$$

$$V_{x_A} = (\epsilon x + 1) V_0 \quad \cdots \text{(At any } x)$$

$\because V \propto N_T$

$$\frac{V}{V_0} = \frac{N_T}{N_{T_0}}$$

in general, $-r_A = -\frac{1}{V}\frac{dN_A}{dt}$ ... (design eq for batch reactor)

$$= \frac{N_{A0}}{V}\frac{dx_A}{dt} \quad \cdots (\because N_A = N_0(1-x_A))$$

$$= \frac{N_{A0}}{V_0(1+\epsilon x_A)} \cdot \frac{dx_A}{dt}$$

$$-r_A = \frac{C_{A0}}{(1+\epsilon x_A)} \cdot \frac{dx_A}{dt}$$

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

22. For 1st order rxn variable vol batch reactor:

from pt (21)

$$t = \int^{x_A} \frac{C_{A0} \cdot dx_A}{-kC_A \; (1-\epsilon x_A)} \quad \cdots (1)$$

☆☆☆

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

$$\therefore \quad \boxed{1+\epsilon X_A = \frac{C_{A0}(1-X_A)}{C_A}} \quad \text{imp} \quad \ldots (2)$$

putting this in (1)

$$t = \int_0^{X_A} \frac{\cancel{C_{A0}}}{-k\,\cancel{C_A}} \cdot \frac{dX_A \cdot \cancel{C_A}}{\cancel{C_{A0}}(1-X_A)}$$

$$t = \int_0^{X_A} \frac{dX_A}{-k(1-X_A)}$$

$$t = \frac{1}{-k} \ln\left(\frac{1-X_A}{1}\right)$$

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

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

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

Same as for const vol reaction system

$\therefore$ for 1st order conversion in a batch reactor is not influenced by change in volume

2nd order rxn :

$$t = \int_0^{X_A} \frac{C_{A0}}{k C_A^2} \cdot \frac{dX_A}{(1+\epsilon X_A)} \quad \ldots (3)$$

we know, $\quad C_A = \dfrac{C_{A0}(1-X_A)}{1+\epsilon X_A} \quad \ldots$ from (2)

putting this in (3)

$$t = \int_0^{X_A} \frac{C_{A0}(1+\epsilon X_4)^2}{k C_{A0}^2 (1-X_4)^2} \cdot \frac{dX_A}{\cancel{(1+\epsilon X_A)}}$$

$$\therefore \quad t = \frac{1}{k C_{A0}} \int_0^{X_A} \frac{1+\epsilon X_A}{(1-X_A)^2} \cdot dX_4$$

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$$\therefore t = \frac{1}{kC_{A0}} \int_0^{X_A} \left[\underbrace{\frac{1}{(1-X_A)^2}}_{A} + \underbrace{\frac{\epsilon X_A}{(1-X_A)^2}}_{B} \right] \cdot dX_A$$

integration of (B)

$$\epsilon \int \frac{X_A}{(1-X_A)^2}$$

$$= \epsilon \int \frac{X_A}{1 - 2X_A + X_A^2}$$

$$= \epsilon \int \frac{1}{\cancel{2}} \left(\frac{\cancel{2}X_A - 2 + 2}{1 - 2X_A + X_A^2} \right)$$

$$= \epsilon \int \frac{1}{2} \left(\frac{2X_A - 2}{1 - 2X_A + X_A^2} + \frac{2}{(1-X_A)^2} \right)$$

$$= \epsilon \frac{1}{2} \left[\ln (1-X_A)^2 + \frac{2}{(1-X_A)} \right]_{0}^{X_A} \quad \ldots \left(\because \int \frac{f'(x)}{f(x)} = \ln f(x) \right)$$

$$= \epsilon \left[\ln (1-X_A) + \frac{1}{1-X_A} \right]_0$$

$$= \epsilon \left(\ln (1-X_A) + \frac{1}{1-X_A} - 1 \right)$$

integration of (A)

$$\int \frac{1}{(1-X_A)^2} = \left[\frac{1}{1-X_A} \right]_0^{X_A} = \frac{1}{1-X_A} - 1$$

$$\therefore t = \frac{1}{kC_A} \int_0^{X_A} \left[\frac{1}{1-X_A} - 1 + \epsilon \ln (1-X_A) + \frac{\epsilon}{1-X_A} - \epsilon \right]$$

$$= \frac{1}{kC_{A_0}} \left[\frac{\epsilon + 1}{1-X_A} - (\epsilon + 1) + \epsilon \ln (1-X_A) \right]$$

$$ktC_{A_0} = \epsilon + 1 \left[\frac{1}{1-X_A} - 1 \right] + \epsilon \ln (1-X_A)$$

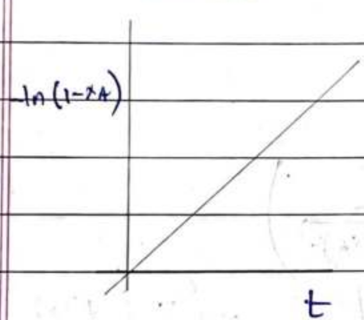
$$ktC_{A_0} = \epsilon + 1 \left[\frac{\cancel{1} - \cancel{1} + X_A}{1-X_A} \right] + \epsilon \ln (1-X_A)$$

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

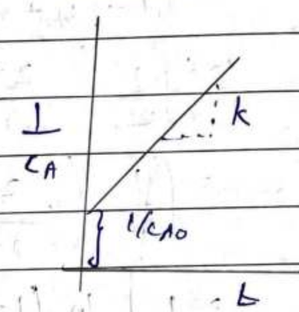
23. integral method

(i) Const vol Batch reactor

1st order



2nd order.



nth order

$$t_f = \frac{F^{1-n} - 1}{k(n-1)} C_{A0}^{(1-n)}$$ ... from pt (19)

log t_F v/s log C_{A0}

(ii) $A + B \rightarrow P$

$$M = \frac{C_{B0}}{C_{A0}}, \quad M \neq 1$$

$$C_{A0} X_A = C_B X_B$$

$$-r_A = -\frac{dC_A}{dt} = C_{A0} \cdot \frac{dX_A}{dt} = k\, C_{A0}(1-X_A)(C_{B0} - C_{A0}X_A)$$

$$= k\, C_{A0}(1-X_A)(M C_{A0} - C_{A0}X_A)$$

$$C_{A0} \cdot \frac{dX_A}{dt} = k\, C_{A0}^2 (1-X_A)(M-X_A)$$

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

Partial fractions :

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

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

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

$\therefore \quad A + B = 0 \quad , \quad MA + B = 1$

$A = -B \qquad -MB + B = 1$

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

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

$$\therefore \quad kC_{A0} \cdot dt = \int_0^{X_A} \left(\frac{-1/1-M}{1-X_A} + \frac{1/1-M}{M-X_A} \right) \cdot dX_A$$

$$= \frac{-1}{1-M} \frac{\ln(1-X_A)}{-1} + \frac{(-1)}{1-M} \ln\left(\frac{M-X_A}{M}\right)$$

