

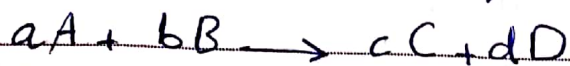


REACTION 1

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general reaction equation: (irreversible Rxns)



Categories of reaction:

homogenous Rxn

heterogenous Rxn (2 phase, catalytic reaction)

Reversible Rxn

Irreversible Rxn

Isothermal Rxn

non-Isothermal Rxn

Rate of reaction:

General form of Rate of reaction

$$r_i = \frac{1}{V} \frac{dN_i}{dt}$$

Rate of Reaction

V: volume

N_i: number of mol. of species

t: time

$$r_A = \frac{1}{V} \frac{dN_A}{dt}$$

; constant volume rxn, we can write it with concentration term

$$= \frac{dCA}{dt}$$

$$r_B = \frac{1}{V} \frac{dN_B}{dt}$$

$$r_C = \frac{1}{V} \frac{dN_C}{dt}$$

$$r_D = \frac{1}{V} \frac{dN_D}{dt}$$

From general rxn eq, we have:

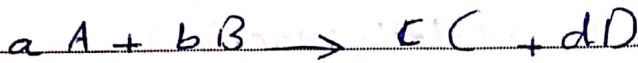
$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

19th Oct

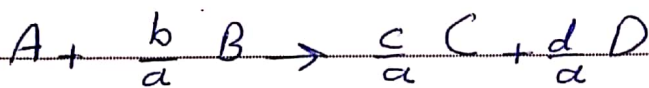
$$-\frac{1}{a} \frac{dN_A}{dt} = -\frac{1}{b} \frac{dN_B}{dt} = \frac{1}{c} \frac{dN_C}{dt} = \frac{1}{d} \frac{dN_D}{dt}$$

* Rate Rxn that is using in design ; depends on nature of component (substance) that disappears first :

A Key of rxn



If A is a key reactant ; $\div$ stoichiometry



$$r_A = -k_1 C_A^a C_B^b \quad (\text{elementary rxn})$$

Rxn $\swarrow$ Elementary
 $\searrow$ non-Elementary

$$r_A = -k_1 C_A^a C_B^b$$

$\downarrow$ disappearing
 $\downarrow$ reaction constant.

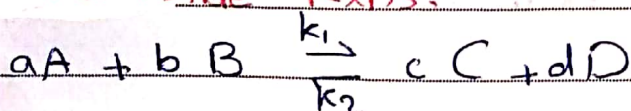
$$-\frac{r_B}{b} = -\frac{r_A}{a} \Rightarrow r_B = \frac{b}{a} r_A = -\frac{b}{a} k_1 C_A^a C_B^b$$

$$\frac{\text{Rate of rxn}}{\text{stoichiometry}} = \frac{\text{Rate of rxn}}{\text{stoichiometry}}$$

$$\frac{r_C}{c} = \frac{r_A}{-a} \Rightarrow r_C = -\frac{c}{a} r_A = \frac{c}{a} k_1 C_A^a C_B^b$$

$$\frac{r_D}{d} = -\frac{r_A}{a} \Rightarrow r_D = -\frac{d}{a} r_A = \frac{d}{a} k_1 C_A^a C_B^b$$

* reversible Rxns:

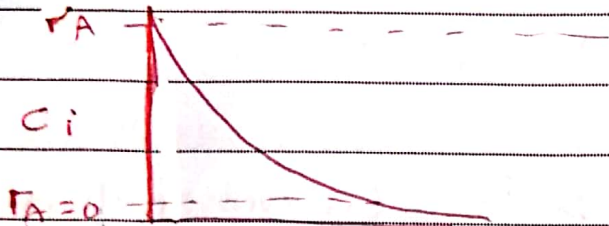


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$$r_A = -k_1 C_A^a C_B^b + k_2 C_C^c C_D^d$$

reactant Disappear Appear

* what does make it different from reversible?



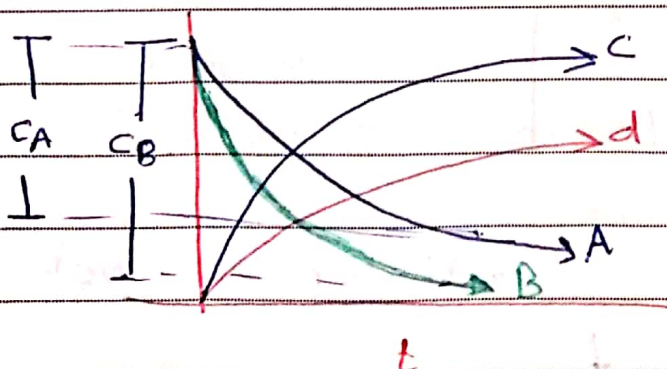
@ equilibria:

$$r_A = 0 = k_1 \left[-C_A^a C_B^b + \frac{1}{K_c} C_C^c C_D^d \right]$$

K_c : equilibrium constant.

$$K_c = \frac{C_C^c C_D^d}{C_A^a C_B^b} = \frac{k_1}{k_2} \quad \begin{matrix} \text{Forward} \\ \text{backward} \end{matrix}$$

$$\therefore r_A = -k_1 \left[C_A^a C_B^b - \frac{1}{K_c} C_C^c C_D^d \right]$$

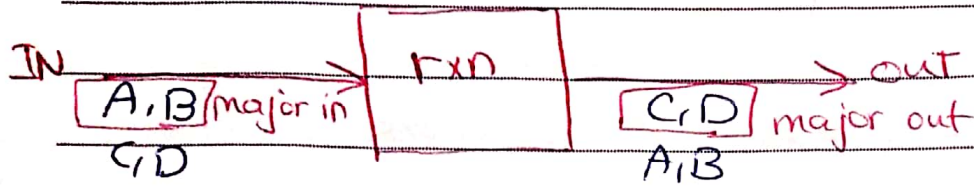


Why is concentration of A different from conc. B?

* Depend on stoichiometry

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The general mol. balance:



$$\text{Rate in} - \text{rate out} + G = \text{Accumulation}$$

Molar flowrate of species $i \Rightarrow F_i$ (conversion of mass)

$$\begin{matrix} i_0 & i \\ F_{i0} & F_i \end{matrix}$$

$$\frac{\text{mol}}{\text{time}} - F_i + G_i = \frac{dN_i}{dt}$$

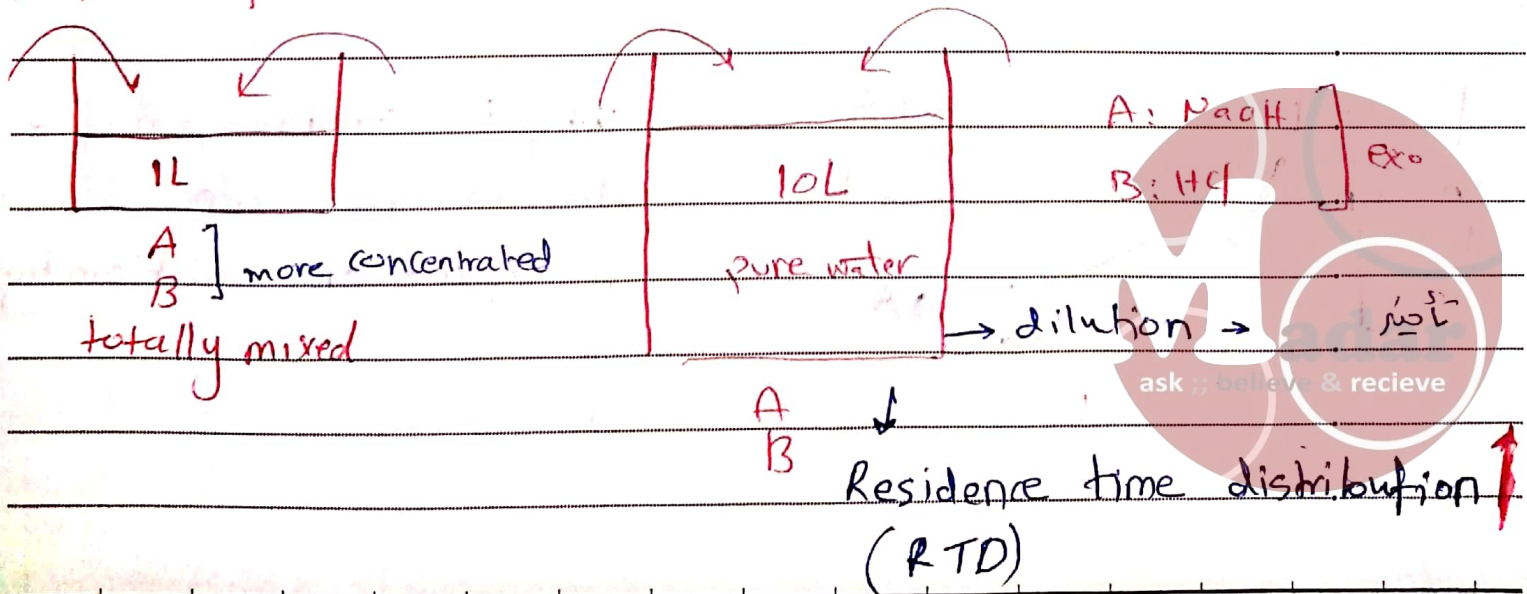
mol mol
time time

$$G_i = r_i V$$

$$\frac{\text{mol}}{\text{time}} = \frac{\text{mol}}{\text{time} \cdot \text{vol}} \times \text{vol (ex: m}^3\text{)}$$

$$r_i \rightarrow \frac{\text{mol}}{\text{time} \cdot \text{vol}} \quad \bar{a}_{\text{eq}}$$

* Rate of rxn:



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$$Q_i = r_i V = \int r_i dv$$

non constant volume

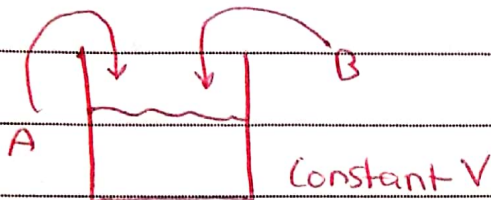
constant volume

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

most important

If we don't have in or out:

1. Batch reactor
2. Constant STR
3. Tubular Reactor
4. Packed bed reactor
5. Semi-batch rxn.



$$\frac{dN_i}{dt} = \int r_i dv$$

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

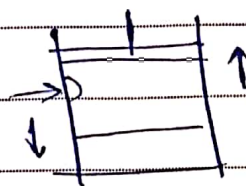
$$\frac{dN_i}{dt} = r_i V$$

design eq. for constant volume.

for batch: $\frac{1}{V} \frac{dN_i}{dt} = \frac{r_i V}{V} \rightarrow \frac{dC_i}{dt} = r_i$ general design equation for constant volume batch reactor.

* Batch reactor with variable volume: (ex: piston in car engine)

$$\frac{dN_i}{dt} = r_i V$$



$$\frac{d(C_i V)}{dt} = C_i \frac{dV}{dt} + V \frac{dC_i}{dt} = r_i V ; \div (V)$$

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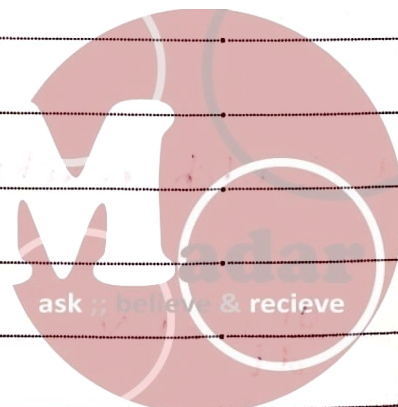
$$\therefore \frac{dc_i}{dt} + \frac{c_i}{v} \frac{dv}{dt} = r_i$$

Note: $N_i = C_i v$ so $C_i = \frac{N_i}{v}$

but: $\frac{1}{v} \frac{dv}{dt} = \frac{d \ln v}{dt}$

So, $\frac{dc_i}{dt} + \frac{c_i d \ln v}{dt} = r_i$

Internal non-constant engine.



wed

21st - Oct - 2020

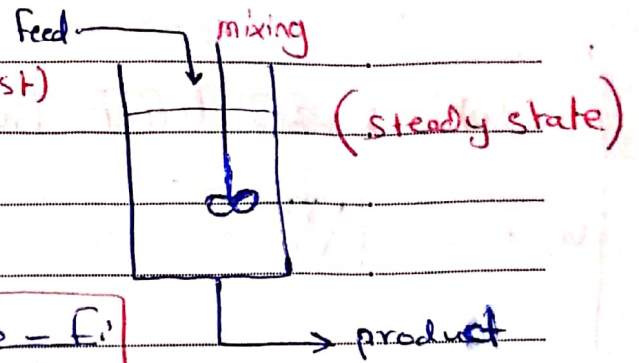
CSTR

mole balance:

$$F_{i0} - F_i + \int_V r_i dv = \frac{dN_i}{dt} \rightarrow 0 \text{ (st. st)}$$

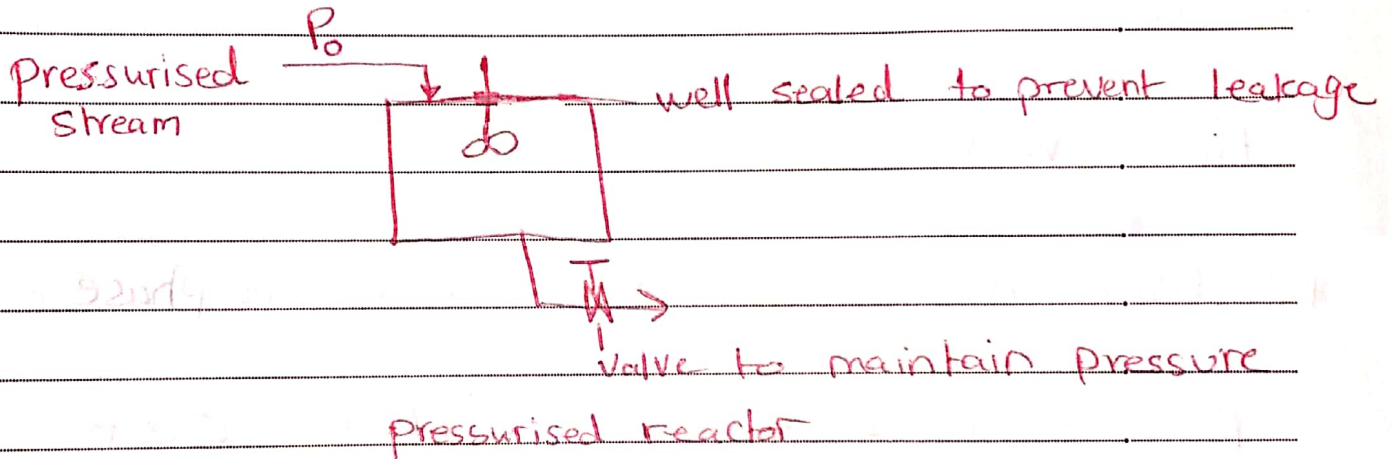
 $r_i V$
constant volume

$$F_{i0} - F_i + r_i V = 0 \Rightarrow V = \frac{F_{i0} - F_i}{-r_i}$$



that for liquid phase

What about gas phase?



so; we should change this eq $V = \frac{F_{i0} - F_i}{-r_i}$ to fit gas reactor (CSTR)

$$F_i = C_i V_i$$

C_i — concentration (mol/vol)
 V_i — volumetric flowrate (vol/time)
 F_i — molar flowrate (mol/time)

$$V = \frac{F_{i0} - F_i}{-r_i} = \frac{C_{i0} V_0 - C_i V_i}{-r_i}$$

wed

21 Oct

under steady state condition so,
and liquid phase rxn

$$v_0 = v_i$$

$v_0 \neq v_i$ If there is a pressure drop
(packed bed reactor)



$$= v_0 \frac{C_{i0} - C_i}{-r_i} \quad \text{that's valid with liquid phase}$$

For gas phase system:

$$F_{i0} = v_0 C_{i0}$$

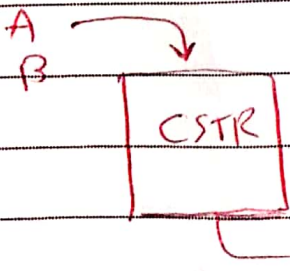
* Assumption: system with Ideal gas condition.

$$\frac{P \cancel{V}}{\cancel{V}} = \frac{n R T}{V} \rightarrow P = \left(\frac{n}{V} \right) R T = C R T$$

$$\therefore C_i = \frac{P_i}{R T_i}$$

$$F_{i0} = v_0 \frac{(P_{i0})}{R T_0} \rightarrow \text{partial pressure of component } i$$

(P_0)
total



Can I measure partial pressure for A?
no.

until I measure mol. fraction for A

ask :: believe & recieve

$$P_i = y_i P_0 \quad \text{mol. fraction}$$

total pressure

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$$F_{A0} = v_0 C_{A0} = v_0 \frac{y_{A0} P_0}{RT_0}$$

$$V = v_0 \frac{C_{A0} - C_A}{-r_A} = v_0 \frac{P_0}{R} \left[\frac{\frac{y_{A0}}{T_0} - \frac{y_A}{T}}{-r_A} \right]$$

When ($T_0 = T$)

$$V = \frac{v_0 P_0}{RT} \left[\frac{y_{A0} - y_A}{-r_A} \right]$$

Example: A mixture of gas A and B enters a Reactor at total Pressure of 7 bar and 800 K. The volumetric flowrate of both gases is 5 L/s. $y_{A0} = 0.2$. Calculate the entering concentration and molar flowrate of both gases?!