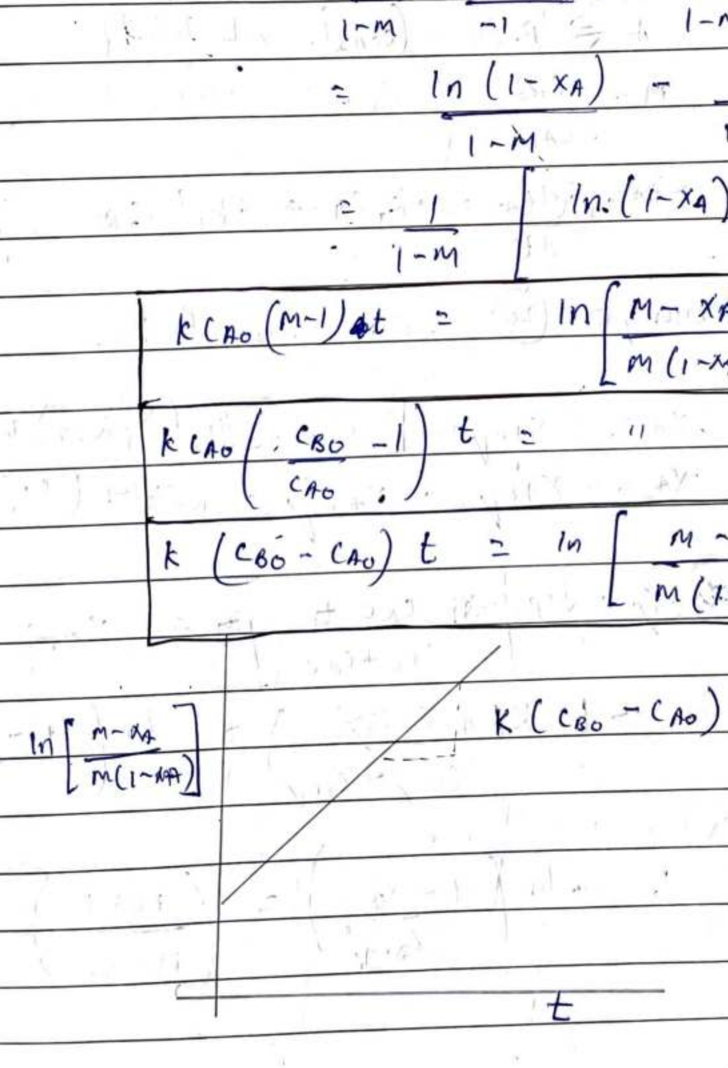
$$= \frac{\ln(1-X_A)}{1-M} - \frac{1}{1-M} \ln\left(\frac{M-X_A}{M}\right)$$

$$= \frac{1}{1-M}\left[\ln(1-X_A) - \ln\left(\frac{M-X_A}{M}\right)\right]$$

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

$$\boxed{kC_{A0}\left(\frac{C_{B0}}{C_{A0}} - 1\right)t = \text{''}}$$

$$\boxed{k(C_{B0} - C_{A0})t = \ln\left[\frac{M-X_A}{M(1-X_A)}\right]}$$



(const vol.)

similarly for, $A + 2B \rightarrow P$, $M = \frac{C_{B0}}{C_{A0}}$

$$-r_A = \frac{-dC_A}{dt} = C_{A0} \cdot \frac{dX_A}{dt} = k\, C_{A0}(1 - X_A)(C_{B0} - 2X_A C_{A0})$$

$$\therefore C_{A0} \cdot \frac{dX_A}{dt} = k\, C_{A0}(1 - X_A)(M C_{A0} - 2X_A C_{A0})$$

$$\therefore C_{A0} \frac{dX_A}{dt} = k\, C_{A0}^2 (1 - X_A)(M - 2X_A)$$

$$\therefore \frac{dX_A}{(1 - X_A)(M - 2X_A)} = k\, C_{A0} \cdot dt$$

similarly

$$\ln\left[\frac{M - 2X_A}{M(1 - X_A)}\right] = C_{A0}(M - 2)kt$$

(iii) $A \rightleftharpoons R$ (const. vol batch)

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

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

from pt (20), we can write.

$$X_A = X_{Aeq}\left[1 - e^{-k_1 (K^?/K_{eq}) t}\right]$$

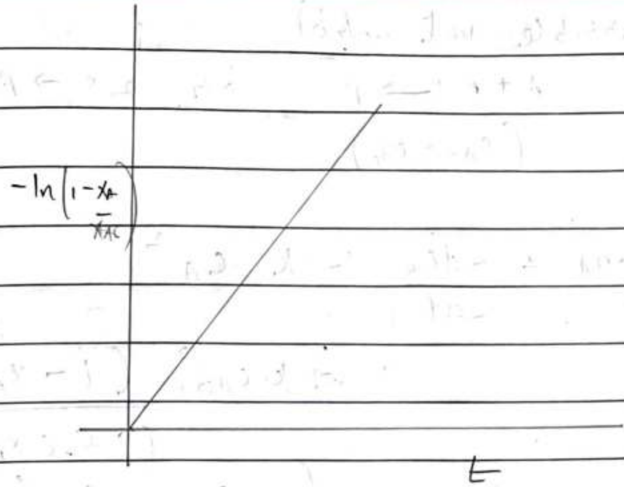
$$X_A = X_{Aeq} - X_{Aeq} \cdot \exp\left[-k_1 \left(\frac{\frac{C_{Re}}{C_{Ae}}}{\frac{C_{Re}}{C_{Ae}} + 1}\right)\right]$$

$$X_{Aeq} \cdot \exp\left[-k_1 \frac{C_{Re}\, t}{C_{Re} + C_{Ae}}\right] = X_{Aeq} - X_A$$

$$-t\, k_1 \left(\frac{C_{Req}}{C_{Req} + C_{Aeq}}\right) = \ln\left(1 - \frac{X_A}{X_{Aeq}}\right)$$

??

$$\therefore -\ln\left(1 - \frac{X_A}{X_{Aeq}}\right) = \left(\frac{M + 1}{M + X_{Ae}}\right) k_1\, t$$



(iv) $A \rightarrow P$ (variable vol. batch)

Zeroth order.

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

$$t = \int_0^{x_A} \frac{C_{A0}}{-r_A} \frac{dx_A}{(1+\epsilon x_A)} \quad \text{... from pt (21)}$$

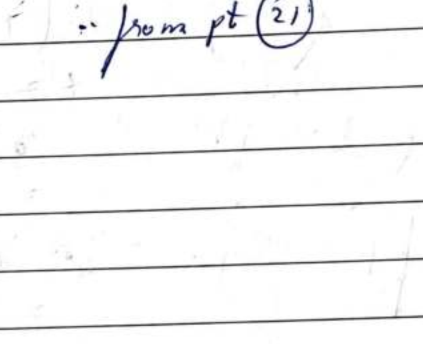
$$\therefore t = \int_0^{x_A} \frac{C_{A0}}{k} \frac{dx_A}{(1+\epsilon x_A)}$$

$$= \frac{C_{A0}}{k} \frac{\ln(1+\epsilon x_A)}{\epsilon}$$

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

$$kt = \frac{C_{A0}}{\epsilon} \ln(1+\epsilon x_A)$$

$$\frac{C_{A0}}{\epsilon} \ln\left(\frac{V}{V_0}\right) = kt$$



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(v) (variable vol batch)

$$A + B \rightarrow P \quad \text{or} \quad 2A \rightarrow P$$

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

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

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

$$\ldots\left(\because C_A = \frac{C_{A0}(1-X_A)}{1+\epsilon_A}\right)$$

$$\therefore \frac{C_{A0}\cdot dX_A}{dt} = k\,C_{A0}^2 \frac{(1-X_A)^2}{(1+\epsilon X_A)^2}$$

$$\cancel{\left(\frac{1+\epsilon X_A}{1-X_A}\right)^2 \frac{dX_A}{dt} = k\,C_{A0}\cdot dt}$$

$$t = \int_0^{X_{A0}} \frac{C_{A0}}{-r_A\,(1-\epsilon X_A)}\cdot dX_A$$

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

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

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

$$t = \frac{1}{kC_{A0}} \int_0^{X_A} \left[\frac{1}{(1-X_A)^2} + \frac{\epsilon X_A}{(1-X_A)^2}\right]\cdot dX_A$$

$$\therefore \boxed{k t\,C_{A0} = \frac{(\epsilon+1)X_A}{1-X_A} + \epsilon \ln(1-X_A)}$$

~~this~~ Refer to pt (22) integration part.

* even though the rxn is gas phase, but if $\epsilon = 0$ i.e vol. change is 0 or moles on products - moles on reactant = 0

24. enzyme - catalytic reaction

$$A \rightarrow P + Q$$

rate : $-r_A = \dfrac{kC_A}{1+k_P C_P}$ ... similar to michelle ment's

$$\frac{-dC_A}{dt} = \frac{kC_A}{1+k_P C_P}$$

we know, $C_P = C_{A0} - C_A$

$$-\int_{C_{A0}}^{C_A} \frac{(1+k_P C_P)\,dC_A}{k\,C_A} = \int_0^t k\,dt$$

$$-\int \frac{dC_A}{C_A} - \int k_P \frac{(C_{A0}-C_A)}{C_A} \cdot dC_A = kt$$

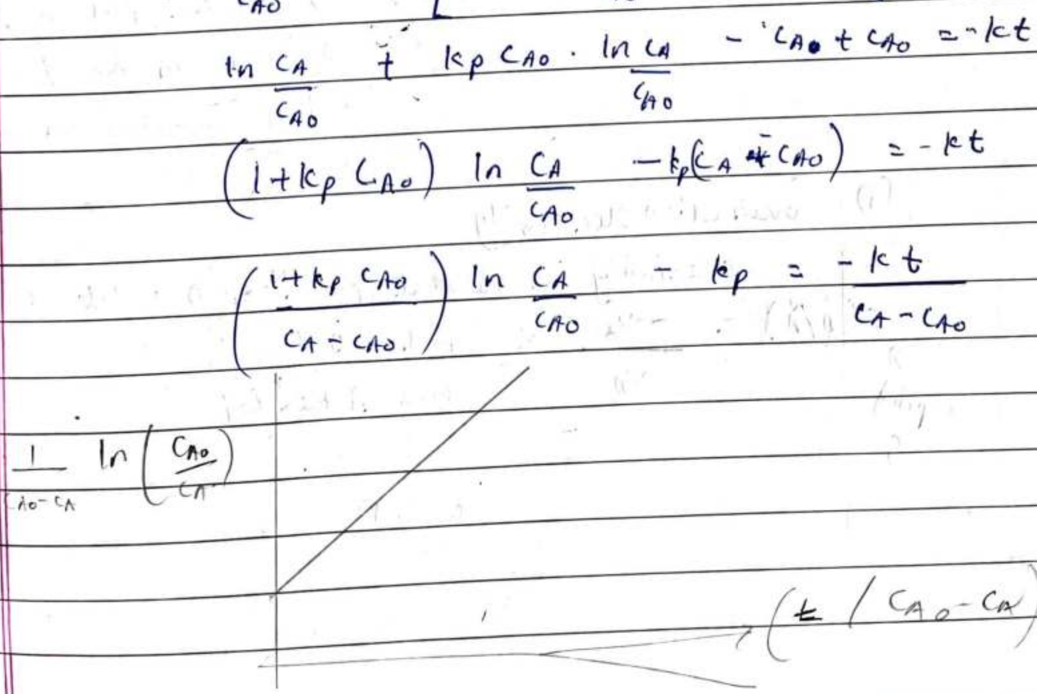
$$-\ln \frac{C_A}{C_{A0}} - \int k_P \left[\frac{C_{A0}}{C_A} \cdot dC_A - 1 \cdot dC_A \right] = kt$$

$$-\ln \frac{C_A}{C_{A0}} - k_P \left[C_{A0} \cdot \ln \frac{C_A}{C_{A0}} - (C_A - C_{A0}) \right] = kt$$

$$\ln \frac{C_A}{C_{A0}} + k_P C_{A0} \cdot \ln \frac{C_A}{C_{A0}} - C_{A0} + C_{A0} = -kt$$

$$(1+k_P C_{A0}) \ln \frac{C_A}{C_{A0}} - k_P (C_A - C_{A0}) = -kt$$

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



$-r_A = dq\, C_A$

* when ever k & n are asked use $-r_A = k C_A^n$ relation no matter which reactor.

25 Single reactions

$$P + 2Q \rightarrow R + 3S \qquad \sum \nu_{ki} A_i = 0$$

$\nu_P = -1 \qquad \nu_R = 1$

$\nu_Q = -2 \qquad \nu_S = 3$

Batch : $\Delta N_i = N_i - N_{i0}$

$$\frac{\Delta N_P}{\nu_P} = \frac{\Delta N_Q}{\nu_Q} = \frac{\Delta N_R}{\nu_R} = \frac{\Delta N_S}{\nu_S} = \xi \quad (\text{zeta})$$

Flow : $$\frac{\Delta F_P}{\nu_P} = \frac{\Delta F_Q}{\nu_Q} = \cdots = \xi$$

ξ is the extent of reaction

26. Multiple reaction

for batch reactor : $$\Delta N_i = N_i - N_{i0} = \sum_{k=1}^{n} \nu_{ki}\, \xi_k$$

where, n is the total no. of reactions in the batch reactor. k is a particular reaction.

(i) over all selectivity

selectivity of desired prod. D w.r.t reactant A.

$$S(D/A) = \frac{-\nu_A}{\nu_D} \times \frac{\text{mols D formed}}{\text{mols A reacted}}$$

capital S

$$A \rightarrow D$$

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(ii) Point / instantaneous selectivity

selectivity in a reactor at any given point

$$s(D/A) = \frac{(-\nu_A)}{\nu_D} \times \frac{(\text{Rate of formation of } D)}{(\text{Rate of consumption of } A)}$$

small s

* for PFR & Batch : S & s may be diff.
for CSTR : $S = s$.

(iii) Yield :

$$Y(D/A) = \frac{(-\nu_A) \times (\text{mol } D \text{ formed})}{(\nu_D) \times (\text{mol } A \text{ fed / charged})}$$

Yield = conversion × selectivity

$Y(D/A) = X_A \times S(D/A)$

ν_A & ν_D are the stoichiometric coeff of D & A

* objectives of multiple reaction study:
→ To maximize selectivity
→ To maximize rate of reaction.

27. Series (consecutive) reactions

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \qquad , \quad C_{R_0} = C_{S_0} = 0$$

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

$$-\int \frac{dC_A}{C_A} = \int k_1 \, dt$$

$$-\ln \frac{C_A}{C_{A0}} = k_1 t \quad \Rightarrow \quad C_A = C_{A0} \cdot e^{-k_1 t} \quad \ldots (1)$$

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

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

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

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0}\, e^{-k_1 t} \quad \cdots (2)$$

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

for linear DE, we know (12th integration)

Integrating factor = I.F = $e^{\int P \cdot dx}$

& multiply the eq. by I.F on both sides.

∴ Here,

$$I.F = e^{\int k_2 dt} = e^{k_2 t}$$

Multiplying this on both sides of (2)

$$\therefore \int \Big[\underbrace{\frac{dC_R}{dt} \cdot e^{k_2 t}}_{\frac{d(I)}{dt} \cdot II} + \underbrace{k_2 C_R \cdot e^{k_2 t}}_{\frac{d(II)}{dt} \cdot I} \Big] = \int k_1 C_{A0}\, e^{-k_1 t} \cdot e^{k_2 t}$$

$$\therefore \int \left[\frac{dC_R}{dt} \cdot e^{k_2 t} + C_R \cdot \frac{d(e^{k_2 t})}{dt} \right] dt = k_1 C_{A0} \int e^{(k_2 - k_1)t}$$

$$\therefore \int \frac{d\left(C_R \cdot e^{k_2 t}\right)}{dt} \cdot dt = k_1 C_{A0} \int e^{(k_2 - k_1)t} \cdot dt + C$$

$$C_R \cdot e^{k_2 t} = k_1 C_{A0} \frac{e^{(k_2 - k_1)t}}{k_2 - k_1} + C \quad \cdots (3)$$

At, $t = 0$ $C_R = 0$ ...(boundary condition)

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

$$\therefore C = \frac{k_1 C_{A0} \cancel{e^{(k_2-k_1)t}}}{k_1 - k_2} \quad \cdots (4)$$

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subs (4) in (3)

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

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

$$\therefore C_R = \frac{k_1 C_{A0}}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \quad \cdots (5) \quad k_1 \neq k_2$$

$$S_R = \frac{-(-1)}{1} \cdot \frac{C_R}{C_{A0}-C_A}$$

selectivity of R

here we consider only this part of rxn $A \to R$.