Sol.

$$P_0 = 7 \text{ bar} = 700 \text{ kPa}$$

$$1 \text{ bar} = 100 \text{ kPa}$$

$$T_0 = 800 \text{ K}$$

$$y_{A0} = 0.2 \rightarrow y_{B0} = 1 - 0.2 = 0.8$$

$$R = 8.314 \frac{\text{L} \cdot \text{kPa}}{\text{mol} \cdot \text{K}}$$

$$C_{A0} = \frac{P_{A0}}{RT_0} = \frac{y_{A0} P_0}{RT_0} = \frac{(0.2)(700 \text{ kPa})}{8.314 \left(\frac{\text{L} \cdot \text{kPa}}{\text{mol} \cdot \text{K}} \right) (800 \text{ K})}$$

$$= 0.02 \frac{\text{mol}}{\text{L}}$$

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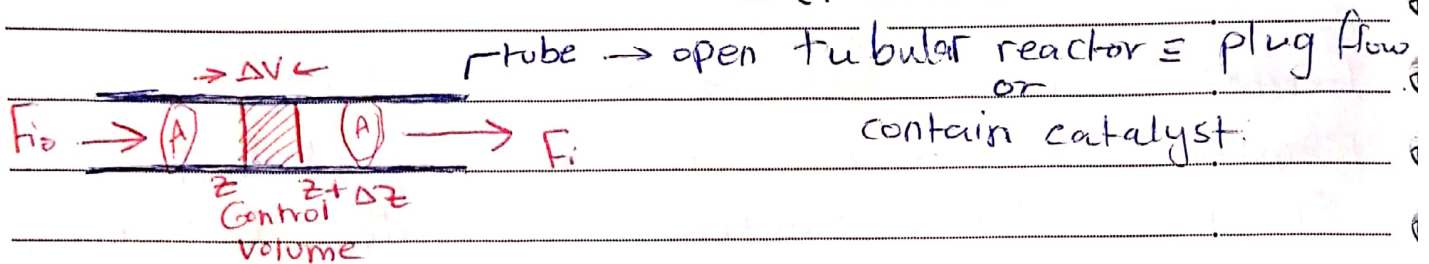
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$$F_{A0} = C_{A0} V_0 = \left(0.02 \frac{\text{mol}}{\text{L}}\right) \left(5 \frac{\text{L}}{\text{s}}\right) = 0.1 \frac{\text{mol}}{\text{s}}$$

$$C_{B0} = \frac{y_{B0} P_0}{R T_0} = \frac{0.8 (700)}{8.314 (800)} = 0.08 \text{ mol/L}$$

$$F_{B0} = C_{B0} V_0 = (0.08) (5 \text{ L/s}) = 0.42 \frac{\text{mol}}{\text{L}}$$

* Plug flow Reactor $\rightarrow$ (Tubular reactor)
(Packed bed reactor)



$$\Delta V = \Delta z \cdot A$$

$$F_{i0} - F_i + \int_{V_i} r_i dV = \frac{dN_i}{dt} \rightarrow 0 \text{ No accumulation (steady-state)}$$

$$F_{i0} - F_i + r_i \Delta V = 0$$

$\downarrow \quad \quad \downarrow$
 $z \quad \quad z+\Delta z$

when ΔV very small

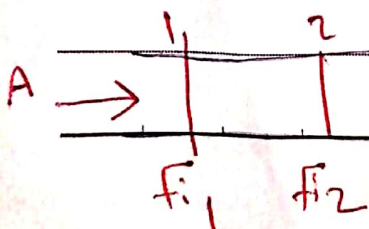
$$\cancel{\frac{dF_i}{dV}} = \cancel{r_i} \text{ generally}$$

but most reactor constant volume

$$\frac{dF_i}{A dz} = r_i$$

$$\rightarrow \boxed{\frac{dF_i}{dz} = r_i A}$$

different areas
general eq. for tubular rxr

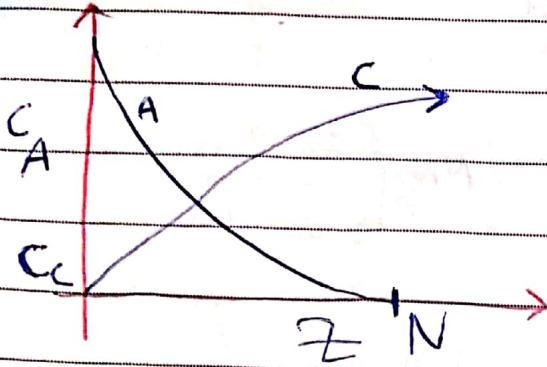
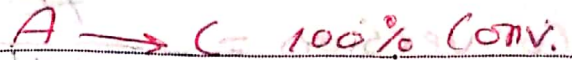
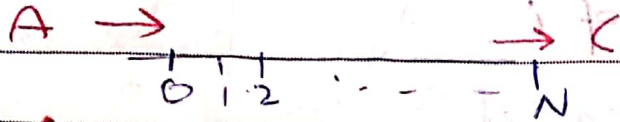


$$F_{A1} > F_{A2} \text{ consumed } (F_{AN} = 0)$$

conversion 100%

wed

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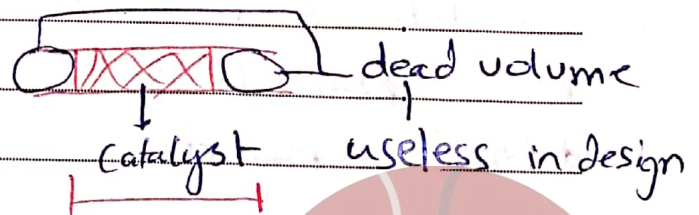
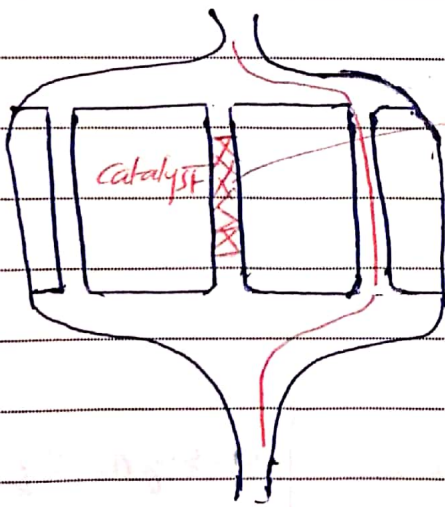


Packed bed r_{xr} :

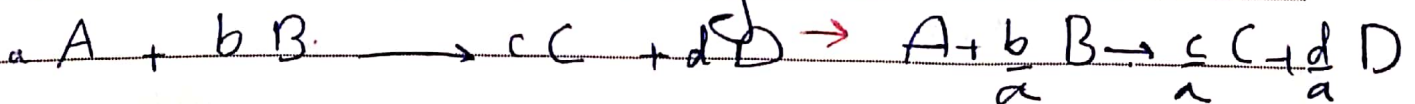
$$\frac{dF_i}{dw} = r_i^*$$

$\downarrow$ (weight of catalyst)

Why are we relating rate of change of molar flowrate of species i with rate of catalyst, instead of volume?
Packed bed is filled with catalyst



conversion and rxr sizing.



wed

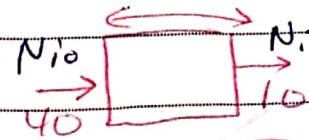
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Conversion = $\frac{\# \text{ of moles of } i \text{ reacted}}{\text{initial } \# \text{ moles of } i}$
(X)



$$X = 80 - 20 = 60$$

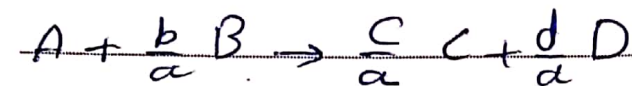
if $i = A$ initial
 $\Rightarrow X = \frac{N_{i0} - N_i}{N_{i0}}$



$$X = 30!!$$

Why differ?

we should compare the number of moles that reacted with respect to initial number of number of that species.



$$X = \frac{N_{A0} - N_A}{N_{A0}} \quad \text{batch / CSTR}$$

$$\Rightarrow N_A = N_{A0} - N_{A0} X$$

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

Ex: if $X = 0.7$ (needed) $N_{A0} = 100 \text{ mol}$

$$N_A = 100 (1 - 0.7) = 30 \text{ mol left}$$

Batch Rxr, $\frac{dN_A}{dt} = r_A V$

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

$$dN_A = -N_{A0} dX$$

$$-N_{A0} \frac{dX}{dt} = r_A V$$

$$\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$$

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

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

design eq for batch reactor

ask, believe & receive

wed

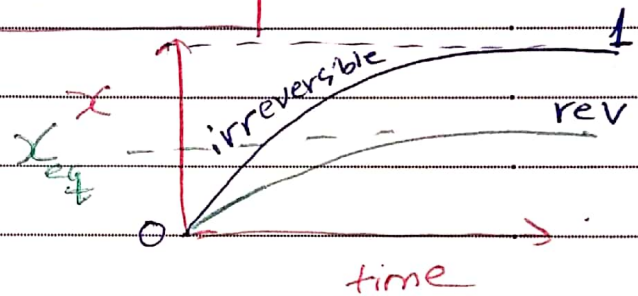
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in batch reactor we are not going to measure the volume, so my design parameter is the volume but my design parameter is related to how long it takes for that reactant to disappear to a product so design parameter is the time for batch rxr

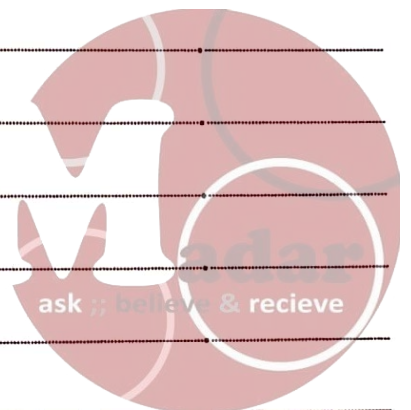
$$N_A \frac{dx}{dt} = -r_A V$$

$$C_{A0} \frac{dx}{dt} = -r_A \rightarrow \boxed{C_A \frac{dx}{dt} = -r_A}$$

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



* eq. rxn no way to reach 1

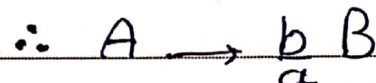
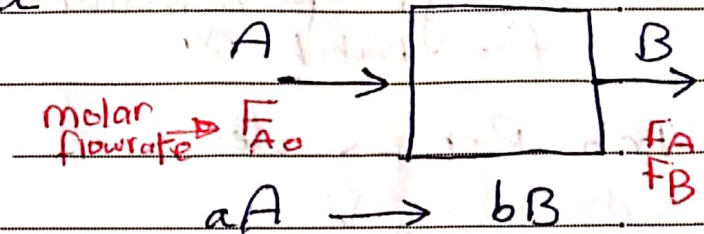


How to relate Inlet number of mol and exit species 26th Oct

$$t = N_{A_0} \int_0^x \frac{dx}{-r_A v} \quad \text{batch rxr}$$

* Design of Flow reactor:

$$X = \frac{\text{mole A reacted}}{\text{mole of A Fed}}$$

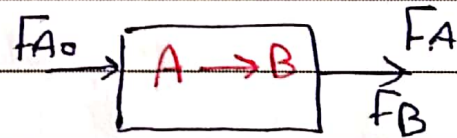


$$\frac{\text{mole of A reacted}}{\text{time}} = \frac{\text{mole of A Fed}}{\text{unit time}} * \frac{\text{mole of A reacted}}{\text{mol of A Fed}}$$

$$\frac{\text{mole of A reacted}}{\text{time}} = F_{A_0} * X$$

$$\frac{\text{moles of A left rxr}}{\text{time}} = \text{moles A Fed} - (\text{moles reacted})$$

$$F_A = F_{A_0} - F_{A_0} X$$



Suppose we do have a gas phase rxn:

$$F_{A_0} = C_{A_0} v \quad \leftarrow \begin{array}{l} \text{volume flowrate} \\ \text{concentration} \end{array}$$

$$F_{A_0} = \frac{P_{A_0}}{RT_0} v = \frac{Y_{A_0} P_T^0}{RT_0} v$$

Similarly for B:

$$F_{B_0} = F_{B_0} + \frac{b}{a} (F_{A_0} X) \quad \text{moles of A reacted to produce moles of B}$$

ask :: believe & recieve

26th Oct

Example :-

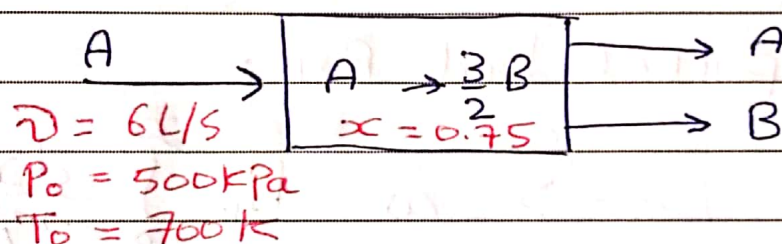
For a reaction $2A \rightarrow 3B$ in a gas phase rxn, where pure A is introduced at 500 kPa and volumetric flowrate 6 L/s. The inlet temp = 700 K. The conversion for this reaction $x = 0.75$.

Calculate : ① Inlet molar flowrate

② exit molar flowrate of A

③ exit " " of B.

assume $F_{B_0} = 0$



SOL :

$$F_{A_0} = C_{A_0} v_0 = \frac{y_{A_0} P_0}{R T_0} v_0 = \frac{(1) (500 \text{ kPa})}{8.314 \left(\frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right) (700 \text{ K})} \left(\frac{6 \text{ L}}{\text{s}} \right)$$

$$= 0.515 \frac{\text{mol}}{\text{s}}$$

$F_A = ??$

$$F_A = F_{A_0} - F_{A_0} x = F_{A_0} (1 - x) = 0.515 (1 - 0.75) = 0.128 \frac{\text{mol}}{\text{s}}$$

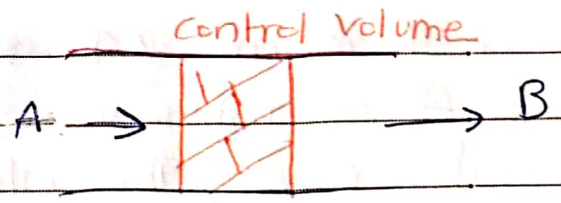
$$F_B = F_{B_0} + \frac{b}{a} F_{A_0} x = 0 + \frac{3}{2} (0.515) (0.75)$$

$$= 0.579 \frac{\text{mol}}{\text{s}}$$

* $aA + bB \rightarrow cC + dD \rightarrow$ similar manner

Design of PFR (Plug Flow Reactor)

$$- \frac{dF_A}{dV} = r_A \iff \frac{dF_A}{dV} = r_A$$



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

$$dF_A = -F_{A_0} dx \div dV$$

$$-F_{A_0} \frac{dx}{dV} = r_A \iff F_{A_0} \frac{dx}{dV} = -r_A$$

$$\left. F_A \right|_z - \left. F_A \right|_{z+\Delta z}$$

$$V = F_{A_0} \int_0^x \frac{dx}{-r_A}$$

design eq. for tubular rxr and plug flow rxr.

Similarly for packed bed Rxr:

$$F_{A_0} \frac{dx}{dW} = -r_A^* \iff W = F_{A_0} \int_0^x \frac{dx}{-r_A^*}$$

Example :-

A Rxn $A \rightarrow B$, $r_A = -k_1 C_A$ in a tubular Rxr

Sol:

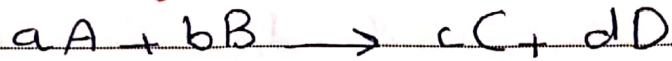
$$C_A = C_{A_0}(1-x) \rightarrow r_A = -k_1 C_A = -k_1 C_{A_0}(1-x)$$

$$V = F_{A_0} \int_0^x \frac{dx}{k_1 C_{A_0}(1-x)}$$

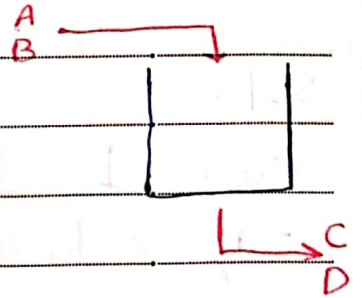
$$F_{A_0} = C_{A_0} v_0 \text{ so; } \frac{F_{A_0}}{C_{A_0}} = v_0$$

$$= \frac{v_0}{k_1} \int_0^x \frac{dx}{1-x} = -\frac{v_0}{k_1} \ln(1-x) \Big|_0^x \quad (\text{tubular})$$

Design of CSTR (conversion)



limiting reactant



$$V = \frac{F_{A0} - F_A}{-r_A}$$

$$F_A = F_{A0} - F_{A0}X \rightarrow F_{A0} - F_A = F_{A0}X$$

$$\therefore V = \frac{F_{A0}X}{-r_A} \Big|_{\text{exit}}$$

Example: :-

$A \rightarrow B$ is to be carried out Isothermally in CSTR and PFR. If 99% is consumed for A, what will be the reactor volume for the following cases.

1. Assume Zero order rxn, $k_0 = 0.05 \text{ mol L}^{-1}\text{hr}$
molar flowrate = 5 mol hr

volumetric flowrate = 10 L hr

NOTE

* The objective of this example:

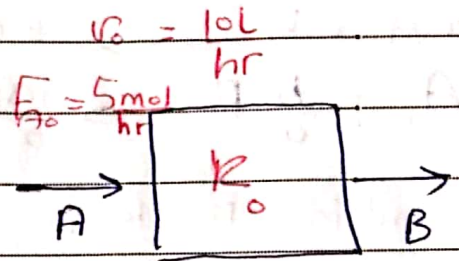
To compare the size of CSTR and the size of the plug flow reactor based on given info. Is the size of CSTR higher than PFR or vice versa?

based on zero order rxn, is that type of rxn, has a pronounced effect on the conversion.
 → For a given conversion, Is the size of CSTR greater than the PFR, For zero order rxn?

Soln:

Case I: zero-order rxn

$$-r_A = k_0 = 0.05 \frac{\text{mol}}{\text{L} \cdot \text{hr}}$$



$$C_A = 0.01 C_{A0}$$

(because 99%
Converted to
product B.)



$$C_{A0} = \frac{\text{molar flowrate}}{\text{volumetric flow}} = \frac{5}{10} = 0.5 \frac{\text{mol}}{\text{L}}$$

$$C_A = (0.01)(0.5) = 0.005 \frac{\text{mol}}{\text{L}}$$

For CSTR:

$$V = \frac{F_{A0} - F_A}{-r_A} = \frac{C_{A0} v_0 - C_A v}{-r_A} = \frac{v_0 (C_{A0} - C_A)}{-r_A}$$

* If It doesn't mention the type of rxn gas phase or liquid phase we assume it is liquid rxn.

∴ liquid in must = liquid out, no accumulation
 incompressible fluid → volume flowrate is const.

$$V_{\text{CSTR}} = \frac{(10)(0.5 - 0.005)}{0.05} = 99 \text{ L}$$

ask : better & receive

PFR:

$$\frac{dF_A}{dV} = r_A \rightarrow V = \int_{F_{A_0}}^{F_A} \frac{dF_A}{r_A} = \int_{F_{A_0}}^{F_A} \frac{dF_A}{-k_0} = -\left(\frac{F_{A_0} - F_A}{-k_0}\right) = 99L$$

Conclusion for zero-order Rxn

$$V_{STR} = V_{PFR} \text{ (For any given condition)}$$

Case II: 1st order rxn

$$r_A = -k_1 C_A$$

$$\text{given } k_1 = 0.0001 \text{ s}^{-1}$$

SOL:

$$\text{For CSTR, } V = \frac{F_{A_0} - F_A}{-r_A} = \frac{C_{A_0} v_0 - C_A v}{k_1 C_A} = \frac{v_0}{k_1} \left[\frac{C_{A_0} - C_A}{C_A} \right]$$

$$C_A = 0.01 C_{A_0}$$

$$V = \frac{v_0}{k_1} \left[\frac{C_{A_0} - 0.01 C_{A_0}}{0.01 C_{A_0}} \right] = \frac{v_0}{k_1} \left(\frac{1 - 0.01}{0.01} \right)$$

* For first order rxn; NO need to know the initial concentration

$$V = \frac{0.99 v_0}{0.01 k_1} = \frac{0.99 \times 10L/hr \times \left(\frac{1hr}{3600s}\right)}{0.01 \times 0.0001 s^{-1}}$$

$$= 2750L \leftrightarrow \text{Volume of CSTR}$$

For PFR:

$$\frac{dF}{dV} = r_A \rightarrow V = \int_{C_A}^{C_{A_0}} \frac{v dC_A}{k_1 C_A} = \frac{v}{k_1} \ln C_A \Big|_{C_A}^{C_{A_0}}$$

$$\text{So; } V = \frac{(10L/hr) \left(\frac{1hr}{3600s}\right)}{0.0001 s^{-1}} \ln \frac{C_{A_0}}{C_A} = 27.77 \ln \left(\frac{C_{A_0}}{0.01 C_{A_0}} \right)$$

$$= 127.9L \leftrightarrow \text{Vol PFR}$$

$$\therefore \underline{V_{PFR} < V_{CSTR}} \text{ for the same condition above}$$

0, 1st, 2nd order

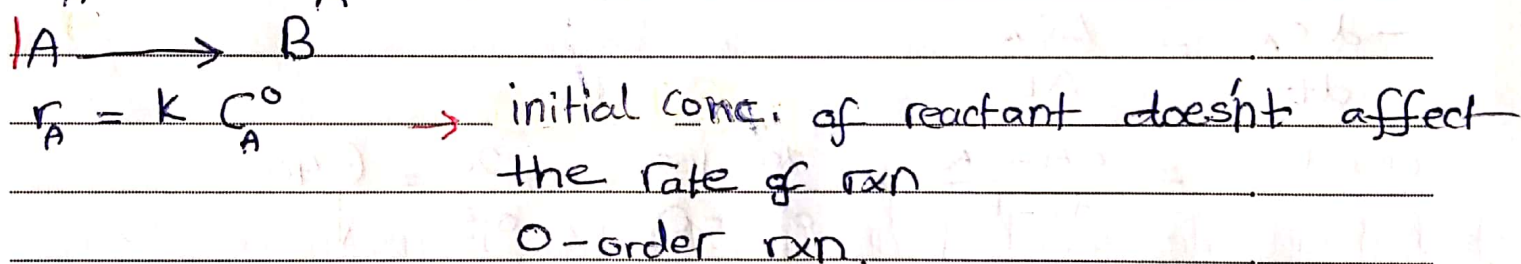
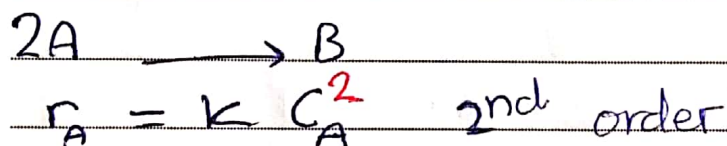
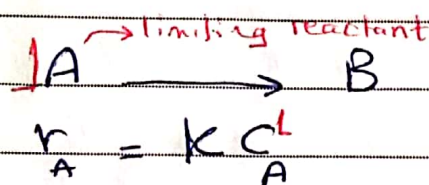
28th - Oct - 2020