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

$$S_R = \frac{k_1}{k_2-k_1}\left(\frac{e^{-k_1 t} - e^{-k_2 t}}{1 - e^{-k_1 t}}\right) \quad \cdots (6)$$

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

$$Y_R = \frac{k_1}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \quad \cdots (7)$$

$$= S_R \cdot X_A$$

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

$$\int_0^{C_S} dC_S = \frac{k_2 k_1 C_{A0}}{k_2-k_1} \int_0^t \left(e^{-k_1 t} - e^{-k_2 t}\right) dt$$

$$C_S = \frac{k_2 k_1 C_{A0}}{k_2-k_1}\left(\left[\frac{e^{-k_1 t}}{-k_1}\right]_0^t - \left[\frac{e^{-k_2 t}}{-k_2}\right]\right)$$

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

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

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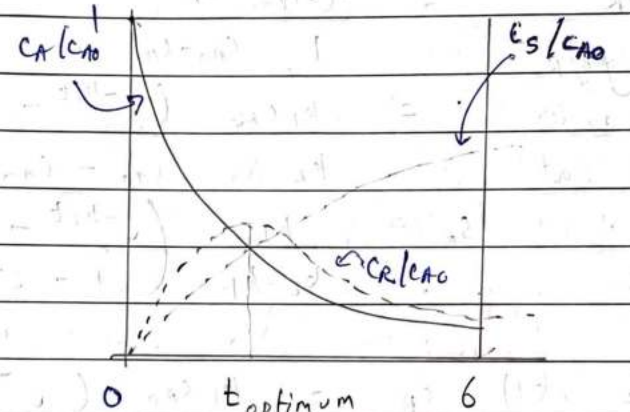
$$C_S = \left[-\frac{k_2\left(e^{-k_1 t}-1\right)}{k_2-k_1} + \frac{k_1\left(e^{-k_2 t}-1\right)}{k_2-k_1} \right] C_{A0}$$

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

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

$$C_S = C_{A0}\left[\frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2-k_1} + 1\right] \quad \dots (8)$$



if $k_1 = k_2$,

$$C_R = k_1 t \, C_{A0} \, e^{-k_1 t} \quad \dots (9)$$

For t_{opt}

for t_{opt} take (C_R/C_{A0}) $\rightarrow$ $\left(\frac{C_R}{C_{A0}}\right) = \frac{k_1}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$ (10) ... from (5)

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

$$\frac{d}{dt}\left(\frac{C_R}{C_{A0}}\right) = 0 \quad \dots \text{for Maximum yield.}$$

$$\therefore k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$$

$$\therefore \frac{k_1}{k_2} = e^{(-k_2 + k_1)t}$$

$$\therefore \ln\frac{k_1}{k_2} = (k_1-k_2)\, t_{opt}$$

$$\therefore \boxed{t_{opt} = \frac{\ln(k_1/k_2)}{k_1-k_2}} \quad \dots (11)$$

putting this in (10)

$$\therefore \left(\frac{C_R}{C_{A0}}\right)_{max} = \frac{k_1}{k_2-k_1}\left[e^{\frac{-k_1}{k_1-k_2}\ln(k_1/k_2)} - e^{-\frac{k_2}{k_1-k_2}\ln(k_1/k_2)}\right]$$

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

$$\left(\frac{C_R}{C_{A0}}\right)_{max} = \frac{k_1}{k_2-k_1}\left(\frac{k_1}{k_2}\right)^{\frac{1}{k_1-k_2}}\left[\left(\frac{k_1}{k_2}\right)^{-k_1} - \left(\frac{k_1}{k_2}\right)^{-k_2}\right]$$

??

$$\left(\frac{C_R}{C_{A0}}\right)_{max} = \left(\frac{k_1}{k_2}\right)^{k_2/k_2-k_1}$$

if, $k_1 = k_2$

$$\frac{C_R}{C_{A0}} = k_1 t\, e^{-k_1 t} \quad \dots \text{from (9)}$$

$$\frac{d}{dt}\left(\frac{C_R}{C_{A0}}\right) = k_1 t\, e^{-k_1 t}\cdot(-k_1) + k_1 e^{-k_1 t} = 0$$

$$\cancel{k_1^2} t\, \cancel{e^{-k_1 t}} = \cancel{k_1}\, \cancel{e^{-k_1 t}}$$

$$k_1 t = 1$$

$$t_{opt} = \frac{1}{k_1}$$

$$\therefore \left(\frac{C_R}{C_{A0}}\right)_{max} = \cancel{k_1}\times\frac{1}{\cancel{k_1}}\, e^{-\cancel{k_1}\frac{1}{\cancel{k_1}}} = e^{-1}$$

$$\therefore \left(\frac{C_R}{C_{A0}}\right)_{max} = \frac{1}{e}$$

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28. Time - independent analysis $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

(1)

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

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$ redone in pt (30)

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

$$\therefore \frac{dC_R}{dC_A} = -1 + \frac{k_2}{k_1}\left(\frac{C_R}{C_A}\right)$$

$$\frac{dC_R}{dC_A} - \frac{k_2}{k_1}\left(\frac{C_R}{C_A}\right) = -1 \quad \text{---(1)}$$

$$\left(\frac{dY}{dx} + PY = Q\right)$$

wrong

$$I.F = e^{\int P \cdot dx} = e^{\int -k_2/k_1 \cdot dC_A} = e^{-\frac{k_2}{k_1}(C_{A0}-C_A)}$$

$$\int \frac{dC_R}{dC_A} \cdot e^{-k_2/k_1 (C_{A0}-C_A)} - \frac{k_2}{k_1}\left(\frac{C_R}{C_A}\right) e^{-k_2/k_1 (C_{A0}-C_A)} = \int -e^{-k_2/k_1 (C_{A0}-C_A)} \cdot dC_A$$

$$\int \frac{d\left((C_R/C_A) \cdot e^{-k_2/k_1 (C_{A0}-C_A)}\right)}{dt} = \frac{-e^{-(k_2/k_1)(C_{A0}-C_A)}}{-\frac{k_2}{k_1}}$$

wrong

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

At, $t=0$, $C_R = 0$ & $C_A = C_{A0}$

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

$$\frac{dC_B}{d\tau} = k_1 C_{A0} e^{-k_1 \tau} - k_2 C_B^{\,2}$$ ← (How to solve in excel)

$$\therefore \left(\frac{C_R}{C_A}\right) e^{-k_2/k_1 (C_{A0}-C_A)} = \frac{k_1}{k_2} e^{\frac{-k_2}{k_1}(C_{A0}-C_A)} - \frac{k_1}{k_2}$$

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

$$\frac{C_R}{C_A}\cdot\frac{k_2}{k_1} = 1 - e^{k_2/k_1 (C_{A0}-C_A)}$$

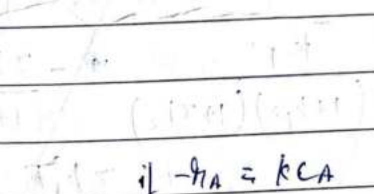
$$\ln\left(\frac{C_R}{C_A}\cdot\frac{k_2}{k_1}\right)$$

$$\frac{C_R}{C_{A0}} = \frac{1}{\left(1-\frac{k_2}{k_1}\right)}\left[\left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} - \frac{C_A}{C_{A0}}\right]$$

check if this is correct

Remember!
$$\boxed{\frac{C_R}{C_{A0}} = \left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1}\cdot\frac{C_{R0}}{C_{A0}} + \frac{1}{\left(1-\frac{k_2}{k_1}\right)}\left[\left(\frac{C_{A0}}{C_{A0}}\right)^{k_2/k_1} - \frac{C_A}{C_{A0}}\right]}$$ ✓

(ii) PFR



Rate in − Rate out + generation = Acc.

$$Q C_A - Q(C_A + dC_A) + r\cdot dV = 0$$

$$Q[C_A - C_A - dC_A] = -r_A \cdot dV$$

$$\frac{-dC_A}{-r_A} = \frac{dV}{Q} = d\tau$$

if $-r_A = kC_A$, $\displaystyle\int \frac{-dC_A}{kC_A} = \int d\tau$

$$\ln\frac{C_A}{C_{A0}} = -k\tau$$

$$C_A = C_{A0}\, e^{-k\tau}$$

(iii) CSTR

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

for A : $\tau = \dfrac{C_{A0} - C_A}{-r_A} = \dfrac{C_{A0} - C_A}{k_1 C_A}$

$$C_A = \frac{C_{A0}}{(1+k_1\tau)} \quad \dots (i)$$

for R : Rate of R in − Rate of R out + Generation of R = 0

$$0 - Q C_R + v(k_1 C_A - k_2 C_R) = 0$$

$$C_R = \tau(k_1 C_A - k_2 C_R)$$

$$C_R + \tau k_2 C_R = \tau k_1 C_A$$

$$C_R = \frac{\tau k_1 C_A}{1+\tau k_2}$$

$$C_R = \frac{\tau k_1 C_{A0}}{(1+k_1\tau)(1+\tau k_2)} \quad \dots \text{from (i)}$$

$$\frac{C_R}{C_{A0}} = \frac{\tau k_1}{[(1+k_1\tau)(1+\tau k_2)]} \quad \dots (2)$$

$$\frac{d}{d\tau}\left(\frac{C_R}{C_{A0}}\right) = \frac{k_1}{(1+k_1\tau)(1+\tau k_2)} + \left[\frac{\tau k_1 (-1)(k_2)}{(1+k_1\tau)(1+\tau k_2)^2} + \frac{\tau k_1 (-1)(-k_1)}{(1+\tau k_2)(1-k_1\tau)^2}\right]$$

$$0 = \frac{k_1}{(1+k_1\tau)(1+\tau k_2)} - \frac{\tau k_1 k_2}{(1+k_1\tau)(1-\tau k_2)^2} + \frac{\tau k_1^2 k}{(1+\tau k_2)(1-k_1\tau)^2}$$

$$0 = 1 k_2 - \frac{\tau k_2}{(1-\tau k_2)^2} + \frac{\tau k_1}{(1-k_1\tau)^2}$$

$$0 = \frac{(1-\tau k_2)^2 - 2k_2}{(1-\tau k_2)^2} + \frac{\tau k_1}{(1-k_1\tau)^2}$$

$$\frac{\tau k_1}{1 - 2k_1\tau + k_1^2\tau^2} = \frac{2k_2 - (1 - 2\tau k_2 + \tau^2 k_2^2)}{1 - 2\tau k_2 + \tau^2 k_2^2}$$

$$\frac{\tau k_1}{1 - 2k_1\tau + k_1^2\tau^2} = \frac{2k_2 - 1 + 2\tau k_2 - \tau^2 k_2^2}{1 - 2\tau k_2 + \tau^2 k_2^2}$$

$$0 = (1-\tau k_2)^2 (1 - k_1\tau)^2 - \tau k_2 (1 - k_1\tau)^2 + \tau k_1 (1 - \tau k_2)^2$$

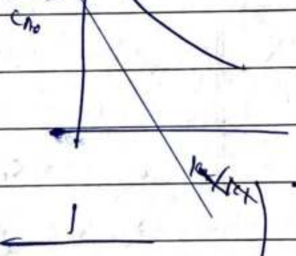
$$\tau\left[k_2 (1 - k_1\tau)^2 - k_1(1-\tau k_2)^2\right] = \left[(1-\tau k_2)(1 - k_1\tau)\right]^2$$

$$\tau\left[(k_2^2 - k_2^2 k_1\tau + k_1^2 - \tau k_2 k_1^2)(k_2^2 - k_2^2 k_1 \tau - k_1^2 + \tau k_2 k_1^2)\right] = [\ \dots\ ]$$

$a^2 - b^2 = (a+b)(a-b)$

$$\tau_{opt} = \frac{1}{\sqrt{k_1 k_2}}$$

$$\frac{C_{R\,max}}{C_{A0}} = \frac{1}{\left(1 + \sqrt{\frac{k_2}{k_1}}\right)^2}$$



differentiating (2),

$$\frac{d}{d\tau}\left(\frac{C_R}{C_{A0}}\right) = \frac{k_1}{(1+k_1\tau)(1+\tau k_2)} + \left[\frac{\tau k_1}{1}\, \frac{d}{d\tau}\left(\frac{1}{(1+k_1\tau)(1+\tau k_2)}\right)\right]$$

$$= \frac{k_1}{(1+k_1\tau)(1+\tau k_2)} \times \left\{\tau k_1\left[\frac{1}{(1+\tau k_2)} \times \frac{(-1)(k_1)}{(1+k_1\tau)^2} + \frac{1}{(1+\tau k_1)} \times \frac{(-1 k_2)}{(1+\tau k_2)^2}\right]\right\}$$

$$\frac{d}{d\tau}\left(\frac{C_R}{C_{A0}}\right) = \frac{k_1}{(1+k_1\tau)(1+\tau k_2)} - \frac{\tau k_1^2}{(1+\tau k_2)(1+k_1\tau)^2} - \frac{\tau k_1 k_2}{(1+\tau k_1)(1+\tau k_2)^2}$$

for maximizing C_R/C_{A0}, $\frac{d}{d\tau}\left(\frac{C_R}{C_{A0}}\right) = 0$

at τ_{opt}

$$\therefore \quad 0 = \frac{\cancel{k_1}}{\cancel{(1+k_1\tau)}\cancel{(1+\tau k_2)}} - \frac{\tau k_1^{\cancel{2}}}{\cancel{(1+\tau k_2)}(1+k_1\tau)^{\cancel{2}}} - \frac{\tau \cancel{k_1} k_2}{\cancel{(1+\tau k_1)}(1+\tau k_2)^{\cancel{2}}}$$

$$\therefore \quad 0 = 1 - \frac{\tau k_1}{(1+k_1\tau)} - \frac{\tau k_2}{(1+\tau k_2)}$$

$$\therefore \quad \frac{\tau k_1}{1+k_1\tau} + \frac{\tau k_2}{1+\tau k_2} = \cancel{\frac{\tau k_1}{1+k_1\tau}} \; 1$$

$$\therefore \quad \cancel{\tau k_1} + \cancel{\tau^2 k_1 k_2} + \cancel{\tau k_2} + \tau^2 k_1 k_2 = 1 + \cancel{k_2\tau} + \cancel{k_1\tau} + \cancel{k_1 k_2 \tau^2}$$

$$\therefore \quad \tau^2 k_1 k_2 = 1$$

$$\therefore \quad \tau_{opt} = \frac{1}{\sqrt{k_1 k_2}}$$

substituting τ_{opt} in (2)

$$\therefore \frac{C_{Rmax}}{C_{A0}} = \frac{\frac{1}{\sqrt{k_1 k_2}} \times k_1}{\left(1 + k_1 \times \frac{1}{\sqrt{k_1 k_2}}\right)\left(1 + k_2 \times \frac{1}{\sqrt{k_1 k_2}}\right)}$$