Rxn $\rightarrow$ elementary
 $\rightarrow$ non-elementary

* Elementary



Rate of rxn changes with consider the stoichiometry
rate of rxn: $r_A = k C_A^1 C_B^1$ order of all rxn: $\therefore$ 2nd



Non-elementary rxn:



$$r_A = k \frac{C_A C_B}{(1 + K_2 C_A)}$$

$\leftarrow$ experimental $\longleftrightarrow$ related to: catalytic rxn

non elementary ex:

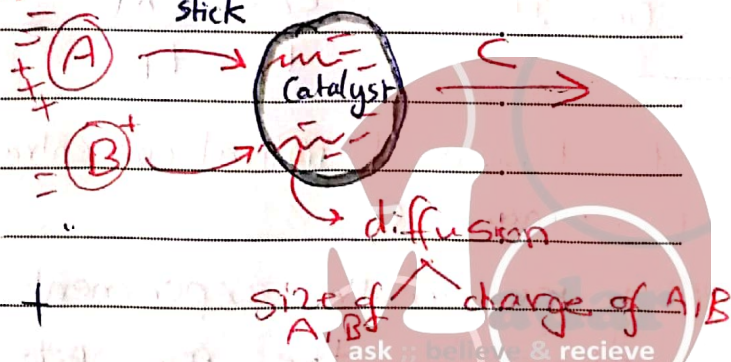
* enzymatic: in body

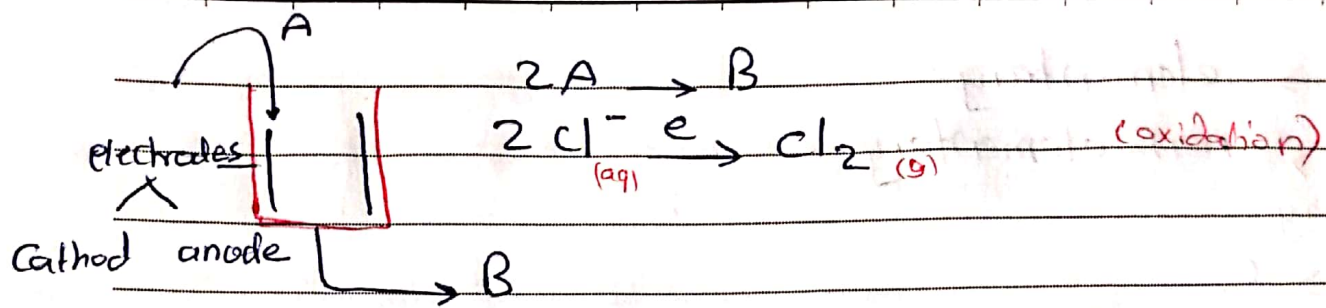
* polymerization:

* complexation: heavy metal + hydroxide

$\Rightarrow$ lead hydroxide $\rightarrow$ lead hydroxide-3

base





Stopwatch

nanosec microsec decade	t	C _A	$-\frac{dC_A}{dt}$
	0	C _{A0} 100	
	0.5	C _{A1} 80	40
	1	C _{A2} 65	30
	:	:	↓ rate = 0

$$-\frac{dC_A}{dt} = \frac{\Delta C_A}{\Delta t}$$

Case I

$$= \frac{C_{A1} - C_{A0}}{t_1 - t_0} = \frac{80 - 100}{0.5 - 0} = \frac{-20}{0.5} = -40$$

↓

that's why there is a (-) sign in $(-\frac{dC_A}{dt})$ to compensate the result

Case II

$$= \frac{C_{A2} - C_{A1}}{t_2 - t_1} = \frac{65 - 80}{1 - 0.5} = \frac{-15}{0.5} = -30$$

to know if initial concentration affects the rate C_{A0}?

① change C_{A0}

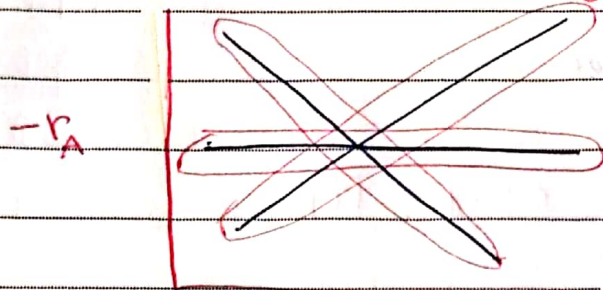
② make another experiment instead of 100 → 200
then is the new rate is consistence?

③ doing different runs with different concentration

④ Take the rate of rxn for each run then graph with concentration

@ $C_A \uparrow$ $r_A \uparrow$ not linearly $\rightarrow$ 2nd order

@ $C_A \uparrow$ $r_A \uparrow \rightarrow$ 1st order linearly



if the plotting looks like this there is not effect of initial rate

C_{A0}

based on C_{A1}
 C_{A2}

soon

In reality, we can't find a reaction with first order

$$r = k C_A^1$$

$$r = k C_A^{0.96}$$

$$r = k C_A^{1.05}$$

we can see experimentally
Approximately first order

$$* r = k C_A^1$$

rate constant k_1

$$* r_0 = k_0 C_A^1$$

the first concentration
the initial no effect

$$r_2 = k_2 C_A^2$$

Zero order:



$$\frac{dC_A}{dt} = k_0$$

$$\frac{\text{mol}}{\text{vol}} = \frac{\text{mol}}{L}$$

t

$$\left[\frac{\text{mol}}{L \cdot s} \right]$$

First order:

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

$$\frac{\text{mol}}{L \cdot s} = k \frac{\text{mol}}{L}$$

$$\left[\frac{1}{s} \right]$$

2nd order

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

$\rightarrow \frac{\text{mol}}{L \cdot s} = k \frac{\text{mol}}{L} \rightarrow \frac{L}{\text{mol} \cdot s}$

Continue: $A \rightarrow B$

0th order
1st "
2nd " CSTR PFR

Size?

As $V \downarrow$ @ required $x \Rightarrow$ good

why? Save FCI

Fixed capital investment

Save COM

Save Maintenance

Save location

easy to be fabricated

* $A \rightarrow B$
staying in
the rxr

with the same Temp.

Condition of Rxr
 $\downarrow$ degradation

C

PFR

$\rightarrow F_A$
Flowrate

$\uparrow$ flow rate $\downarrow$ undesired product

but $\downarrow \downarrow$ time to produce
product B

FCI

Size

avoid this region

CSTR



ask :: believe & recieve

Back to the example of PFR and CSTR

$$x = 0.99, C_{A0} = 100$$

if then 99 is consumed left 1%

$$C_A = C_{A0}(1-x) = 100(1-0.99) = 1$$

molar flowrate, $F_{A0} = 5 \text{ mol/hr}$

volumetric flowrate, $v_0 = 10 \text{ L/hr}$

0 order $\rightarrow V_{\text{CSTR}} = 99 \text{ L}$
 $\rightarrow V_{\text{PFR}} = 99 \text{ L}$

1st order $\rightarrow V_{\text{CSTR}} = 2750 \text{ L}$
 $\rightarrow V_{\text{PFR}} = 127.9 \text{ L}$

2nd order rxn:

Assume: $C_{A0} = 100 \frac{\text{mol}}{\text{L}}, k_2 = 0.001 \frac{\text{L}}{\text{mol} \cdot \text{s}}$ $0.001 \frac{\text{L}}{\text{mol} \cdot \text{s}}$

$$V_{\text{CSTR}} = \frac{F_{A0} - F_A}{-r_A} = v_0 \frac{C_{A0} - C_A}{-r_A} = \frac{v_0 C_{A0} x}{-r_A}$$

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

$$\therefore C_{A0} - C_A = C_{A0} x$$

$$V = \frac{v_0 x C_{A0}}{K (C_A)^2}$$

$$= 9900 \frac{10/3600}{0.001 * 100} = 275 \text{ L} \rightarrow \frac{10 \frac{\text{L}}{\text{hr}} * 0.99 * 100 \frac{\text{mol}}{\text{L}}}{(0.001 * 3600 \text{ s})(1)^2}$$

$$V_{\text{PFR}} = - \int_{C_{A0}}^{C_A} v_0 \frac{dC_A}{k_2 C_A^2} = \frac{v_0}{K} \left[\frac{1}{C_A} \right]_{C_{A0}}^{C_A} = \left(\frac{10 \text{ L}}{\text{hr}} \right) \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) \frac{1}{(0.001 \text{ L/mol} \cdot \text{s})}$$

$$\left(\frac{1}{0.01 C_A} - \frac{1}{C_{A0}} \right) = 2.77 * \left(\frac{1}{0.01 * 100} - \frac{1}{100} \right) = 2.75 \text{ L}$$

Volume $\rightarrow$ CSTR, $V = 275\text{L}$ $\xrightarrow{\times 100}$ Required at the same x
 @ $C_{A0} = 100 \frac{\text{mol}}{\text{L}}$ $\rightarrow$ PFR, $V = 2.75\text{L}$

if $C_{A0} = 1000 \text{ mol/L}$ $\rightarrow V_{\text{PFR}} = 0.274\text{L}$ $\downarrow$
 the $V \downarrow$ $\uparrow$ Rate of rxn $\uparrow C_{A0}$

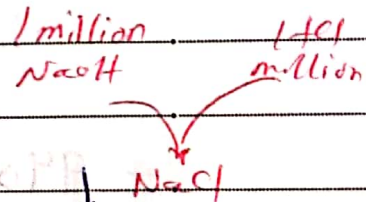
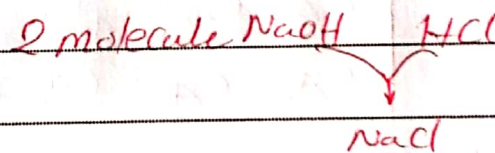
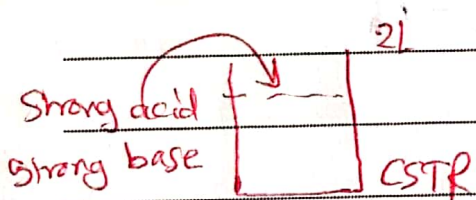
When to need bigger volume?

If the reaction is slow, or order is small

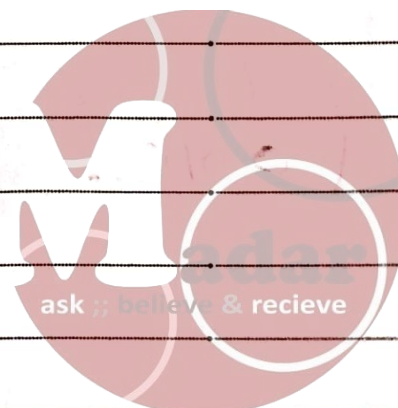
CSTR: perfect mixing need time, but for PFR $\rightarrow$ $\Rightarrow$ flow with each other

* k the reaction constant, indicator of how fast the rxn is.

* Acid-based $\rightarrow$ exothermic $\rightarrow$ highly aggressive $\rightarrow$ very fast



Safety: you can't
Do that



sizing of Rxrs based on exp. data

2nd Nov.

sizing of rxrs based on exp data:

Introduction

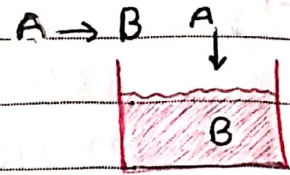
* Batch Rxr:

$$t = f(C_A)$$

$$C_A = C_{A0} (1 - X) \quad \text{given } X = 0.70$$

So the question what is the time required to achieve that conc. or conversion?

at the beginning = C_{A0}
 $(C_{A0} - C_A) / C_{A0}$



Required conversion!
 Time needed!

Design of batch

We need time required to achieve the desired conversion.

$$C_A = f(t) \text{ or } t = f(C_A)$$

t	C_A	X	r_A ($-dC_A/dt$)
0	C_{A0}	0	
t_1	C_{A1}	X_1	$\frac{C_{A1} - C_{A0}}{t_1 - t_0}$
t_2	C_{A2}	X_2	
⋮			

← 0.78 = X

t_n C_{An} $(X_n) = 0.78$

not happen in reality!

∴ for design of batch rxr → experimental data

Time
 Vs
 X or conc.

* CSTR Rxr & PFR Rxr: (Fixed volum then measure rate
 Rate r Vs X Vs X)

Example: Sizing of CSTR vs PFR

given that

X: 0

0.2

0.4

0.6

0.8

0.85

- r_A : 0.0053 ↑

0.005

0.004

0.0025

0.00125

0.001

* ↓ concentration ↓ rate

2nd Nov

$\frac{1}{-r_A}$: 189 200 250 400 800 1000

$v_0 = 6 \text{ L/s}$, $P_0 = 10 \text{ atm}$, $y_{A_0} = 0.5$ why? there is invert-enting
 $T_0 = 422.2 \text{ K}$,
 (A) $\rightarrow$ B

For CSTR $C_{A_0} = 0.144 \text{ M}$ s.l. = isoprl

Size $\rightarrow$ CSTR? and PFR?

⊗ Previously we did such a comparison but

based on a given expression $\rightarrow$ analytically.

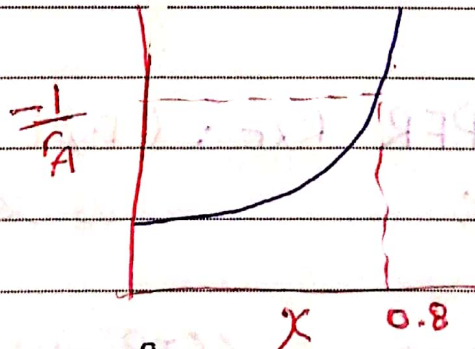
Now we have experimental $\rightarrow$ fitting $\rightarrow$ expression.

Soln:

~~PFR~~: $F_{A_0} = \frac{y_{A_0} P_0}{RT_0} v_0 = \frac{(0.5)(1013 \text{ kPa})(6 \text{ L/s})}{(8.314 \frac{\text{kPa} \cdot \text{L}}{\text{mol} \cdot \text{K}})(422.2 \text{ K})}$

$= 0.866 \text{ mol/s}$

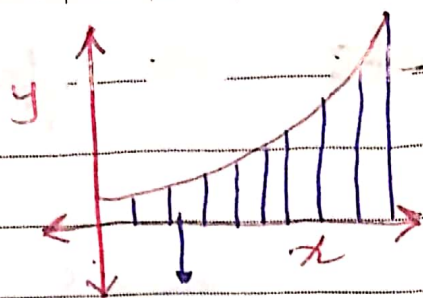
CSTR: $V = \frac{F_{A_0} x}{-r_A}$, if x needed = 0.8, what is V_{CSTR} ?
 $\downarrow$
 (gas: hydrocarbon)
 $= \frac{(0.866)(0.8)}{0.00125} = 552.9 \text{ L}$



PFR: $V = F_{A_0} \int_0^x \frac{dx}{-r_A}$
 $\downarrow$
 by

* Numerical integration:

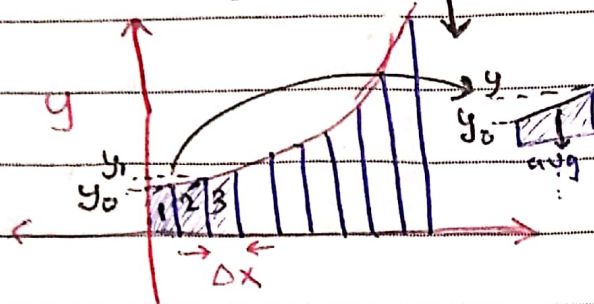
note: (This example is taken from chapter 2 (example 2-2) fogler 3rd edition)



how many of them

gathering $\rightarrow w \times L \times n = \text{Area}$

$I = \text{Area}$



$$A_1 = \Delta x \left(\frac{f_0 + f_1}{2} \right)$$

$$A_2 = \Delta x \left(\frac{f_1 + f_2}{2} \right)$$

$$A_{n-1} = \Delta x \left(\frac{f_{n-2} + f_{n-1}}{2} \right)$$

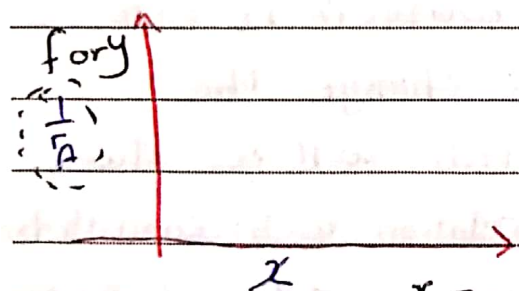
$$A_n = \Delta x \left(\frac{f_{n-1} + f_n}{2} \right)$$

Area 1 + Area 2 + Area 3 $\rightarrow$ Area under the curve

$$\text{Area} = \Delta x \left(\frac{f_0 + f_1}{2} \right) + \Delta x \left(\frac{f_1 + f_2}{2} \right) + \Delta x \left(\frac{f_2 + f_3}{2} \right) + \dots + \Delta x \left(\frac{f_{n-2} + f_{n-1}}{2} \right) + \Delta x \left(\frac{f_{n-1} + f_n}{2} \right)$$

$$= \frac{\Delta x}{2} \left[f_0 + 2f_1 + 2f_2 + \dots + 2f_{n-1} + f_n \right]$$

back to example:



$$V_{pfr} = F_{A0} \int_0^{x=0.8} \frac{dx}{r_A} = F_{A0} \sum_{x=0}^{x=0.8} \Delta x \left(\frac{1}{r_A} \right)$$

$$\text{Area} = 0.2 \left(\frac{189 + 200}{2} \right) + 0.2 \left(\frac{200 + 250}{2} \right) + 0.2 \left(\frac{250 + 400}{2} \right) + 0.2 \left(\frac{400 + 800}{2} \right) = 268.9$$

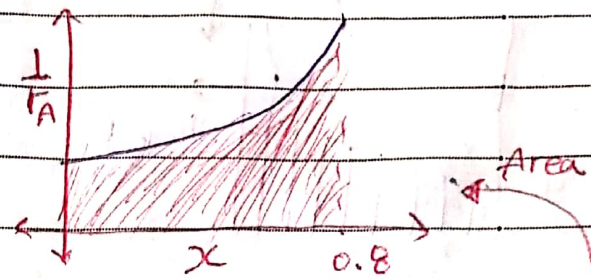
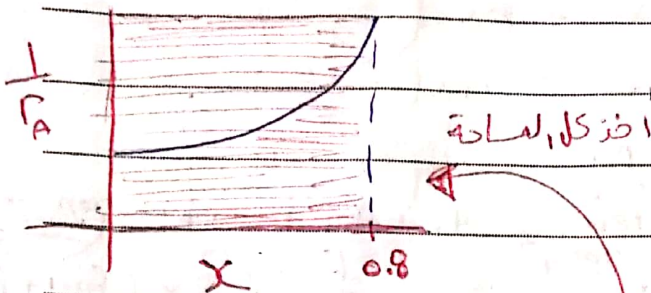
2nd Nov

$$V_{PFR} = 0.866 \times 268.9 = 232.87 \text{ L}$$

* Go to comparison for this Case ①

$$V_{CSTR, x=0.8} = 554.9 \text{ L}$$

$$V_{PFR, x=0.8} = 232.87 \text{ L}$$



In the case of CSTR

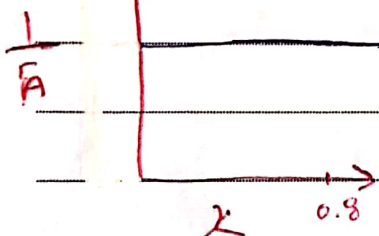
$$V_{CSTR} = \frac{F_{A0} x}{-r_A}$$

In the case of PFR

$$V_{PFR} = F_A \int_0^{0.8} \frac{dx}{-r_A}$$

* So, which is better to be chosen? PFR

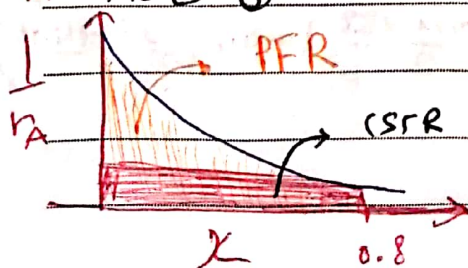
* CASE ②



⇒ based on this kind of rxn, which is better?

- the same, because it is zero order, if we change the conversion the rate will be always constant, No relation with concentration
∴ rate expression is not a fcn of concn.