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

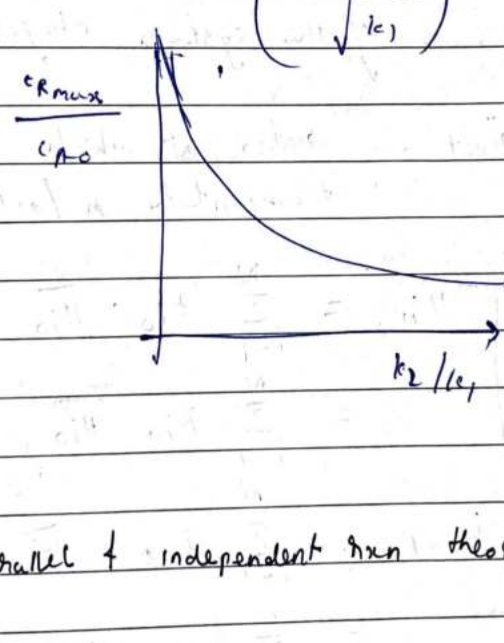
$$\frac{C_{Rmax}}{C_{A0}} = \frac{\sqrt{\frac{k_1}{k_2}}}{1 + \sqrt{\frac{k_2}{k_1}} + \sqrt{\frac{k_1}{k_2}} + 1}$$

= dividing by $\sqrt{\frac{k_1}{k_2}}$ above & below

$$= \frac{1}{\sqrt{\frac{k_2}{k_1}} + \sqrt{\frac{k_2}{k_1} \times \frac{k_2}{k_1}} + 1 + \sqrt{\frac{k_2}{k_1}}}$$

$$= \frac{1}{1 + 2\sqrt{\frac{k_2}{k_1}} + \frac{k_2}{k_1}}$$

$$\therefore \; C_{Rmax} = \frac{1}{\left(1 + \sqrt{\frac{k_2}{k_1}}\right)^2}$$



* Read Parallel & independent rxn theory from notes.

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29. Energy balance

(i) General Macroscopic energy balance:

- energy bal. eq for a reactor with more than one rxn can be written as:

$$0 = Q - W_s + (\dot{H}_{in} - \dot{H}_{out}) = \frac{d}{dt}(U_{sys}) \quad \cdots (1)$$

Q : rate of heat transfer into the reactor (kJ/s)

$\bar{W}_s$: rate at which shaft work is done on the system (eg: by agitator) (usually taken zero)

$\frac{d(U_{sys})}{dt}$: rate at which total internal energy of the system changes w.r.t time.

$\dot{H}_{in}$, $\dot{H}_{out}$: rates at which enthalpies are transported in/out of the reactors.

$$(2) \cdots \begin{cases} \dot{H}_{in} = \sum_{i=1}^{N} F_{i0} \cdot \overline{H_{i0}} \\ \quad = \sum_{i=1}^{N} F_{i0} H_{i0} \\ \dot{H}_{out} = \sum_{i=1}^{N} F_{i} \cdot \overline{H_i} \\ \quad = \sum_{i=1}^{N} F_i \cdot H_i \end{cases}$$

$\overline{H_{i0}}$: Partial molar enthalpy of species i at inlet.

$\overline{H_i}$: ,, at outlet.

∴ for ideal solution $\overline{H_{i0}} = H_i$ & $\overline{H_i} = H_i$ (pure component enthalpy)

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$$F_i - F_{io} = \sum_{k=1}^{R} \nu_{k_i}\, \varepsilon_k$$, where R is the no. of rxns taking place & k is a particular rxn

$$\therefore F_i = F_{io} + \sum_{k=1}^{R} \nu_{k_i}\, \varepsilon_k \quad \cdots (3)$$

$$\dot{H}_{io} - \dot{H}_{out} = \sum_{i=1}^{N} F_{io} \cdot H_{io} - \sum_{i=1}^{N} F_i \cdot H_i \quad \cdots \text{from } (2)$$

$$= \sum_{i=1}^{N} F_{io}\, H_{io} - \sum_{i=1}^{N} \left(F_{io} + \sum_{k=1}^{R} \nu_{k_i}\, \varepsilon_k \right) H_i$$

$$\cdots \text{from } (3)$$

$$= \sum_{i=1}^{N} F_{io} \left(H_{io} - H_i \right) - \sum_{i=1}^{N} \sum_{k=1}^{R} \nu_{k_i}\, \varepsilon_k\, H_i$$

$$\dot{H}_{io} - \dot{H}_{out} = \sum_{i=1}^{N} F_{io} \left(H_{io} - H_i \right) - \sum_{k=1}^{R} \varepsilon_k \sum_{i=1}^{N} \nu_{k_i}\, H_i$$

we know,

$$H_{io} - H_i = \int_{T}^{T_0} c_{p_i}\, dT$$

Assuming avg value of c_{p_i}

$$H_{io} - H_i = \overline{c_{p_i}} \cdot \left(T_0 - T \right)$$

$$\& \quad \sum_{i=1}^{N} \nu_{k_i} H_i = \Delta H_R (T)$$ ← change in enthalpy of rxn at the outlet of system at T

$\therefore$ substituting the above terms in (1) we get.

$$\frac{dU_{sys}}{dt} = Q - W_s - \underbrace{\left(\sum_{i=1}^{N} F_{io}\, \overline{c_{p_i}} \right) \left(T - T_0 \right)}_{\text{Rate at which sensible heat is added or removed to bring the feed from } T_0 \text{ to } T} - \underbrace{\sum_{k=1}^{R} \varepsilon_k\, \Delta H_{R_k} (T)}_{\text{Rate of enthalpy change associated with conv. of reactants to pdt.}} \quad \cdots (4)$$

for single rxn, eq (5) can be written as

$$-\xi = \cancel{-}\, \ell F_{A0}$$

$$\xi = \frac{F_A - F_{A0}}{\nu_A}$$

$\therefore$ if $\nu_A = -1$

$$-\xi = F_A - F_{A0}$$
$$= F_{A0}(1 - X_A) - F_{A0}$$
$$= F_{A0} - F_{A0}X_A - F_{A0}$$
$$\xi = \cancel{F_{A0}}\ \cancel{\ell} \cdot F_{A0} X_A$$

$\therefore$ putting this in eq (5)

$$\dot{Q} - \dot{W_s} - \left(\sum_{i=1}^{N} F_{i0}\,\overline{C_{p_i}}\right)(T - T_0) - F_{A0}X_A\,\Delta H_{Rx}(T) = \frac{dU_{sys}}{dt} \quad \ldots (6)$$

$\uparrow$ for a reactor with single rxn.

(ii) For reactors in series

$$Q - W_s - \left(\sum_{i=1}^{N} F_{i0}\,\overline{C_{p_i}}\right)(T_{out} - T_{in}) - F_{A0}(X_{A\,out} - X_{A\,in})\,\Delta H_R(T) = \frac{dU_{sys}}{dt} \quad \ldots (7)$$

(iii) reactors with more than one reactions occurring in series reactions

$$Q - W_s - \left(\sum_{i=1}^{N} F_{i0}\,\overline{C_{p_i}}\right)(T_{out} - T_{in}) - \sum_{k=1}^{R}\left(\xi_k - \xi_k^{0}\right)\Delta H_{R_k}(T) = \frac{dU_{sys}}{dt} \quad \ldots (8)$$

ξ_k^{0} : extent of rxn at the feed inlet

ξ_k : " " " " exit

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(iv) ~~single flow reactors~~:

Batch reactor

eq for energy bal will be : $Q = \frac{dU_{sys}}{dt}$

we know, $U_{sys} = H_{sys} - \underset{\text{Reactor press.}}{P_{Total}} V \rightarrow$ reactor volume of content

change in PV is negligible

$\therefore \frac{dU_{sys}}{dt} = \frac{dH_{sys}}{dt}$

$\therefore Q = \frac{dH_{sys}}{dt}$, where $H_{sys} = \sum_{i=1}^{N} \bar{H}_i N_i$

$(\bar{H}_i = H_i)$ ideal sol^n

$H_{sys} = \sum_{i=1}^{N} H_i N_i$

$\therefore Q = \frac{d}{dt} \sum_{i=1}^{N} H_i N_i$

$$Q = \sum_{i=1}^{P} H_i \left(\frac{dN_i}{dt}\right) + \sum_{i=1}^{N} N_i \frac{dH_i}{dt} \quad \ldots (9)$$

$\because dH_i = d(c_{p_i} \, T) = c_{p_i} \cdot dT \quad \ldots (10)$ ... Assuming c_{p_i} to be const.

& $$\sum_{i=1}^{N} H_i \frac{dN_i}{dt} = \sum_{i=1}^{N} H_i \sum_{k=1}^{R} \nu_{ik} \frac{d\varepsilon_k}{dt}$$

$$= \sum_{k=1}^{R} \Delta H_{R_k}(T) \frac{d\varepsilon_k}{dt} \quad \ldots (11)$$

Putting (10) & (11) in 9

$$Q = \left(\sum_{i=1}^{N} N_i c_{p_i}\right) \frac{dT}{dt} + \sum_{k=1}^{R} \Delta H_{R_k}(T) \frac{d\varepsilon_k}{dt} \quad \ldots (12)$$

Read isothermal reactors & Adiabatic reactors theory from notes

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(v) ~~Adiabatic Temp. change~~

(v) Single flow reactors:

for a CSTR / PFR with single rxn, at steady state we can write, $\frac{dU_{sys}}{dt} = 0$

shaft work negligible, $W_S \approx 0$

$$\therefore \quad Q - \left(\sum_{i=1}^{N} F_{i0} \overline{C_{p_i}} \right) (T - T_0) - F_{A0} X_A \Delta H_R (T) = 0$$

... (13) from eq (6)

(vi) Adiabatic Temp. change

from eq (13),

$$Q - \left(\sum_{i=1}^{N} F_{i0} \overline{C_{p_i}} \right) (T - T_0) - F_{A0} X_A \Delta H_R (T) = 0$$

$\because$ adiabatic reactor, $Q = 0$

$$-\left(\sum_{i=1}^{N} F_{i0} \overline{C_{p_i}} \right) (T - T_0) = F_{A0} X_A \Delta H_R (T)$$

$$\therefore \quad T = T_0 + \left[\frac{F_{A0} \left(-\Delta H_R (T) \right)}{\sum_{i=1}^{N} F_{i0} \overline{C_{p_i}}} \right] X_A$$

Let $T = T_{adiabatic}$ & $X_A = 1$

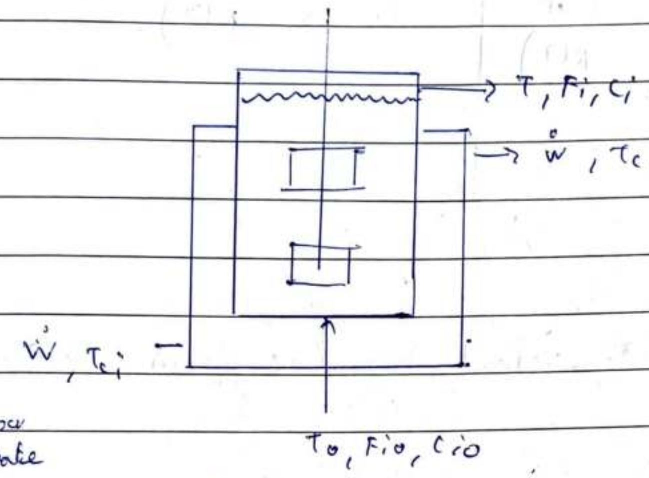
$$\Delta T_{ad} = T_{ad} - T_0 = \underbrace{\left[\frac{F_{A0} \left(-\Delta H_R (T_{ad}) \right)}{\sum_{i=1}^{N} F_{i0} \overline{C_{p_i}} \, (T_0 \to T_{ad})} \right]}_{\text{evaluated at } T_{ad}}$$

$\therefore \quad T = T_0 + (\Delta T_{ad}) X_A$

for most ~~this~~ systems this is not a strong func of temp.

we can similarly show that for ~~batch~~ adiabatic batch reactor

(vii) Energy balance in a CSTR



from eq (6)

$$Q - \cancel{W_s} - \left(\sum_{i=1}^{N} F_{io}\,\overline{C_{pi}}\right)(T - T_0) - F_{A0}\,X_A\,\Delta H_R(T) = \cancel{\frac{dU_{sys}}{dt}}$$

Q will account for cooling water

$$Q - \left(\sum_{i=1}^{N} F_{io}\,\overline{C_{pi}}\right)(T - T_0) = F_{A0}\,X_A\,\Delta H_R(T)$$

Rate of heat tr. Q,

$$Q = U A_h (T_{ci} - T)$$

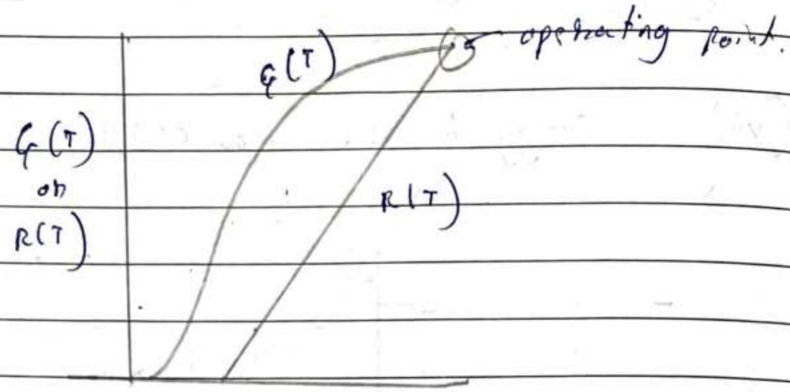
$$\therefore \left[-\Delta H_R(T)\right] F_{A0} X_A = U A_h (T - T_{ci}) + \left(\sum_{i=1}^{N} F_{io}\,\overline{C_{pi}}\right)(T - T_0)$$

above eq can be expressed as

$$G(T) = R(T)$$

$$U A_h (T - T_c) + \left(\sum_{i=1}^{N} F_{io}\,\overline{C_{pi}}\right)(T - T_0) = \left[U A_h + \left(\sum_{i=1}^{N} F_{io}\,\overline{C_{pi}}\right)\right] T + \left[U A_h T_c + \left(\sum_{i=1}^{N} F_{io}\,\overline{C_{pi}}\right) T_0\right]$$

$$R(T) = mT + C$$



* Non-ideal reactors from Notes !!

3a Time - independent analysis of series consecutive reaction

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

(Point 28 (i) redone here)

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

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

$$\therefore \frac{dC_R}{dC_A} = \frac{k_1 C_A - k_2 C_R}{-k_1 C_A}$$

$$\therefore \frac{dC_R}{dC_A} = -1 + \frac{k_2}{k_1}\left(\frac{C_R}{C_A}\right)$$

$$\therefore \frac{dC_R}{dC_A} - \frac{k_2}{k_1}\left(\frac{C_R}{C_A}\right) = -1 \quad (1)$$

~~condition~~ Consider C_R as a function of C_A

$$C_R = V \cdot C_A \quad \ldots (2)$$

$$\therefore \quad \frac{dC_R}{dC_A} = V \cdot \frac{dC_A}{dC_A} + C_A \cdot \frac{dV}{dC_A}$$

$$\therefore \frac{dC_R}{dC_A} = V + C_A \cdot \frac{dV}{dC_A} \quad \ldots (3)$$