* CASE ③

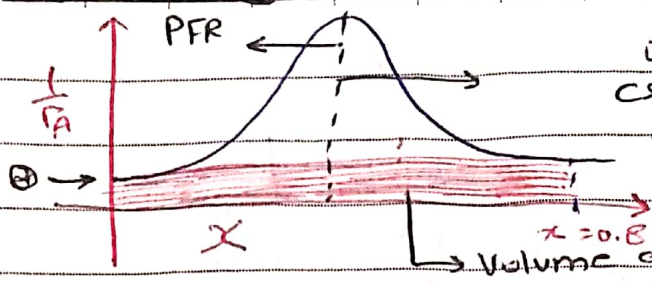


* to give the minimum volum for the same x
PFR or CSTR??

ask receive
CSTR but PFR will take the whole Area under the curve

2nd Nov

* CASE (4)



Volume of CSTR, based on initial C_0

but in this case C_0 is not large!

* Which one? (combination of PFR and CSTR)

* $A \rightarrow B \rightarrow C$: Series rxn. is valid for such a case

desired product undesired product

$x = 0.8$

up the re

Catalyst is used

decomposition

back to our example:

→ what is the size at $x = 0.85$

$$V_{CSTR} = \frac{0.864 (0.85)}{0.001} = 734.4 \text{ L}$$

$$V_{PFR} = F_{A0} \int_0^x \frac{dx}{r_A} = F_{A0} * \left(\int_0^{0.8} \frac{dx}{r_A} + \int_{0.8}^{0.85} \frac{dx}{r_A} \right)$$

$$= 0.866 * \left(268.9 + 0.05 * \left(\frac{1000 + 800}{2} \right) \right) = 271.86$$

what is preferable 0.80 or 0.85? OR what is feasible?

For CSTR → 0.80

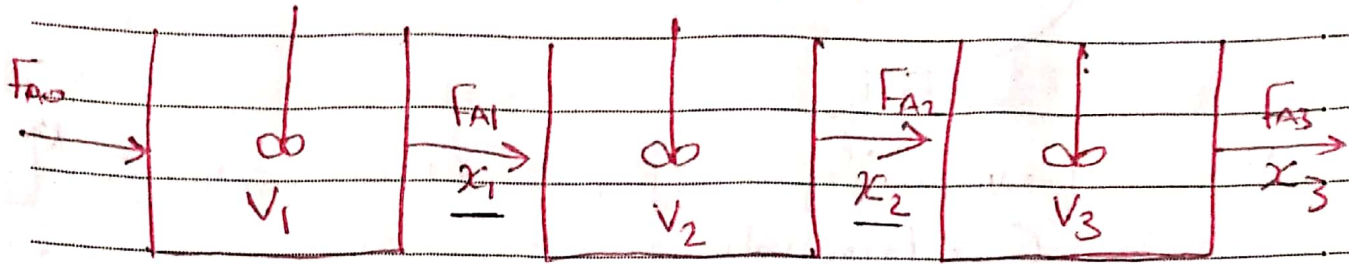
For PFR → 0.85

x	$V \text{ (L)}_{CSTR}$	$V_{PFR} \text{ (L)}$
0.8	552.9	232.87
0.85 (useless)	734.4	271.86
ΔV	181.5	38.99
$\frac{\Delta V}{V_{in}}$	32.83%	16.7%

فقدان في الإنتاج

* Ask & receive
* think from business point of view rather than technical.

CSTR



$$V_1 = \frac{F_{A0} - F_{A1}}{-r_{A1}} = \frac{F_{A0} - F_{A0}(1-x_1)}{-r_{A1}} = \frac{F_{A0} x_1}{-r_{A1}}$$

$$V_2 = \frac{F_{A1} - F_{A2}}{-r_{A2}} = \frac{F_{A0}(1-x_1) - F_{A0}(1-x_2)}{-r_{A2}} = \frac{F_{A0}(x_2 - x_1)}{-r_{A2}}$$

$$V_3 = \frac{F_{A2} - F_{A3}}{-r_{A3}} = \frac{F_{A0}(1-x_2) - F_{A0}(1-x_3)}{-r_{A3}} = \frac{F_{A0}(x_3 - x_2)}{-r_{A3}}$$

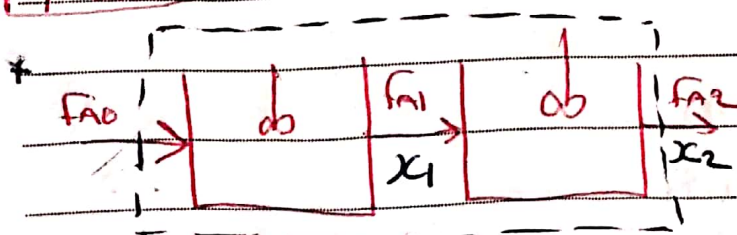
$$V_T = V_1 + V_2 + V_3 = \frac{F_{A0} x_1}{-r_{A1}} + \frac{F_{A0}(x_2 - x_1)}{-r_{A2}} + \frac{F_{A0}(x_3 - x_2)}{-r_{A3}} + \dots$$

$$V_T \text{ for } n\text{-Rxr} = F_{A0} \sum_{i=1}^n \frac{\Delta x}{-r_{Ai}} = F_{A0} \int_{x=0}^{x_T} \frac{dx}{-r_{Ai}} \rightarrow \text{the size of PFR}$$

Note:

- * there is a difference between x_1 and x_2 ;
no. rxr $\uparrow$ = not have enough residence time in rxr
flow rate is constant, no. rxr $\uparrow \Rightarrow$ volume of each
following rxr $\downarrow \downarrow$, $\downarrow$ volume, the difference
between x_1 and x_2 is not that much

Note:



why do we take F_{A0} ??

$$F_{A2} = F_{A0}(1-x_2)$$

consider F_{A2} by F_{A1} initially

$$F_{A2} = F_{A1}(1-x_2)$$

don't (in term of x_1 conversion)
I know it

4th / Nov / 2020

Conclusion I:

The volume of infinite number of CSTR in series = the size of one PFR

Example: last example previous lecture

our expecting:
the same size!!

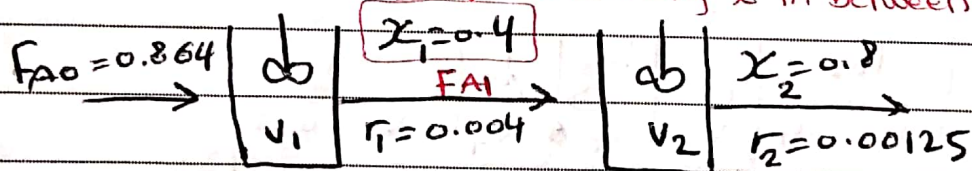
X	0	0.2	0.4	0.6	0.8
$-r_A$	0.0053	0.005	0.004	0.0025	0.00125
$1/r_A$	189	200	250	400	800

$v_0 = 6 \text{ L/s}$, $F_{A0} = 0.864$

* Case I One PFR (CSTR), $X = 0.8$

$$V_1 = F_{A0} \frac{X}{-r_{A1}} = (0.864 \text{ (mol/s)}) \times \frac{0.8}{0.00125} = 552.9 \text{ L}$$

* Case II: we have two CSTRs in series.



$$V_1 = F_{A0} \frac{X_1}{-r_{A1}} = (0.864) \left(\frac{0.4}{0.004} \right) = 86.4 \text{ L}$$

related to F_{A0}

$$= F_{A0} \left(\frac{X_2 - X_1}{-r_{A2}} \right) = (0.864) \left(\frac{0.8 - 0.4}{0.00125} \right) = 276.48 \text{ L}$$

$\uparrow F_{A0}$

$$V_{\text{total}} = V_1 + V_2 = 86.4 + 276.48 = 362.9 \text{ L}$$

* previous case $V_1 = 552.9$ when it was just a one PFR

* Why it's much bigger than the first one? because of the flowrate ($F_{A1} < F_{A0}$)

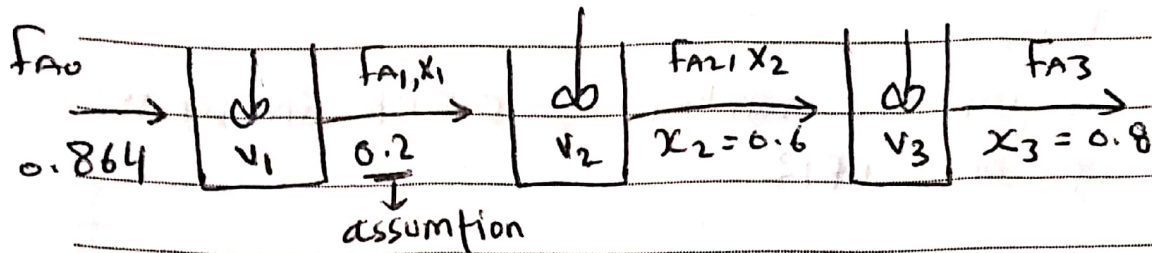
↓ flowrate ↓ conversion

↓ volume with the same performance

Case III: Three CSTRs in Series

Rxr in Series.

Nov 4th

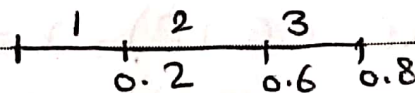


$$V_1 = 0.864 \frac{0.2}{0.005} = 34.56 \text{ L}$$

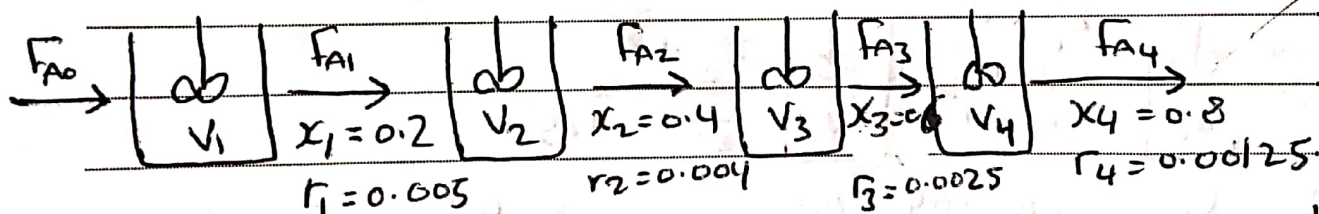
$$V_2 = F_{A0} \frac{x_2 - x_1}{-r_{A2}} = 0.864 \frac{0.6 - 0.2}{0.0025} = 138.24 \text{ L}$$

$$V_3 = F_{A0} \frac{x_3 - x_2}{-r_{A3}} = 0.864 \frac{0.8 - 0.6}{0.00125} = 138.24 \text{ L}$$

$$V_T = 311.04 \text{ L}$$



Case VI: Four CSTRs in Series:

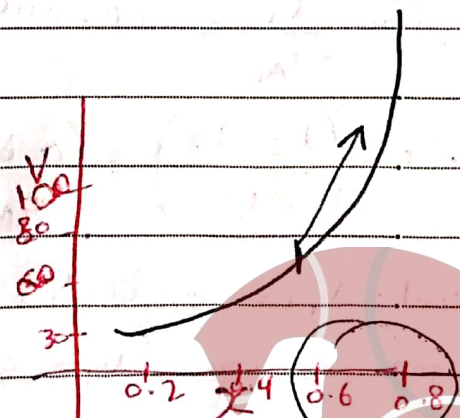


$$V_1 = 0.864 \frac{0.2}{0.005} = 34.56 \text{ L}$$

$$V_2 = 0.864 \frac{0.4 - 0.2}{0.004} = 43.2 \text{ L}$$

$$V_3 = 0.864 \frac{0.6 - 0.4}{0.0025} = 69.36 \text{ L}$$

$$V_4 = 0.864 \frac{0.8 - 0.6}{0.00125} = 138.24 \text{ L}$$

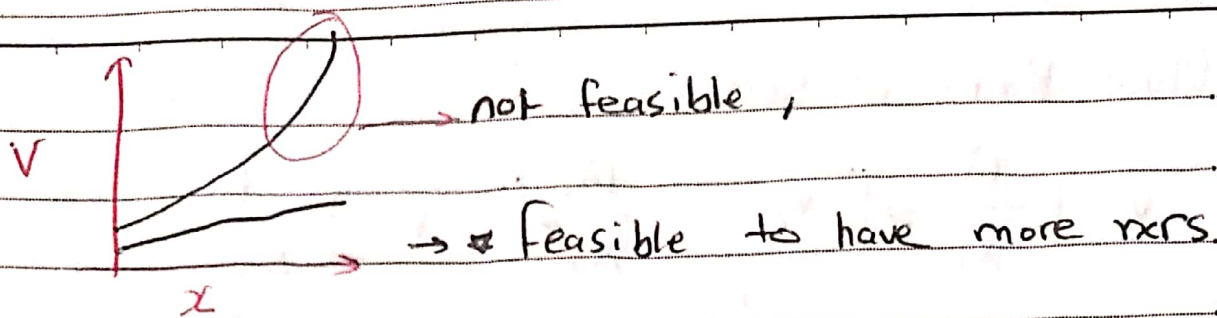


Is that a feasible?

ask : believe & recieve

* Conversion difference = equal 0.2 0.4 0.6 0.8
expecting the volume of rxr

Nov, 4th



$$V_T = V_1 + V_2 + V_3 + V_4 = 285.36 \text{ L}$$

Conclusion:

$$R_1 (552.9 \text{ L}) \quad R_2 (362.9 \text{ L}) \quad R_3 (311.04 \text{ L}) \quad R_4 (286 \text{ L})$$

$V_I \quad V_{II} \quad V_{III} \quad V_{IV}$

→
of rxr

total size ↓ ↓ decrease

= ∞ number of CSTRs in series

$$V_{PFR} = \int_0^{0.8} F_{A0} \frac{dx}{-r_A} = 0.866 * 268.9 = 232.87 \text{ L}$$

$$\square - \square - \square - \square - \dots - \infty \Rightarrow 1 \text{ PFR}$$

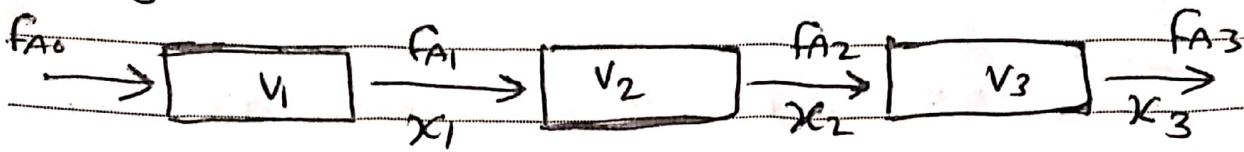
* CSTR: ∞ rxr to reduce the size to 232.87 L (the size of PFR) saving (50 - 60 L), is that feasible to make a design of ∞ of CSTRs to reduce size 60 L (Not feasible)

* Size of CSTR ~~and~~ equals the size of PFR, which is giving the less conversion? (CSTR)

* Size of PFR 1000 L, size of CSTR 1.2, 78 = 1000 L
Conversion ↑↑ : ((PFR))

Nov, 4th

plug flow Rxrs in series:



$$V_1 = \int_0^{x_1} F_{A0} \frac{dx}{-r_{A1}} \quad ; \quad V_2 = \int_{x_1}^{x_2} F_{A0} \frac{dx}{-r_{A2}} \quad ; \quad V_3 = \int_{x_2}^{x_3} F_{A0} \frac{dx}{-r_{A3}}$$

$$V_T = V_1 + V_2 + V_3$$

$$= F_{A0} \left[\int_0^{x_1} \frac{dx}{-r_{A1}} + \int_{x_1}^{x_2} \frac{dx}{-r_{A2}} + \int_{x_2}^{x_3} \frac{dx}{-r_{A3}} \right]$$

(V₁ → Diam 1cm length 1cm) $r_{A1} \quad r_{A2} \quad r_{A3} \quad r_A \text{ at that exist } x$

$$= F_{A0} \left[\int_0^{x_1} \frac{dx}{-r_A} + \int_{x_1}^{x_2} \frac{dx}{-r_A} + \int_{x_2}^{x_3} \frac{dx}{-r_A} \right] \quad \text{Sumation integration}$$

$\underbrace{\text{at that exist } x_1} \quad \underbrace{\text{at that } x_2} \quad \underbrace{\text{at that } x_3}$

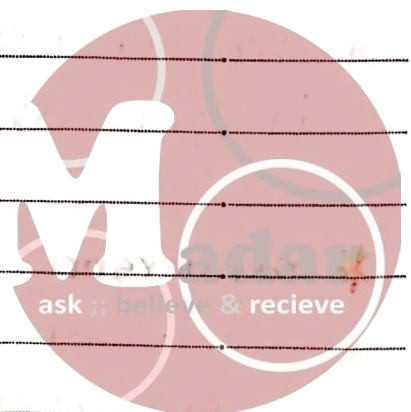
Remember:

$$\int_0^{x_1} y dx + \int_{x_1}^{x_2} y dx = \int_0^{x_2} y dx$$

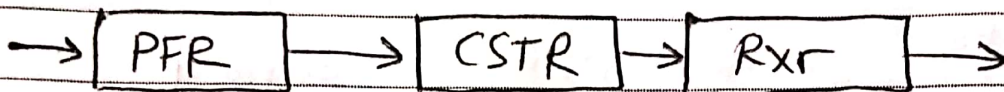
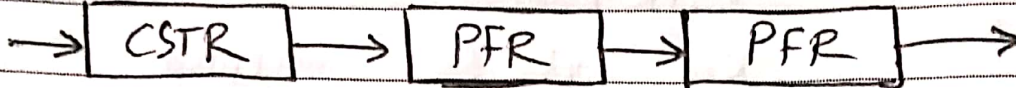
$$V_T = F_{A0} \int_0^{x_3} \frac{dx}{-r_A} \quad \rightarrow F_{A0} \quad \dots \quad \rightarrow F_{A3}$$

conclusion:

Sumation PFRs in series $\equiv$ 1 PFR to achieve the last conversion



Rxrs in Series



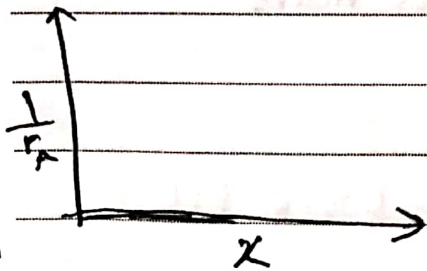
Which one is the best described of my rxn?



object: to have maximum conv.
at minimum volume

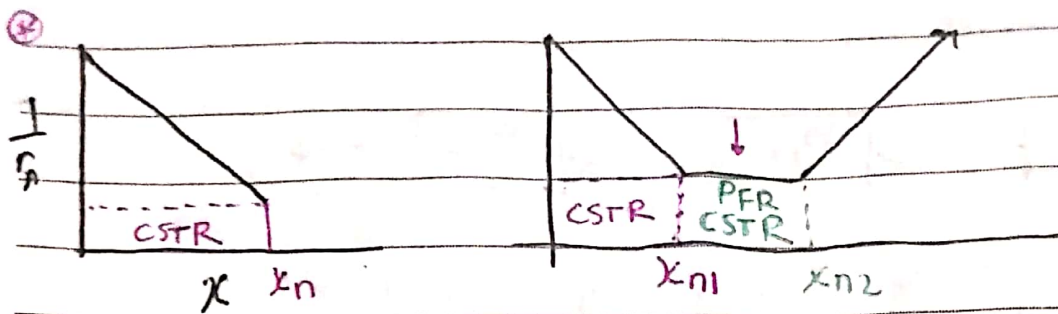
better quality of the product
with minimum fixed capital
investment, the conver. of last
rxr is needed as maximum as
possible.

← → which rxr is first which is the last
x r_A 1/r_A depend on the rate of rxn.



$$V_{CSTR} = \frac{F_{A0} x}{-r_A}$$

$$V_{PFR} = \int_0^{x_r} F_{A0} \frac{dx}{-r_A}, \quad x_1 dx \text{ vs } \frac{1}{A}$$



* but one is the more right?

(1) cost

(2) plant location

CSTR + CSTR

$x=0 \quad x_{n1} \quad x_{n1} \quad x_{n2}$ accepted

CSTR + PFR

$0 \quad x_{n1} \quad x_{n1} \quad x_{n2}$

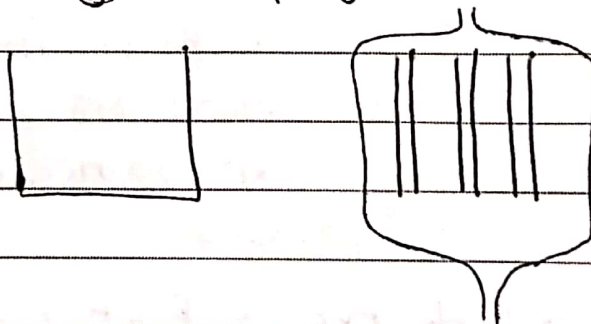
accepted

Note:

* More the one CSTR is more feasible than one

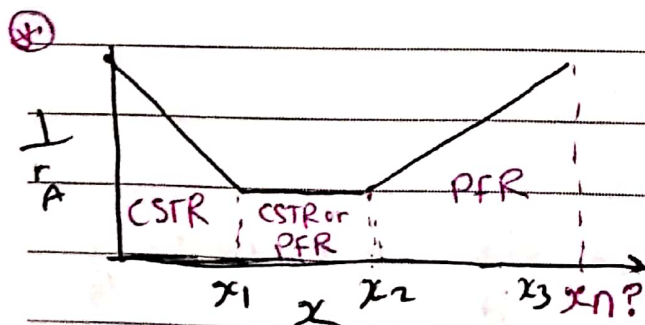
plant location: area of the plant limited

we prefer PFR



Note:

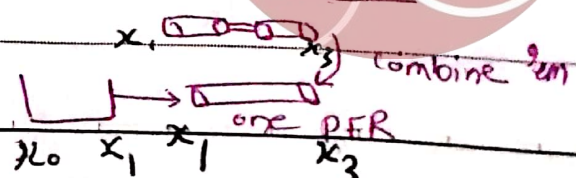
CSTR is easier to maintain, It takes hours.



CSTR - CSTR - PFR

or

CSTR - PFR - PFR



⊗

CSTR - CSTR - PFR

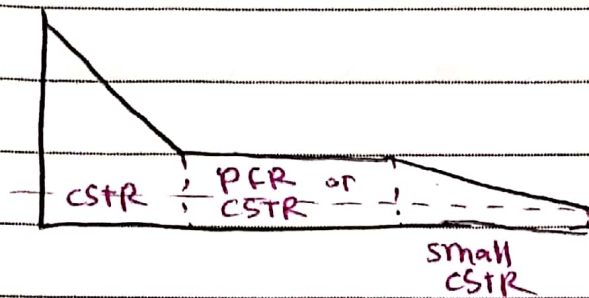
Not efficient compared to next choice

CSTR - PFR - PFR
 $x_0 \quad x_1 \quad x_1 \quad x_2$

combined the both of PFR rxrs

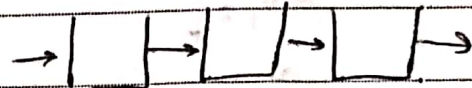
CSTR - PFR
 $x_0 \quad x_1 \quad x_1 \quad x_3$

⊗



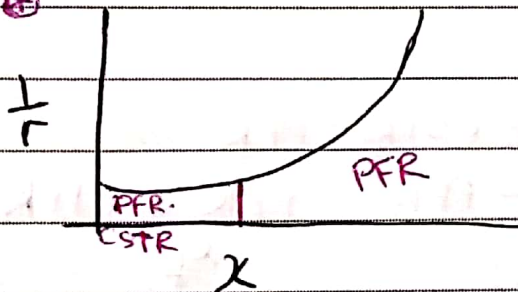
CSTR - PFR - CSTR
 CSTR - CSTR - CSTR

both are correct



3 CSTRs in series

⊗



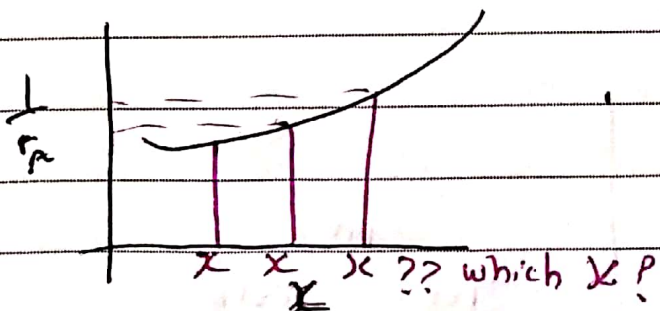
✓ PFR - PFR

longer

CSTR - PFR

NOTE: PFR - PFR is the better in operational point of view

if you're forced to choose the CSTR?

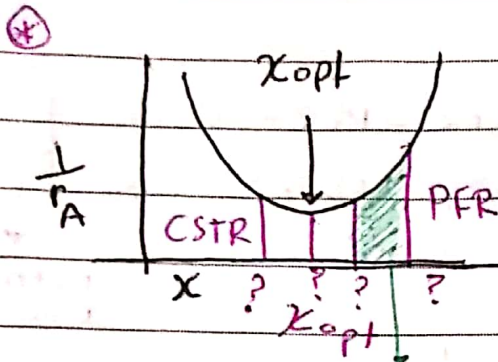


$x_{opt} ?$

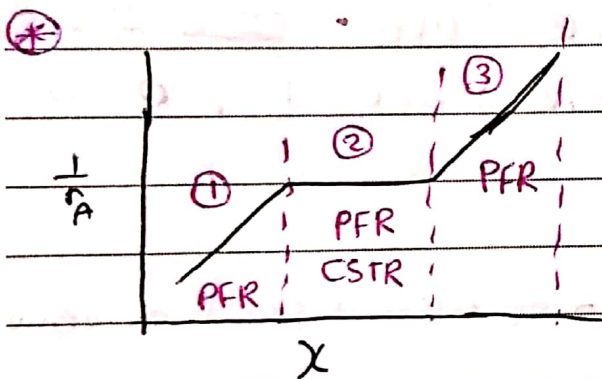
CSTR - PFR

$$V_{CSTR} = F(x_{opt})$$

$$V_{PFR} = \int_{x_{opt}}^{x_f} \frac{dx}{-r_A} F_{A0}$$



the same

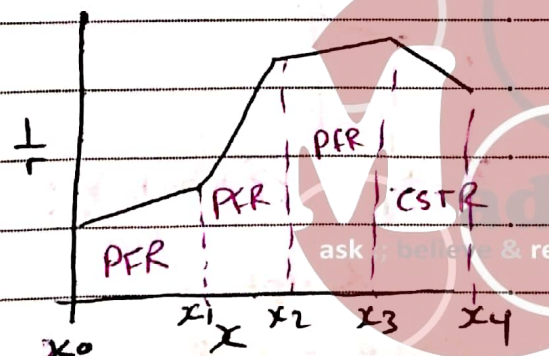
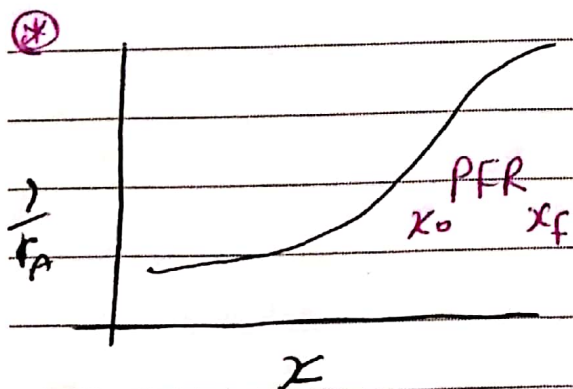


$$PFR - CSTR - PFR$$

$$PFR - PFR - PFR \equiv 1 PFR$$

x_0

x_f

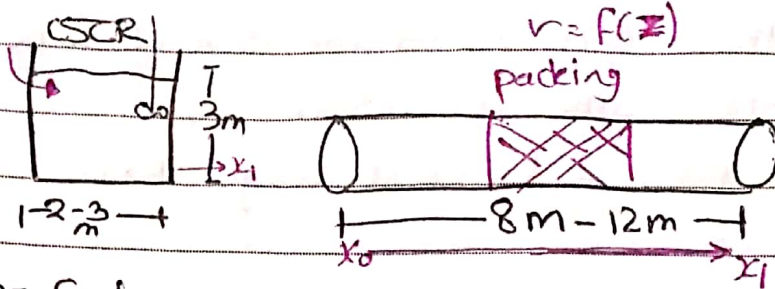


$$PFR - PFR - PFR - CSTR$$

$$\equiv PFR - CSTR$$

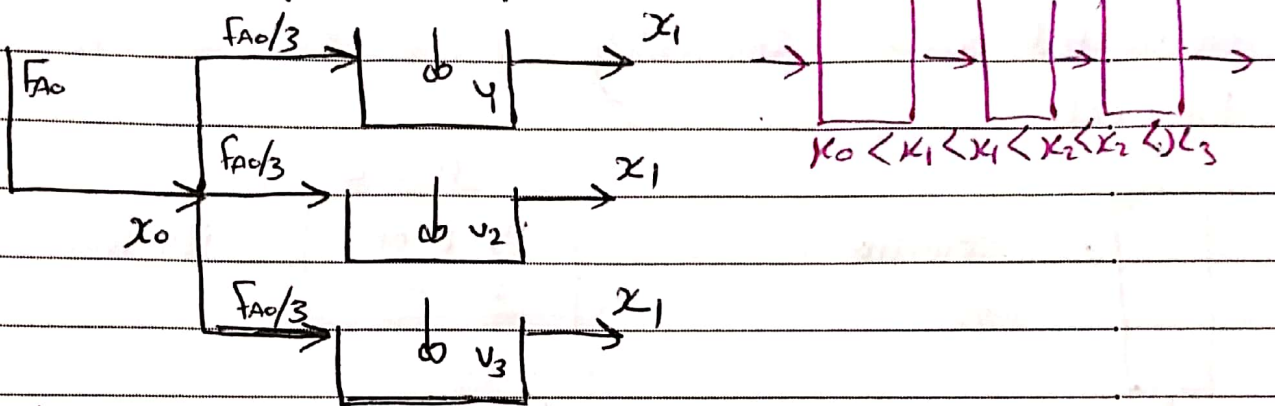
In Parallel

9th Nov



Perfect mixing

CSTRs in Parallel:



Assume: $V_1 = V_2 = V_3$

* The conversion of CSTRs in series > The conversion of CSTRs in parallel

but the yield / flowrates for parallel CSTRs > flowrates for Series CSTRs

* total design to achieve higher flowrate:

$$1^{st} \text{ CSTR : } V_1 = \frac{F_{A0} x_1 / 3}{-r_{A1}} = \frac{1}{3} \frac{F_{A0} x_1}{-r_{A1}}$$

$$V_2 = \frac{1}{3} F_{A0} \frac{x_1}{-r_{A1}} =$$

$$V_3 = \frac{1}{3} F_{A0} \frac{x_1}{-r_{A1}}$$

$$\therefore V_{\text{Total}} = \frac{F_{A0} x_1}{-r_{A1}}$$

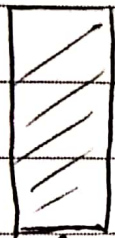
3 CSTRs in parallel, their size equal the size of one CSTR to achieve the same conversion.

Each small r_{xr} converts $\frac{1}{3} F_{A0}$ but large R_{xr} converts F_{A0}

* $\swarrow$ quality $\searrow$ conversion
 $\swarrow$ quantity $\searrow$ production rate

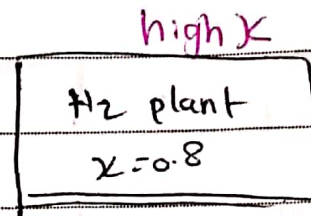
* $A \rightarrow B$, $X = 60\%$ we don't care about conversion
activated carbon industry

lig-cell $\rightarrow C$



selective
0.95

Filtration of water



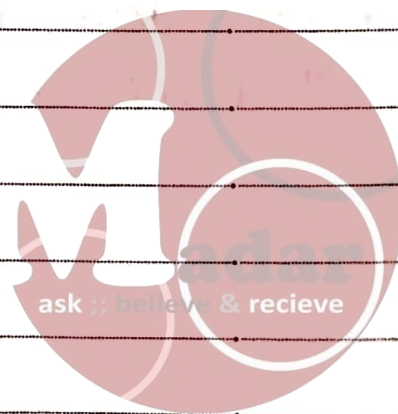
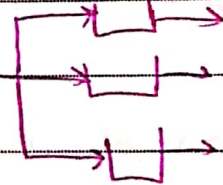
high X

Petroleum

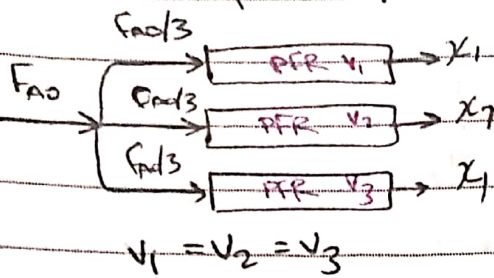
large F_{A0}

bulk

to rid off odor



PFR in Parallel:-



$$V_1 = \frac{F_{A0}}{3} \int_0^{X_1} \frac{dX}{-r_A}$$

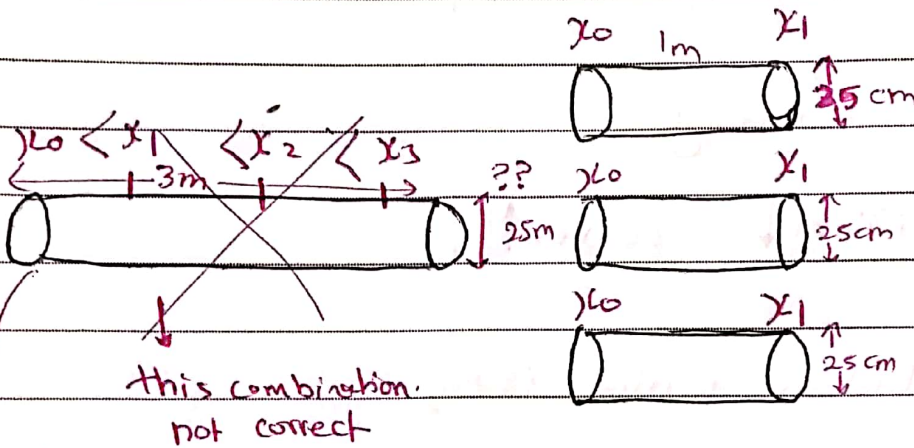
$$V_2 = \frac{F_{A0}}{3} \int_0^{X_2} \frac{dX}{-r_A}$$

$$V_3 = \frac{F_{A0}}{3} \int_0^{X_3} \frac{dX}{-r_A}$$

$$V_T = V_1 + V_2 + V_3$$

$$= \frac{F_{A0}}{3} \left[\int_0^{X_1} \frac{dX}{-r_A} + \int_0^{X_2} \frac{dX}{-r_A} + \int_0^{X_3} \frac{dX}{-r_A} \right]$$

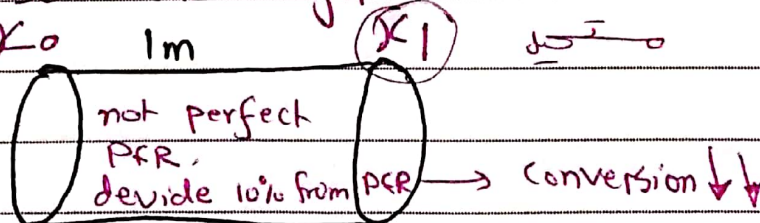
Note $\int_0^{X_1} y dx + \int_0^{X_1} y dx = 2 \int_0^{X_1} y dx$ so, $= \frac{3}{3} F_{A0} \int_0^{X_1} \frac{dX}{-r_A} = F_{A0} \int_0^{X_1} \frac{dX}{-r_A}$



$V_T = V_T$ is this real?

length $\rightarrow$ conversion

So the right combination or design.



what is the difference between these ^{big} PFR and three small vars?!!

$$V_{T(\text{big } r \times r)} = V_{T(3 \text{ } r \times r \text{ small})}$$

$$\pi r^2 l = \pi \left(\frac{1}{4}\right)^2 (1) = \frac{\pi}{16} \begin{matrix} r \times r_1 \\ r \times r_2 \\ r \times r_2 \end{matrix}$$

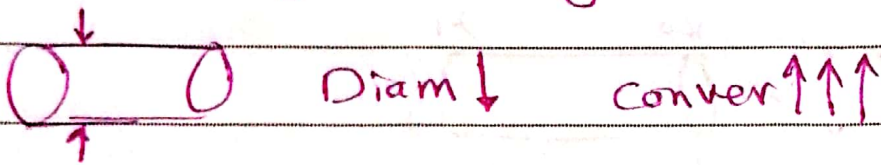
$$\text{So } V_{(3 \text{ } r \times r)} = \frac{3\pi}{16} \Rightarrow \frac{3\pi}{16} = \pi r^2 (1)$$

$$r^2 = \frac{3}{16} \Rightarrow r = \sqrt{\frac{3}{16}} = 0.433 \text{ m}$$

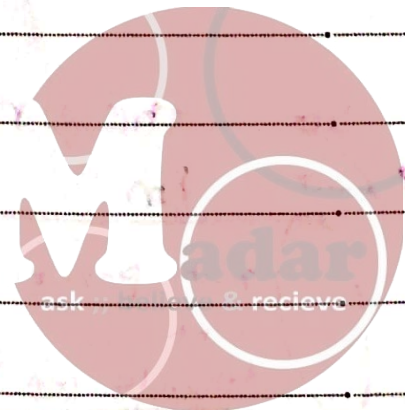
Size of (1m, 0.433 Diam) = size (3 $r \times r$ 25cm, 1m)
 the X_1 conversion from X_1

Why?

There is not good mixing.



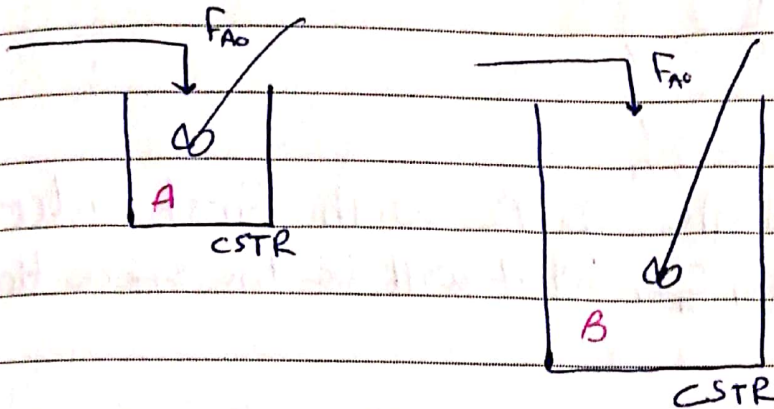
choosing multistage parallel PFRs



Space time ^{rxr or τ}

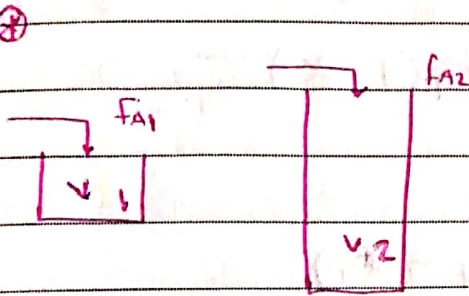
Nov, 16

space time : the time necessary to process one rxr volume of fluid on entrance conditions ($X, V_{dume}, \text{volumetric flowrate}$)



↑
comparison
molar flowrate the same for both rxrs

$A \rightarrow B$, 1st order, does rxr A give the same conversion f_B ?
-NO, because the difference of volume



$F_{A2} \text{ molar flowrate} = 2 F_{A1}$

$V_2 = 2 V_1$

which one giving higher conversion?
that's our topic

Note! For CSTR $\uparrow \text{volume}$ $\uparrow x$ but there another factor Space time!

For CSTR:

$$x = f(V, \tau_0)$$

$$V = \frac{F_{A0} x}{-r_{A1}}$$

$$F_{A0} = C_{A0} \cdot \tau_0$$

$$V = \frac{C_{A0} x \cdot \tau_0}{-r_{A1}}$$

↓
we can compare two rxrs based on their

↓
 V τ_0

$$\frac{V}{\tau_0} = \tau = \frac{C_{A0} x}{-r_{A1}}$$

actual design eq. for CSTR & recieve

$$\text{Space time} = \tau = \frac{V}{v_0}$$

$$\text{Space velocity} = \frac{1}{\tau} = \frac{v_0}{V}$$

Compare between CSTRs $\xrightarrow{v}$

Example: Consider a single CSTR with First order rxn $A \rightarrow B$, $r_A = -k_1 C_A$, What will be the space time?