Substituting (2) & (3) in (1)

$$V + C_A \cdot \frac{dV}{dC_A} - \frac{k_2}{k_1}\left(\frac{V \cdot C_A}{C_A}\right) = -1$$

$$V + C_A \cdot \frac{dV}{dC_A} - \frac{V k_2}{k_1} = -1$$

$$V\left(1 - \frac{k_2}{k_1}\right) + 1 = -C_A \cdot \frac{dV}{dC_A}$$

$$\therefore \frac{1}{-C_A} \cdot dC_A = \frac{dV}{V\left(1 - \frac{k_2}{k_1}\right) + 1}$$

$$\therefore \frac{dC_A}{C_A} = \frac{dV}{\left(\frac{k_2}{k_1} - 1\right) V - 1}$$

let $\frac{k_2}{k_1} - 1 = a$

$$\therefore \frac{dC_A}{C_A} = \frac{dV}{(a)V - 1}$$

$$\therefore \frac{dC_A}{C_A} = \frac{1}{a} \frac{a \cdot dV}{aV - 1}$$

$$\therefore \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \frac{1}{a} \int_{V_0}^{V} \frac{a\, dV}{aV - 1}$$

$$\therefore \ln\left(\frac{C_A}{C_{A0}}\right) = \frac{1}{a} \ln\left(\frac{aV - 1}{aV_0 - 1}\right) \quad \ldots \because \left[\int \frac{f'(x)}{f(x)} = \ln f(x)\right]$$

$$\left(\frac{C_A}{C_{A0}}\right)^a = \frac{aV-1}{aV_0-1}$$

substituting $\frac{k_2}{k_1} - 1 = a$

$$\& \quad \frac{C_R}{C_A} = V \quad \& \quad \frac{C_{R0}}{C_{A0}} = V_0$$

$$\therefore \left(\frac{C_A}{C_{A0}}\right)^a = \left[\frac{\left(\frac{k_2}{k_1} - 1\right)\frac{C_R}{C_A} - 1}{\left(\frac{k_2}{k_1} - 1\right)\frac{C_{R0}}{C_{A0}} - 1}\right]$$

$$\left(\frac{C_A}{C_{A0}}\right)^{\frac{k_2}{k_1}-1} = \left[\frac{\frac{C_R k_2}{k_1 C_A} - \frac{k_1 C_R}{k_1 C_A} - \frac{k_1 C_A}{k_1 C_A}}{\frac{k_2 C_{R0}}{k_1 C_{A0}} - \frac{k_1 C_{R0}}{k_1 C_{A0}} - \frac{k_1 C_{A0}}{k_1 C_{A0}}}\right]$$

$$\left(\frac{C_A}{C_{A0}}\right)^{\frac{k_2}{k_1}} \times \cancel{\frac{C_{A0}}{C_A}} = \frac{\cancel{k_1} C_{A0}\left[C_R k_2 - k_1 C_R - k_1 C_A\right]}{\cancel{k_1} C_A\left[k_2 C_{R0} - k_1 C_{R0} - k_1 C_{A0}\right]}$$

$$\left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} = \frac{C_R(k_2 - k_1) - k_1 C_A}{C_{R0}(k_2 - k_1) - C_{A0} k_1}$$

Let $\left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} = M$

$$\therefore M C_{R0}(k_2 - k_1) - M C_{A0} k_1 = C_R(k_2 - k_1) - k_1 C_A$$

$$M \frac{C_{R0}}{C_{A0}}(k_2 - k_1) - M k_1 = \frac{C_R}{C_{A0}}(k_2 - k_1) - k_1 \frac{C_A}{C_{A0}}$$

$$M \frac{C_{R0}}{C_{A0}} - M \frac{k_1}{k_2 - k_1} = \frac{C_R}{C_{A0}} - \frac{k_1}{k_2 - k_1}\frac{C_A}{C_{A0}}$$

$$\therefore \frac{C_R}{C_{A0}} = \frac{M C_{R0}}{C_{A0}} - M \frac{k_1}{k_2 - k_1} + \frac{k_1}{k_2 - k_1}\frac{C_A}{C_{A0}}$$

$$= M \frac{C_{R0}}{C_{A0}} + \frac{k_1}{k_1 - k_2}\left(M - \frac{C_A}{C_{A0}}\right)$$

$$\therefore \frac{C_R}{C_{A0}} = M \frac{C_{R0}}{C_{A0}} + \frac{1}{\left(1 - \frac{k_2}{k_1}\right)}\left[M - \frac{C_A}{C_{A0}}\right]$$

Substituting M

$$\therefore \frac{C_R}{C_{A0}} = \frac{M \, C_{R0}}{C_{A0}}$$

$$\therefore \frac{C_R}{C_{A0}} = \left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} \cdot \frac{C_{R0}}{C_{A0}} + \frac{1}{\left(1 - \frac{k_2}{k_1}\right)} \left[\left(\frac{C_A}{C_{A0}}\right)^{k_2/k_1} - \frac{C_A}{C_{A0}} \right]$$

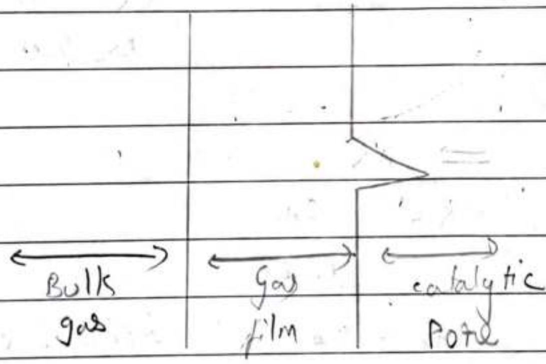
* Non-ideal from notes.

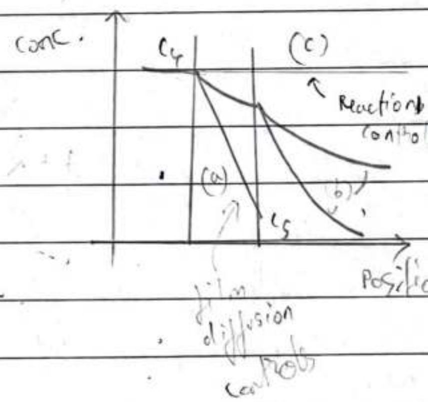
— POST MID-SEM —

31. Heterogenous Reactions

Gas-Solid catalytic Heterogenous reactions:

3-Steps : Adsorption, surface reaction, Desorption





Rate of film diffusion step : $R_A = k_g (C_g - C_s)$ ...(1)

Rate of chemical reaction step : $R_A = \eta k C_s$ ...(2)

effectiveness factor $\eta = 1$ (pore diffusion unimportant) or on non-porous cat.)

At steady state rate is same,

$$C_s = \frac{R_A}{\eta k} \quad \text{... from 2}$$

Substituting C_s in (1), $R_A = k_g \left(C_g - \frac{R_A}{\eta k} \right)$

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$$R_A = k_G C_G - \frac{k_G R_A}{k} \quad (n=1)$$

$$R_A\left(1 + \frac{k_G}{k}\right) = k_G \cancel{C_G}\, C_G$$

$$R_A = \frac{k_G C_G}{1 + \frac{k_G}{k}} = \frac{C_G}{\frac{1}{k_G} + \frac{1}{k}}$$

$$k_G << k \Rightarrow \frac{1}{k_G} >> \frac{1}{k}$$

$$\therefore R_A = k_G C_G \quad (C_S \approx 0)$$

slow mass transfer

$$k_G >> k \Rightarrow \frac{1}{k_G} << \frac{1}{k} \Rightarrow R_A = k\, C_G$$

$$(C_G \approx C_S)$$

Reaction is slow

$$A + X \rightleftharpoons AX$$

$$k = \frac{C_{AX}}{P_A C_X}$$

Let, $C_{AX} = \theta_A$, fractional coverage

$C_X = 1 - \theta_A = \theta_V$ fractional voidage

$$\therefore k = \frac{\theta_A}{P_A(1-\theta_A)}$$

$$kP_A - kP_A\theta_A = \theta_A$$

$$kP_A = \theta_A(1 + kP_A)$$

$$\theta_A = \frac{kP_A}{1 + kP_A}$$

if $kP_A << 1$ — 1st order rxn

if $kP_A >> 1$ — 0th order