Soln:

$$V = \frac{F_{A0} x}{-r_A} = \frac{v_0 C_{A0} x}{k_1 C_A} = \frac{v_0 C_{A0} x}{k_1 C_{A0} (1-x)} = \frac{V}{v_0} = \tau$$

$$\frac{x}{k_1 (1-x)} = \tau \text{ (space time)}, \quad k_1 (1-x) \tau = x$$

$$\tau k_1 - k_1 x \tau = x$$

$$\text{or } \tau k_1 = k_1 x \tau + x = x (1 + \tau k_1)$$

$$x = \frac{\tau k_1}{(1 + \tau k_1)} \quad \text{relates conversion with space time} \quad \text{Based on rxn order (1st-order)}$$

$$C_A = C_{A0} (1-x) = C_{A0} \left(1 - \frac{\tau k_1}{(1 + \tau k_1)} \right)$$

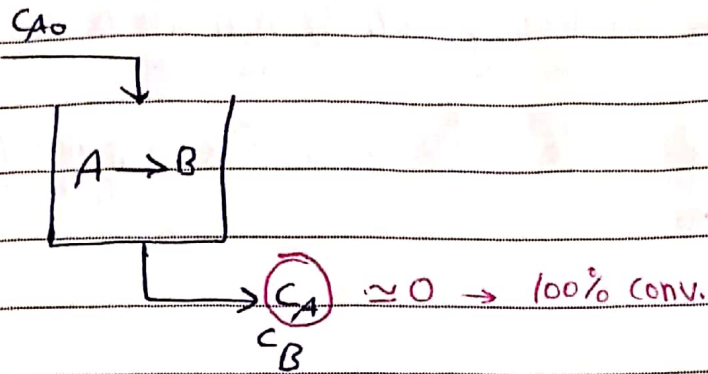
$$= C_{A0} \frac{1 + \tau k_1 - \tau k_1}{1 + \tau k_1}$$

$$\therefore C_A = C_{A0} \frac{1}{1 + \tau k_1}, \quad \tau = \frac{V}{v_0}$$

as $v \uparrow \rightarrow \tau \uparrow$ so the den. $\uparrow$

so $C_A \downarrow$ (that's what we want) $x \uparrow$

Nov, 16th



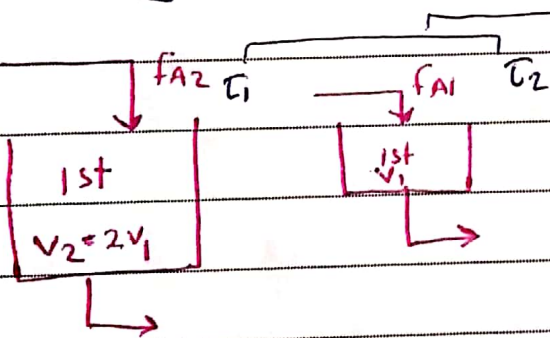
as $v_0 \downarrow \rightarrow \tau \uparrow \rightarrow C_A \downarrow, X \uparrow$

* To increase conversion for first order rxn in CSTR
 $\uparrow V$ or $\downarrow v_0$

* v_0, v_0 clouds $X \uparrow$ inlets (small rxn) possible
 affecting yield $\leftarrow v_0$

Hw: given two rxns, 1st order Rxn, CSTRs, so what is the volume of each rxr and volumetric flowrate that yield similar conversion?

ratio, that conversion the same!



$$V_2 = 2V_1$$

$$X_2 = X_1$$

$$C_{A01} = C_{A02}$$

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const $\rightarrow$ $V_{CSTR} = \frac{F_{A0} X}{-r_{A1}}$ relation
 $\leftrightarrow$ order, 0, 1, 2, non elementary
 plays a significant role

* Note: at constant molar flowrate $\uparrow$ volume, $\uparrow$ X $\rightarrow$ general speaking

HW soln:

$$\tau_1 = \frac{C_{A0} X}{-r_{A1}};$$

$$V = \frac{V_0 C_{A0} X}{-r_{A1}}, \text{ 1st order}$$

$$r_{A1} = -k_1 C_A = -k C_{A0} (1-X)$$

$$\frac{V}{V_0} = \frac{C_{A0} X}{k_1 C_{A0} (1-X)} \Rightarrow \tau_1 = \frac{X}{k_1 (1-X)} \rightarrow \tau_1 k_1 - \tau_1 k_1 X = X$$

$$\tau_1 k_1 = X(1 + \tau_1 k_1)$$

$$X = \frac{\tau_1 k_1}{1 + \tau_1 k_1}$$

R_{xr1}

$$F_{A1} = V_1 C_{A0}$$

R_{xr2}

$$F_{A2} = V_2 C_{A0}$$

$$\frac{\tau_1 k_1}{1 + \tau_1 k_1} = X = \frac{\tau_2 k_1}{1 + \tau_2 k_1}$$

$$\frac{\tau_1 k_1}{1 + \tau_1 k_1} = \frac{\tau_2 k_1}{1 + \tau_2 k_1}$$

$$\frac{\tau_1}{\tau_2} = \frac{1 + \tau_2 k_1}{1 + \tau_1 k_1} \quad \tau_1 = \frac{V_1}{V_{01}} = \frac{1 + \frac{V_1}{V_{01}} k_1}{1 + \frac{V_2}{V_{02}} k_1}$$

$$\tau_2 = \frac{V_2}{V_{02}}$$

$$V_2 = 2V_1 \rightarrow \frac{V_1/V_{01}}{2V_1/V_{02}} = \frac{1 + \frac{V_1}{V_{01}} k_1}{1 + \frac{2V_1}{V_{02}} k_1}$$

$$\frac{V_{02}}{2V_{01}} = \frac{1 + (V_1/V_{01}) k_1}{1 + \frac{2V_1}{V_{02}} k_1}$$

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$$V_{o2} = 2V_{o1} \left(\frac{1 + \frac{V_1}{V_{o1}} k_1}{1 + \frac{2V_1}{V_{o2}} k_1} \right) \text{ if } k_1 = 1 (s^{-1})$$

$$V_{o2} = 2V_{o1} \left(\frac{1 + \frac{V_1}{V_{o1}}}{1 + \frac{2V_1}{V_{o2}}} \right)$$

$$V_{o2} = 2V_{o1} \left(\frac{V_{o1} + V_1}{V_{o1}} \right) = 2V_{o1} \frac{V_{o1} + V_1}{V_{o1}} + \frac{V_{o2}}{V_{o2} + 2V_1}$$

at Note: $\frac{y}{x} = \frac{y}{x}$
 $\frac{z}{k} = \frac{z}{k}$

$$V_{o2} = 2V_{o1} \frac{V_{o1} + V_1}{V_{o2} + 2V_1}$$

$$V_{o2} = 2V_{o2} \frac{V_{o1} + V_1}{V_{o2} + 2V_1}$$

$$\frac{1}{2} = \frac{V_{o1} + V_1}{V_{o2} + 2V_1}$$

$$2(V_{o1} + V_1) = (V_{o2} + 2V_1)$$

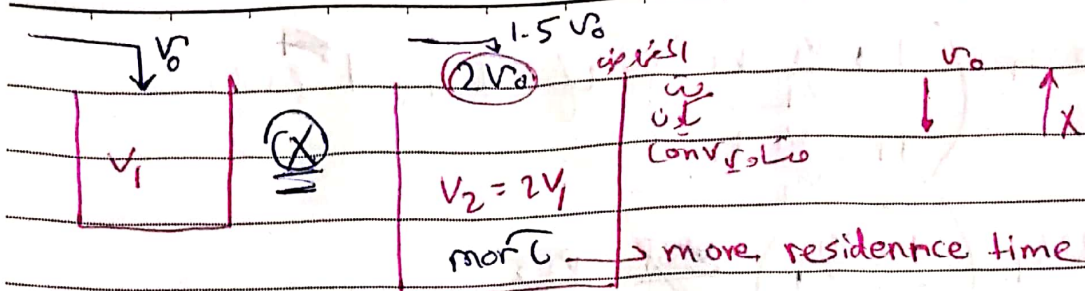
$$2V_{o1} + 2V_1 = V_{o2} + 2V_1$$

$$2V_{o1} = V_{o2}$$

if I have $V_2 = 2V_1$ then
 $V_{o2} = 2V_{o1}$ to get similar
conversion



Nov 16



$\uparrow \uparrow \tau \rightarrow X \uparrow$

$$\tau_2 = \frac{V_2}{v_{02}} = \frac{2V_1}{1.5v_0} = \left(\frac{2}{1.5}\right) \tau_1 \quad \tau_2 > \tau_1$$

more than one

$\uparrow \uparrow \tau \therefore X \uparrow$

* $X_1 = X_2$ but $\downarrow v_0$ for $\tau \rightarrow \uparrow \uparrow$ Residence time $\rightarrow \uparrow X$
based on if first order rxn

Hw: τ for 2nd order, $-r_2 = k_2 C_A^2$

$$V = \frac{v_0 C_{A0} X}{K_2 C_A^2} = \frac{V}{v_0} = \tau = \frac{C_{A0} X}{K_2 C_{A0}^2 (1-X)^2}$$

$$\tau = \frac{X}{K_2 C_{A0} (1-X)^2} \quad ; \alpha = K_2 C_{A0}$$

second order

$$\tau_2 = \frac{X}{\alpha(1-X)(1-X)} = \frac{X}{\alpha(1-2X+X^2)}$$

$$\tau_2 \propto (1-2X+X^2) = X, \quad \beta = \alpha \tau_2$$

$$\beta - 2\beta X + \beta X^2 = X$$

$$\beta - 2\beta X - X + \beta X^2 = 0$$

$$\beta^c - X(1+2\beta) + \beta X^2 = 0$$

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Nov, 16

$$X = \frac{+(1+2\beta) \pm \sqrt{(1+2\beta)^2 - 4\beta^2}}{2\beta}$$
$$= \frac{(1+2\beta) - \sqrt{(1+2\beta)^2 - (2\beta)^2}}{2\beta}$$

depend (-) sign
 $X < 1$

let $A = (1+2\beta)$
 $B = 2\beta$

$$X = \frac{A - \sqrt{A^2 - B^2}}{B} = \frac{A - \sqrt{(A-B)(A+B)}}{B}$$

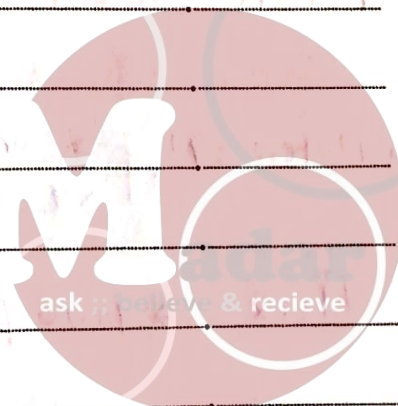
$$= \frac{(1+2\beta) - \sqrt{(1+2\beta-2\beta)(1+2\beta+2\beta)}}{2\beta}$$

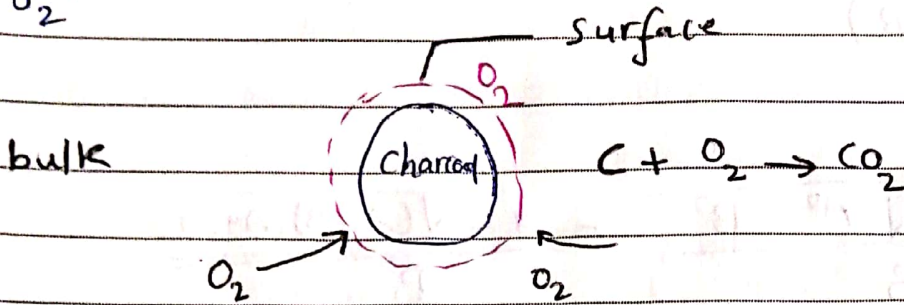
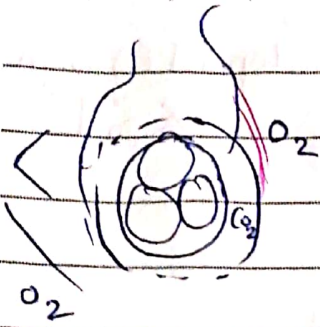
$$= \frac{(1+2\beta) - \sqrt{(1+4\beta)(1)}}{2\beta}$$

$$X = \frac{(1+2k_2\tau_2C_{A0}) - \sqrt{(1+4k_2\tau_2C_{A0})}}{2k_2\tau_2C_{A0}}$$

conversion for 2nd order

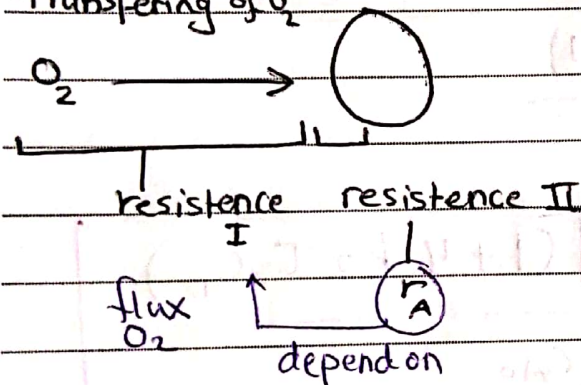
HW: If we have Zero-order!





Suppose $r_A = k C_A^2$, $C_A \downarrow \rightarrow r_A \downarrow$

transferring of O_2



* rxn doesn't depend just on the rate of rxn, but also on flux on surface

* Note: $N_A \rightarrow$ convective $\rightarrow -k_c (C_{As} - C_{\infty})$ (almost zero)
 $\rightarrow$ Diffusion $\rightarrow$ gradient $\rightarrow r_A = k C_A^2$

Flux $\rightarrow$ two factors $\rightarrow$ difference of conc. = driving force
 as driving force $\uparrow$ resistance $\downarrow$

$\rightarrow k_c$, how fast the reactant (material) to move, (unit of velocity)

resistance $= \frac{1}{k_c}$

- * Rxn not necessarily is affected by the rate of rxn itself
 It is affected by ~~the~~ diffusion rate of a reactant to the surface of the second reactant

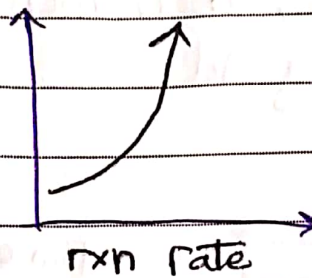
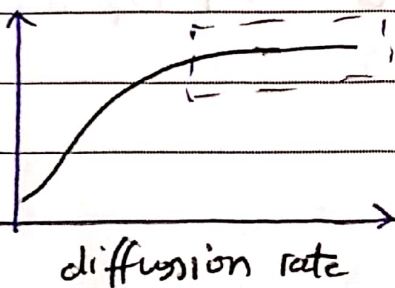
$$Da = \frac{\text{Rxn Rate}}{\text{Diffusion rate}}$$

$$= \frac{\text{Diffusion time}}{\text{reaction time}}$$

- * If $Da < 0.1$, then $x < 0.1$ Conversion

* rxn rate as fast as possible compared to Diffusion rate

- * If $Da > 10$, then $x > 0.9$



Damköhler number is a useful ratio for determination whether diffusion rate or rxn rate is more important for defining a steady state chemical distribution over the length and time scale of interest.

Example: 1st order rxn $A \rightarrow B$

$$Da = \frac{-r_{A0} V}{F_{A0}} \rightarrow \text{rxn rate at the entering at the beginning of that rxn}$$

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$$Da = \frac{-r_{A0} V}{F_{A0}} = \frac{-r_{A0}}{\frac{F_{A0}}{V}} = \frac{-r_{A0}}{\frac{V_0 C_{A0}}{\tau}} = \frac{-r_{A0}}{\frac{C_{A0}}{\tau}}$$

Exn Rate
diffusion rate

$$Da \approx 0.1 \rightarrow \approx 10$$

we assumed 1st order, $r_{A0} = -k_1 C_{A0}$

$$\therefore Da \approx \frac{k_1 C_{A0}}{\frac{C_{A0}}{\tau}} = \tau k_1$$

$\uparrow \tau$ time $\uparrow X$
 $\uparrow \tau$ increasing $\uparrow Da$
 $\times 10^{-4}$ small number
 so

* If k_1 is small, then increase $\tau \rightarrow \uparrow Da$
 BUT Less yield

* $\tau \uparrow$ yield $\downarrow$

$$k_n = A e^{-E_a/RT}$$

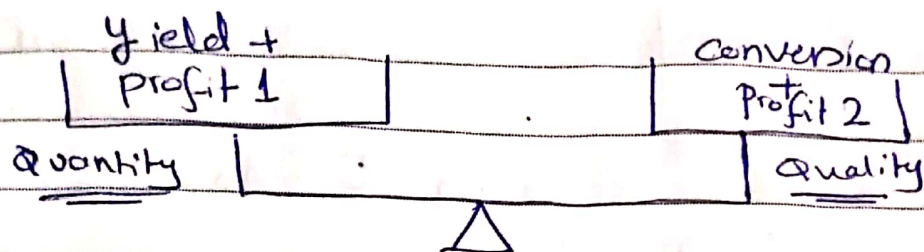
Activation energy
 Temp
 Ideal gas constant
 frequency constant

as $T \uparrow$ $(E_a/RT) \downarrow$ so $e^{-E_a/RT} \uparrow$

$\therefore k \uparrow$

* Operational Point of view:

first order: $Da_1 = \tau k_1$ to get large yield so, getting more profit
 BUT $Da \downarrow X \downarrow$ i so we need balance.

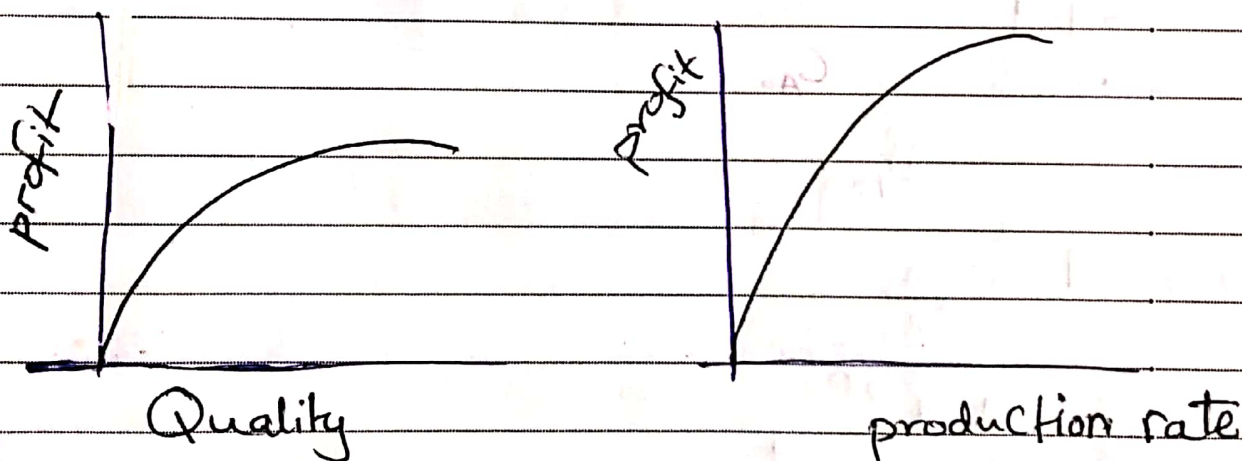


Profit 1 $\rightarrow$ mass production (Quantity) $\rightarrow$ bulk $\downarrow$
 Profit 2 $\rightarrow$ Quality $\uparrow \uparrow$

* activated carbon $\rightarrow$ water filtration $\rightarrow$ expensive: more porous $\uparrow$ active
 $\downarrow$ also using to store H_2 less - expense: less porous

* rxn $\rightarrow$ lectures $\rightarrow$ Da $\rightarrow$ make Da constant with specific conversion. with rxn order k_1 or k_2

$T??$
 $10\% = X \rightarrow T \downarrow \rightarrow$ bulk
 $\uparrow X \rightarrow \uparrow T \rightarrow$ product rate



1st order $Da = T k_1$

$Da: (0.1 - 9)$

$X: (0.1 - 0.9)$

CASE II : 2nd order

$$Da_2 = \frac{-r_{A0} V}{F_{A0}} = \frac{k_2 C_{A0}^2 V}{V_0 C_{A0}} = k_2 \tau C_{A0}$$

$$Da_2 = k_2 \tau \underline{\underline{C_{A0}}}$$

$$Da_1 = k_1 \tau \begin{matrix} \rightarrow \text{quality} \\ \rightarrow \text{quantity} \end{matrix}$$

to $\uparrow Da_2$ we have three choices: $k_2 \uparrow$
 $\tau \uparrow$
 $C_{A0} \uparrow$

* $\tau \downarrow$ more production rate $\uparrow C_{A0} \rightarrow$ desired Da

$$10 = k_2 \tau \underbrace{C_{A0}}_{\substack{?? \\ = 100}}$$

$$10 = 0.1 \frac{\tau}{C_{A0}} \underbrace{C_{A0}^2}_{\substack{? \\ = 50}}$$

conversion $\leftarrow \tau$ $\leftarrow$ C_{A0}

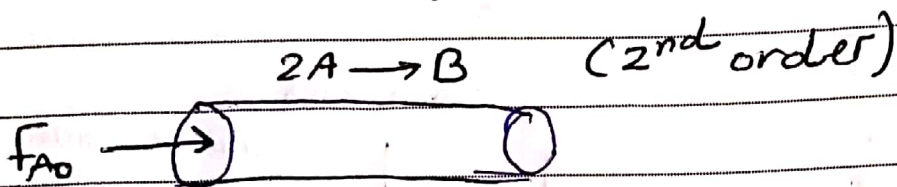
* Note : $\downarrow$ space time $\downarrow$ Conv.

$\uparrow$ high concentration at once = achieving desired Conversion
 or Fixed convr. $\tau \uparrow$ or $\downarrow$ C_{A0} for the 2nd order

$$\boxed{Da_n = k_n \tau C_{A0}^{n-1}} \quad \text{general relation for } Da \text{ number}$$

Example:

Consider the following second order rxn ^{no-changing in k} 2nd rxn,
 takes place in a tubular rxr at isothermal condition
 what will be the volume, space time, and conv.
 as a function of Damkohler no.



$2A \rightarrow B$

$$V = F_{A0} \int_0^x \frac{dx}{-r_A} \quad , \quad r_A = -k_2 C_A^2 \quad (\text{at the entrance})$$

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

$$V = F_{A0} \int_0^x \frac{dx}{k_2 C_{A0}^2 (1-x)^2} = \frac{F_{A0}}{k_2 C_{A0}^2} \left(\frac{x}{1-x} \right)$$

$$\boxed{F_{A0} = v_0 C_{A0}}$$

$$V = \frac{v_0 C_{A0}}{k_2 C_{A0}^2} \left(\frac{x}{1-x} \right)$$

$$V = \frac{v_0}{k_2 C_{A0}} \left(\frac{x}{1-x} \right) \quad , \quad \tau = \frac{V}{v_0} = \frac{1}{k_2 C_{A0}} \left(\frac{x}{1-x} \right)$$

Rearrange;

$$\boxed{x = \frac{\tau k_2 C_{A0}}{1 + \tau k_2 C_{A0}}} \quad \text{but} \quad \boxed{Da_2 = \tau k_2 C_{A0}}$$

$$X = \frac{Da_2}{1 + Da_2}$$

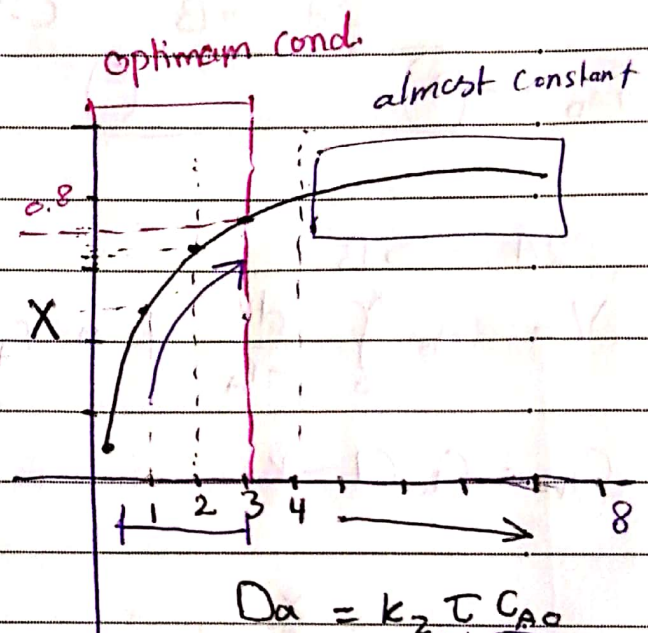
in tubular rxr.
for Second order

X → Can't make significant change x = $\frac{Da_2 \uparrow \downarrow}{1 + Da_2 \uparrow \downarrow}$
for x

* X → rxr rate of rxn ↓ with time → tubular rxr ✓

in tubular rxr $k = \frac{Da_2}{1 + Da_2}$

Da_2	X
0.1	0.09
1	0.5
2	0.66
3	0.75
4	0.8
5	0.83
6	0.85
7	0.87
8	0.88
9	0.9
10	0.91



$$Da = k_2 \tau \frac{C_{A0}}{C_A}$$

↑ production rate
↑ raw material

* not necessarily achieving high convr. by ↑↑ Da
= because of nature of rxr

not feasible ↑ Da → because little ↑ x

* Can we do that 1st PFR, 1st CSTR, 2nd CSTR??

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last time, CSTR, 2nd order

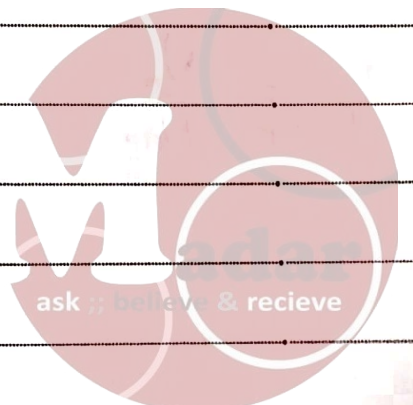
$$X = \frac{(1 + 2\tau k_2 C_{A0}) - \sqrt{1 + 4\tau k_2 C_{A0}}}{2\tau k_2 C_{A0}}$$

For 2nd order $Da_2 = \tau k_2 C_{A0}$, substitute.

$$X = \frac{(1 + 2Da_2) - \sqrt{1 + 4Da_2}}{2Da_2}$$

(plot Da vs x)
for 2nd order rxn
in CSTR

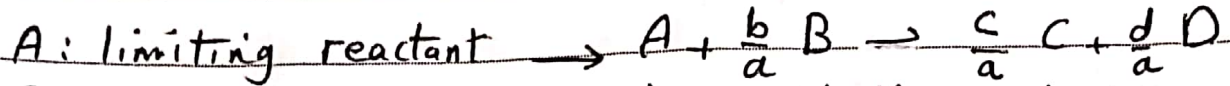
K



Rate laws & stoichiometry Nov, 25



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



For batch rxr: $N_A = N_{A0} - N_{A0}X = N_{A0}(1-X)$

number of moles

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

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

$$= N_{A0} \left(\frac{N_{B0}}{N_{A0}} - \frac{b}{a}X \right)$$

$$= N_{A0} \left(\theta_B - \frac{b}{a}X \right)$$

$$N_C = N_{C0} + \frac{c}{a}N_{A0}X = N_{A0} \left(\theta_C + \frac{c}{a}X \right)$$

$$\theta_B = \frac{N_{B0}}{N_{A0}}$$

$$N_D = N_{A0} \left(\theta_D + \frac{d}{a}X \right)$$

$$\theta_C = \frac{N_{C0}}{N_{A0}}$$

$$N_T = \left(N_{A0} + N_{B0} + N_{C0} + N_{D0} \right)$$

$$\theta_A = 1$$

$$+ \left(\frac{d}{a} + \frac{c}{a} + \frac{-b}{a} - 1 \right) N_{A0}X$$

in case $\rightarrow \theta_{Inert} = \frac{N_{I0}}{N_{A0}}$

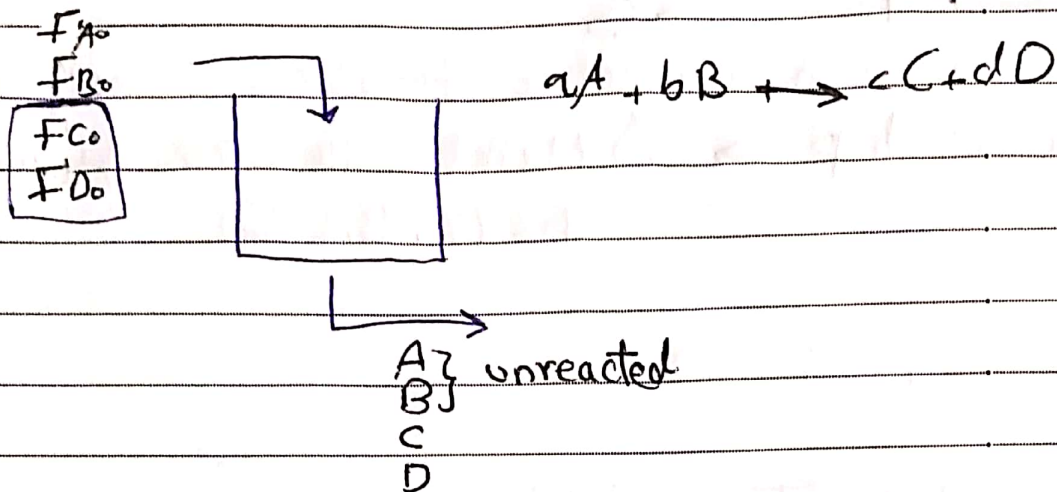
$$N_T = N_{T0} + \delta N_{A0}X$$

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

Nov 25

Flow system: $\begin{cases} \rightarrow \text{Incompressible} \\ \rightarrow \text{Compressible} \end{cases}$ flow

liquid flow ~~compressible~~



In case we have PFR



* Semibatch: material already inside the rxr

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

$$F_B = F_{A0}(\theta_B - \frac{b}{a}X)$$

$$F_C = F_{A0}(\theta_C + \frac{c}{a}X)$$

$$F_D = F_{A0}(\theta_D + \frac{d}{a}X)$$

$$F_I = F_{A0}(\theta_I + \text{zero})$$

$$F_T = F_{T0} + \delta F_{A0}X$$

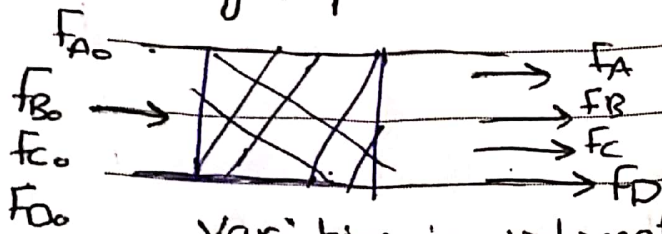
$$F_{T0} = F_{A0} + F_{B0} + F_{C0} + F_{D0}$$

$$= \sum_{i=1}^n F_{i0} = F_{A0}(1 + \theta_B + \theta_C + \theta_D)$$

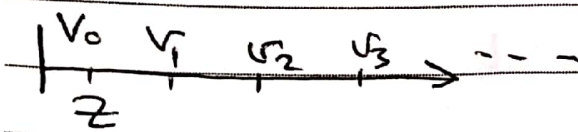
$$= F_{A0} \sum_{i=1}^n \theta_i$$

Compressible fluid:

gas phase rxn $\rightarrow$ compressed within the bed
 $\rightarrow \Delta P \rightarrow$ Pressure drop



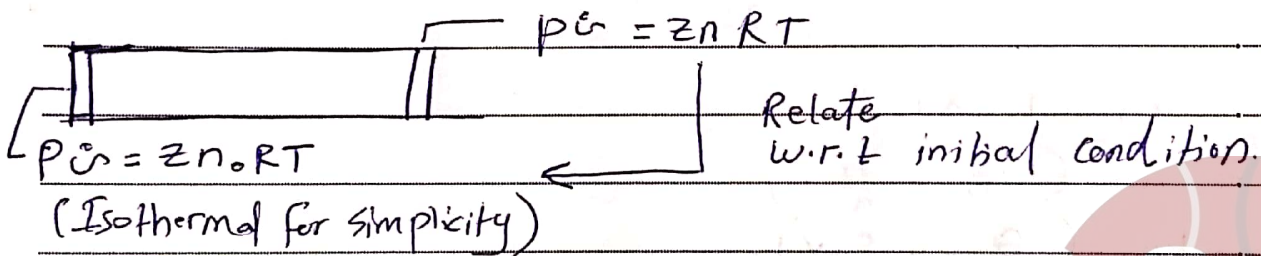
Variation in volumetric flow rate, ΔP is changed
 $\rightarrow$ pressure drop $\rightarrow$ Δ volumetric flowrates of that total gas (A, B, C, D)



$$PV = zn RT \quad \div \text{time}$$

$$P \dot{V} = z \dot{n} RT$$

to find molar flowrate, conc.



$$\text{So; } \frac{P \dot{V}}{P \dot{V}_0} = \frac{z n RT}{z_0 n_0 R T_0}$$

But:

$$N_T = N_{T_0} + \sum N_{A_0} X \div N_{T_0}$$

$$\frac{N_T}{N_{T_0}} = 1 + \sum \frac{N_{A_0}}{N_{T_0}} X = 1 + \sum y_{A_0} X \quad \text{mole fraction}$$

let $\varepsilon = \frac{\text{change in } N_T \text{ for complete conversion}}{\text{Total } N_T \text{ fed to the Rxx}}$

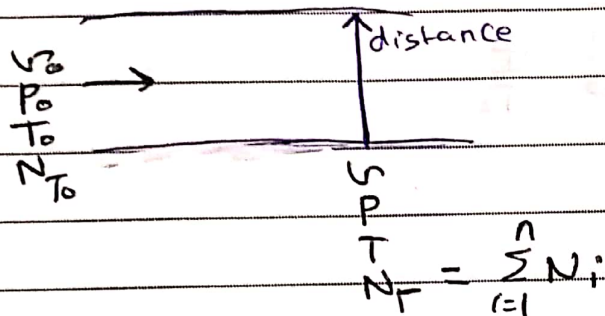
$$\epsilon = \sum y_{A_0} = \left(\frac{d}{a} + \frac{c}{a} + -\frac{b}{a} - 1 \right) \frac{N_{A_0}}{N_T}$$

back to compressible case

$$\frac{P v}{P_0 v_0} = \frac{z \cancel{N_T} R T}{z_0 \cancel{N_T} R T} \quad \text{or } n \quad \text{But} \quad \frac{N_T}{N_{T_0}} = 1 + \sum y_{A_0} X$$

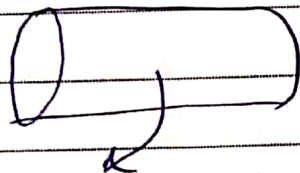
$$v = v_0 \frac{P_0}{P} \frac{T}{T_0} (1 + \epsilon X)$$

↓
volumetric flowrate of Reactant and product initially
↓
volumetric flowrate at any distance within the rxr
↓
for Reactants and product



$$v = v_0 \frac{P_0}{P} \frac{T}{T_0} (1 + \epsilon X) \quad y_{A_0} \delta$$

v fn of distance



$$X = f(z)$$

$$v = f(X)$$

$$= J(z)$$

$$C_T = \frac{F_T}{V} \text{ at any given time or distance}$$

$$C_{T_0} = \frac{F_{T_0}}{V_0} = \frac{P_0}{Z_0 R T_0} \quad \boxed{P V_0 = Z_0 R T_0}$$

$$\frac{C_T}{C_{T_0}} = \frac{F_T / V}{F_{T_0} / V_0} = \frac{P / Z R T}{P_0 / Z_0 R T_0}$$

$$V = V_0 \frac{N_T}{N_{T_0}} \frac{P_0}{P} \frac{T}{T_0} = (1 + \epsilon X) \frac{P_0}{P} \frac{T}{T_0} = \frac{V_0 F_T P_0 T}{F_{T_0} P T_0}$$

$$F_T = F_{T_0} + F_{A_0} \delta X$$

$$V = V_0 \frac{F_{T_0} + F_{A_0} \delta X}{F_{T_0}} \frac{P_0}{P} \frac{T}{T_0}$$

$$V = V_0 \left(1 + \frac{F_{A_0}}{F_{T_0}} \delta X \right) \frac{P_0}{P} \frac{T}{T_0}$$

For conc

$$C_j = \frac{F_j}{V} = C_{T_0} \frac{F_{A_0} (\Theta_j + U_j X)}{F_{T_0} + F_{A_0} \delta X} \frac{P}{P_0} \frac{T_0}{T}$$

$$= C_{T_0} \frac{F_{A_0} (\Theta_j + U_j X)}{F_{T_0} \left(1 + \frac{F_{A_0} \delta X}{F_{T_0}} \right)} \frac{P}{P_0} \frac{T_0}{T}$$

$N_T \rightarrow$ no flow

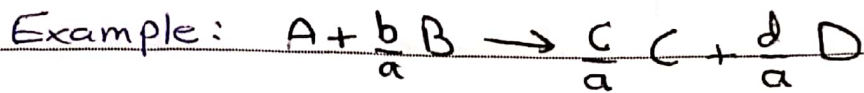
$F_T \rightarrow$ flow / per time

$$= C_T \frac{F_{A_0} (\Theta_j + U_j X)}{F_{T_0} \left(1 + \frac{F_{A_0} \delta X}{F_{T_0}} \right)} \frac{P}{P_0} \frac{T_0}{T}$$

Now $\frac{F_{A_0}}{F_{T_0}} = y_{A_0}$ -ve rxnt
+ve product

$$C_j = \frac{y_{A_0} C_{A_0} (\Theta_j + U_j X)}{y_{A_0} (1 + y_{A_0} \delta X) P_0 T} \quad \boxed{C_{A_0} = y_{A_0} C_{T_0}} \quad \boxed{F_{A_0} = y_{A_0} F_{T_0}}$$

$$C_j = C_{A0} \frac{(\theta_j + \nu_j X)}{(1 + \epsilon X)} \frac{P}{P_0} \frac{T_0}{T}$$



$$C_A = C_{A0} \frac{(1 - X)}{(1 + \epsilon X)} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{A0} \frac{(\theta_B - b/a X)}{(1 + \epsilon X)} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_C = C_{A0} \frac{(\theta_C + c/a X)}{(1 + \epsilon X)} \frac{P}{P_0} \frac{T_0}{T}$$

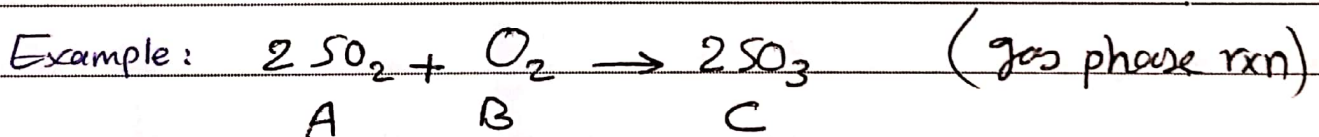
⋮

$$C_T = F_T/P$$

Notes:

$$\begin{aligned} \nu_A &= -1 \\ \nu_B &= -b/a \\ \nu_C &= c/a \\ \nu_D &= d/a \end{aligned}$$

$$\begin{aligned} \theta_A &= 1 \\ \theta_B &= \frac{C_{B0}}{C_{A0}} = \frac{F_{B0}}{F_{A0}} \\ \theta_C &= \frac{C_{C0}}{C_{A0}} = \frac{F_{C0}}{F_{A0}} \\ \theta_D &= \frac{C_{D0}}{C_{A0}} = \frac{F_{D0}}{F_{A0}} \end{aligned}$$



initially

28% SO_2 + 72% Air, $P_T = 1485 \text{ kPa}$, $T = 227^\circ \text{C}$

Soln: $F_{A0} = 0.28 F_{T0}$ (SO_2)

$F_{B0} = (0.72)(0.21)(F_{T0})$ (O_2)

$\theta_B = F_{O_2}^0 / F_{SO_2}^0 = \frac{(0.72)(0.21) F_{T0}}{0.28 F_{T0}} = 0.54$

we do have inert N_2

$$\Theta_I^\circ = f_I^\circ / f_A^\circ = \frac{(0.72)(0.79)}{0.28} = 2.03$$

$$F_A = f_{A0} (1 - X)$$

$$F_B = f_{A0} (\Theta_B - \frac{1}{2} X)$$

$$F_C = f_{A0} (\Theta_C + X)$$

$$f_I = f_{A0} (\Theta_I)$$

$$F_T = F_{T0} - \frac{F_{A0}}{2} X$$

$$C_A = \frac{f_{A0} (1 - X)}{v_0 (1 + \epsilon X)} = C_{A0} \frac{(1 - X)}{(1 + \epsilon X)}$$

Assume for simplicity $P = P_0$ $T = T_0$

$$C_{A0} = y_{A0} C_{T0} = y_{A0} \frac{P_0}{RT_0} = (0.28) \frac{1485 \text{ kPa}}{8.314 (\text{KPa} \cdot \text{L} / \text{mol} \cdot \text{K}) * 500 \text{ K}}$$
$$= 0.1 \frac{\text{mol}}{\text{L}}$$

$$C_T = \frac{F_T}{v} = \frac{F_{T0} + y_{A0} \delta X F_{A0}}{v_0 (1 + \epsilon X)} = \frac{F_{T0} (1 + \epsilon X)}{v_0 (1 + \epsilon X)} = \frac{F_{T0}}{v_0}$$

$$C_{T0} = \frac{P_0}{RT_0} = \frac{1485}{8.314 * 500} = 0.357 \frac{\text{mol}}{\text{L}}$$

why $C_T = C_{T0}$: Because P constant, T constant
at given distance given
No rxn happens in this case



25 Nov

$$\varepsilon = y_{A0} \delta = 0.28 \left(1 - \frac{1}{2} - 1\right) = -0.14$$

$$C_A = \frac{0.1(1-x)}{1-0.14x}$$

$$C_B = \frac{0.1(0.54 - 0.5x)}{1-0.14x}$$

$$C_C = \frac{0.1(x)}{1-0.14x}$$

$$C_I = \frac{0.1(2.03)}{1-0.14x}$$

ex @ $x=0$

$$C_A = 0.1$$

$$C_B = 0.054$$

$$C_C = 0$$

$$C_I = 0.203$$

$$C_T = 0.357$$

ex @ $x=0.78$

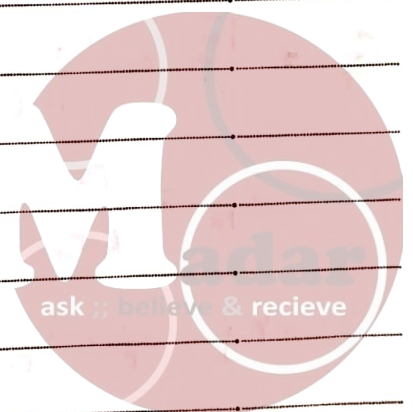
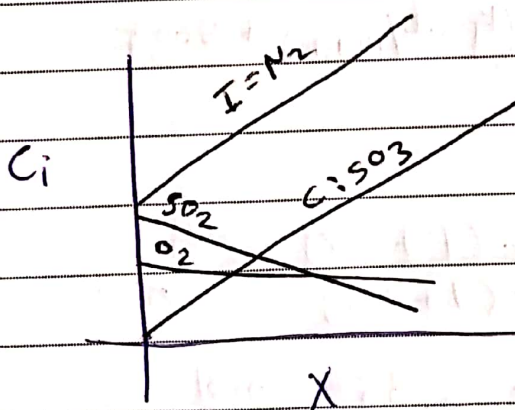
$$C_A = 0.025$$

$$C_B = 0.017$$

$$C_C = 0.0875$$

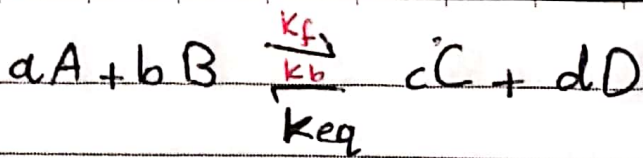
$$C_I = 0.2278 \approx 0.228$$

$$C_T = 0.357$$

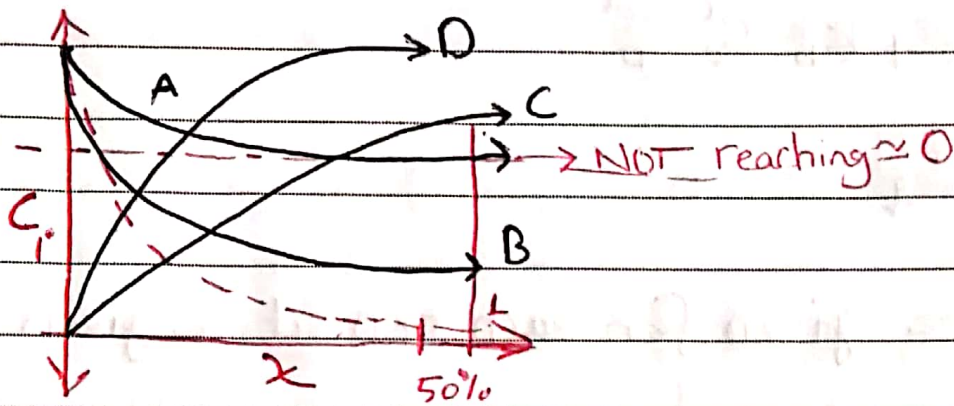


Equilibrium Conversion

2nd Dec



$$K_{eq} = \frac{k_{forward}}{k_{backward}}$$

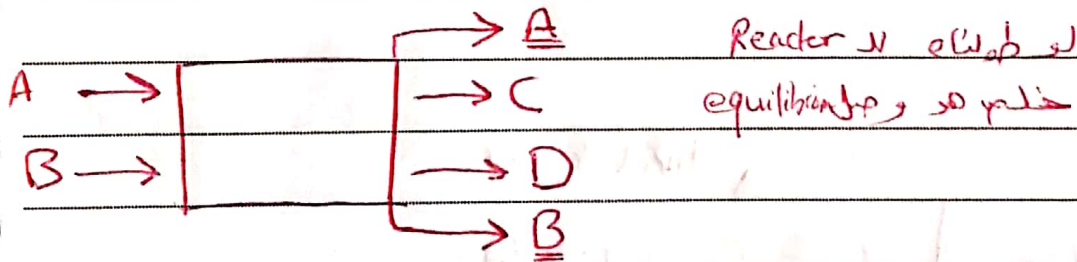


if I have r_1 $x_{eq} = 0.5$

r_2 $x_{eq} = 0.78$

maximum that can be achieved

there are
 x x_{eq}



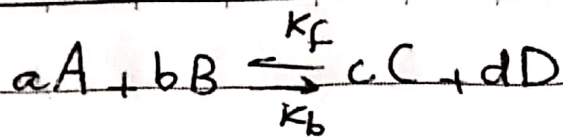
conversion x_e ← max achieved conversion at equilibrium

* Conversion $x_{eq} \hat{=} \frac{K_{eq}}{1 + K_{eq}} = A e^{-G/RT}$

$$x \leq x_e$$

one required

Vibration $\hat{=} \frac{1}{2} \rho \omega^2 r^2$

2nd Dec

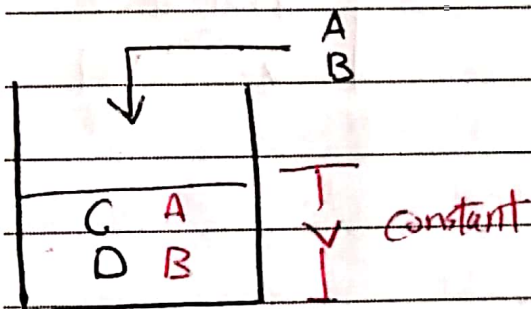
$$r = -k_f C_A^a C_B^b + k_b C_C^c C_D^d$$

@ eq $r = 0$

$$0 = -k_f C_A^a C_B^b + k_b C_C^c C_D^d$$

$$\frac{k_f}{k_b} = \frac{C_C^c C_D^d}{C_A^a C_B^b} = K_{eq}$$

Values of K_{eq} are given for each rxn at a given condition (T, P).



batch rxr

$$X = X_{eq}$$

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

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

$$N_B = N_{A0} \left(\theta_B - \frac{b}{a} X \right)$$

$$C_B = C_{A0} \left(\theta_B - \frac{b}{a} X \right)$$

$$N_C = N_{A0} \left(\theta_C + \frac{c}{a} X \right)$$

$$C_C = C_{A0} \left(\theta_C + \frac{c}{a} X \right)$$

$$N_D = N_{A0} \left(\theta_D + \frac{d}{a} X \right)$$

$$C_D = C_{A0} \left(\theta_D + \frac{d}{a} X \right)$$

@ equilibria Substitute the concentration $\rightarrow k_{eq}$

$$K_{eq} = \frac{C_C^c C_D^d}{C_A^a C_B^b} = \frac{C_{A0}^c (\theta_C + \frac{c}{a} X_e)^c C_{A0}^d (\theta_D + \frac{d}{a} X_e)^d}{C_{A0}^a (1-X)^a C_{A0}^b (\theta_B - \frac{b}{a} X_e)^b}$$

Sometimes, $C_C^o = C_D^o = 0$, $\theta_C = \theta_D = 0$

$$K_{eq} = \frac{C_{A0}^{c+d} (\frac{c}{a} X_{eq})^c (\frac{d}{a} X_{eq})^d}{C_{A0}^{a+b} (1-X_{eq})^a (\theta_B - \frac{b}{a} X_{eq})^b}$$

$$K_{eq} = \frac{C_{A0}^{c+d-a-b} (\frac{c}{a})^c (\frac{d}{a})^d X_{eq}^{c+d}}{(1-X_{eq})^a (\theta_B - \frac{b}{a} X_{eq})^b} \rightarrow X_{eq}$$

For any rxn is applicable.

For example:

$$V_{CSTR} = \frac{F_{A0} X}{-r_A}$$

$$V_{eq, CSTR} = \frac{F_{A0} X_{eq}}{+k_f C_A^a C_B^b - k_b C_C^c C_D^d}$$

$$= \frac{F_{A0} X_{eq}}{k_f [C_{A0} (1-X_{eq})]^a [C_{A0} (\theta_B - \frac{b}{a} X_{eq})]^b - k_b [C_{A0} (\theta_C + \frac{c}{a} X_{eq})]^c +$$

$$[C_{A0} (\theta_D + \frac{d}{a} X_{eq})]^d]$$

max. conversion
can be
achieved for
that eq. rxn

ask : balay & recieve

* example (3-8) ch 3, 3rd ed, voglar

example:

The reversible gas-phase decomposition of nitrogen tetroxide, N_2O_4 to nitrogen dioxide NO_2

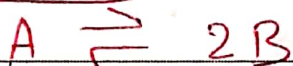


is to be carried out at constant temperature and pressure. the feed consists of pure N_2O_4 at 340 K. The concentration equilibrium constant at 340 K is $0.1 \frac{mol}{dm^3}$

K_c

Calculate the equilibrium conversion of N_2O_4 in a constant-volume batch rxr and in a flow rxr.?

* Soln:



Batch Reactor

species	symbol	initial	change	Remaining
N_2O_4	A	N_{A0}	$-N_{A0}X$	$N_A = N_{A0}(1-X)$
NO_2	B	0	$+2N_{A0}X$	$N_B = 2N_{A0}(X)$ $\downarrow$ $\left(\frac{b}{a}\right)$

$$\frac{N}{T} = \frac{N}{T_0} + N_{A0}X$$

$$\begin{aligned} \frac{N}{T} &= N_{A0} - N_{A0}X + 2N_{A0}X \\ &= N_{A0} + N_{A0}X \end{aligned}$$

pure N_2O_4 , so
 $N_{T0} = N_{A0}$

2nd Dec

$$C_i = N_i / V_i \quad \text{and } V \rightarrow \text{constant}$$

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

$$C_B = C_{A0} + 2X \quad (+)$$

$$C_T = C_{A0}(1 + X)$$

But $C_{A0} = \frac{y_{A0} P_0}{RT_0} = \frac{(1) (2 \text{ atm})}{\left(\frac{0.082 \text{ atm} \cdot \text{L}}{\text{gmol} \cdot \text{K}} \times 340 \text{ K} \right)}$

$$= 0.0717 \frac{\text{mol}}{\text{L}}$$

BUT in kPa units

$$C_{A0} = \frac{(1) (202.6 \text{ kPa})}{\left(8.314 \frac{\text{kPa} \cdot \text{L}}{\text{gmol} \cdot \text{K}} \right) (340 \text{ K})} = 0.0717 \frac{\text{mol}}{\text{L}}$$

$$K_c = \frac{(C_{B \text{ eq}})^2}{(C_{A \text{ eq}})^1} = \frac{(2 C_{A0} X_{\text{eq}})^2}{(C_{A0} (1 - X_{\text{eq}}))^1} = \frac{4 C_{A0} X_{\text{eq}}^2}{(1 - X_{\text{eq}})}$$

$$0.1 = \frac{4 \times 0.0717 \times X_{\text{eq}}^2}{1 - X_{\text{eq}}} \quad (\text{Quadratic eq.})$$

$$X_{\text{eq}} = 0.441 \quad \left(\begin{array}{l} \text{في مفاعل تدفق مستمر} \\ \text{DESIGN} \end{array} \right)$$

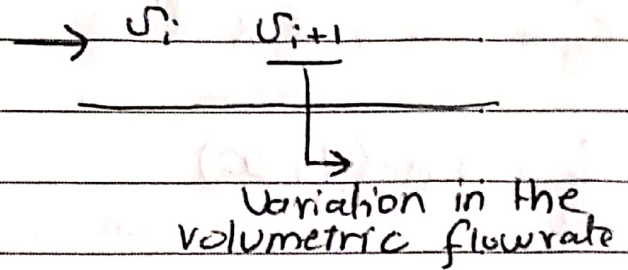
there is another root = -0.79 : negligible

2nd Dec

* Case II :

Flow Rxr:

Soln:



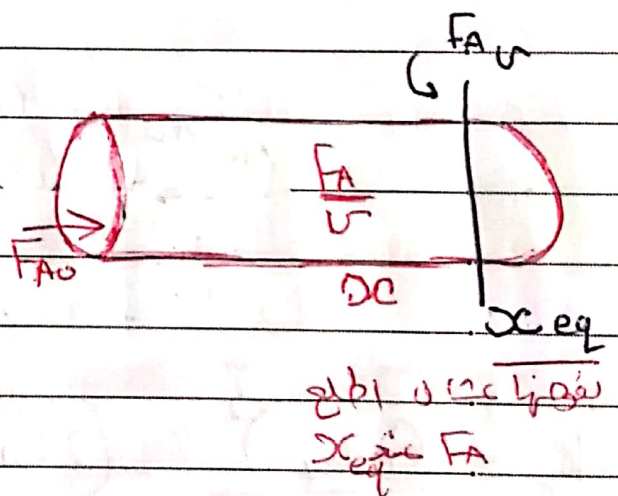
$$v = v_0 (1 + \epsilon X)$$

$$\epsilon = y_{A0} \delta$$

$$\delta = 2 - 1 = 1$$

$$\therefore \epsilon = (1)(1) = 1$$

$$\begin{aligned} C_A = \frac{F_A}{v} &= \frac{F_{A0} (1 - x)}{v} \\ &= \frac{F_{A0} (1 - x)}{v_0 (1 + \epsilon X)} \\ &= \frac{C_{A0} (1 - x)}{1 + \epsilon X} \\ &\quad | = 1 \end{aligned}$$



$$C_A @ \text{equilibra} = C_{A0} \frac{(1 - x_{eq})}{(1 + x_{eq})}$$

$$C_{B_{eq}} = \frac{2 C_{A0} x_{eq}}{1 + x_{eq}}$$

$$[B = 0] \quad [\epsilon = 1]$$

$$K_c = \frac{C_{Be}^2}{C_A} = \frac{\left[2C_{A0} x_{eq} / (1+x_{eq}) \right]^2}{C_{A0} [(1-x_{eq}) / (1+x_{eq})]}$$

$$= \frac{4 C_{A0} x_{eq}^2}{(1-x_{eq})(1+x_{eq})} = 0.1$$

$$= \frac{4 \cdot 0.0717 x_{eq}^2}{(1-x_{eq})(1+x_{eq})} = 0.1$$

check poly math

$$x_{eq} = 0.509 \approx 0.51$$



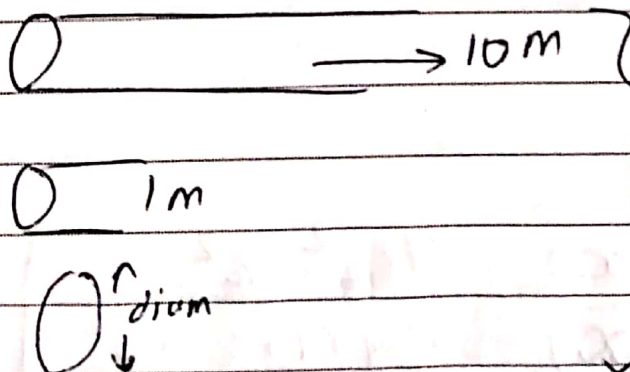
pressure drop → shift the equilibrium rxn

(batch NO pressure drop) so reactant's Partial Pressure ↓↓↓, Partial pressure of the product ↑↑↑

∴ Total Pressure based on difference = Pressure drop



Δ volumetric flowrate

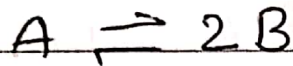


any flow system
the same $x_{eq} = 0.51$

ask : bal & recieve

2nd Dec

* What will be rate of Rvn in a batch Vs flow systems !!



$$r_A = -k_f C_A + k_b C_B^2$$

In Batch Reactor: $-r_A = k_f \left[C_A - \frac{C_B^2}{K_{eq}} \right]$

$$-r_{A_{eq}} = k_f \left[C_{A0} (1 - x_{eq}) - \frac{4 C_{A0}^2 x_{eq}^2}{K_{eq}} \right]$$

In flow system: $-r_A = k_f \left[C_A - \frac{C_B^2}{K_{eq}} \right]$

$$= k_f \left[\frac{C_{A0} (1 - x_{eq})}{(1 + \epsilon x_{eq})} - \frac{4 C_{A0}^2 x_{eq}^2}{K_{eq} (1 + \epsilon x_{eq})^2} \right]$$

* Determine V_{STR} to achieve 80% of equili. conversion.

if $F_A = 3 \frac{\text{mol}}{\text{min}}$, $K_f = 0.5/\text{min}$.

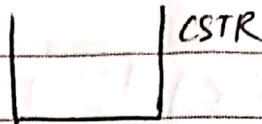
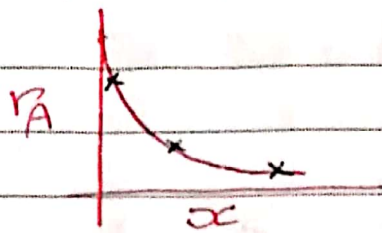
Soln:

$$x = 0.8 x_{eq}$$

$$-r_A = k_f \left[\frac{C_{A0} (1 - x)}{(1 + \epsilon x)} - \frac{4 C_{A0}^2 x^2}{K_{eq} (1 + \epsilon x)^2} \right]$$

General Rate

2nd Dec



CSTR

$0.0712 \approx 0.72$

general eq CSTR: $-r_A = 0.5 \left[\frac{0.072(1-x_e) - 4(0.072)^2 x_e^2}{(1+x_e) \cdot 0.1(1+x_e)^2} \right]$

$-r_A = 0.036 \left[\frac{1-x_e}{1+x_e} - \frac{2.88 x_{eq}^2}{(1+x_{eq})^2} \right]$ (x)

$x_{eq} \text{ for flow system} = 0.51$

$x = 0.8 * x_{eq}$
 $= 0.8 * 0.51$
 $= 0.408 \approx 0.41$

$V = \frac{F_{A0} x}{-r_A|_x} = \frac{3 \left(\frac{\text{mol}}{\text{min}} \right) x}{-r_A|_x}$ (x) ← 0.41

Substitute for above equation $(-r_A)$ (x)

@ $x = 0.41$, $-r_A = 0.00629 \approx 0.0063 \frac{\text{mol}}{\text{L} \cdot \text{min}}$

$V_{@x=0.41} = \frac{3 * 0.41}{0.00629} = 195.32 \text{ L}$ 512

$\uparrow x \uparrow V \propto x_{eq} \rightarrow 1 x_{eq} \approx 44\%$

Now what will be $V @ x_{eq}$ → Rate of rxn @ $x = eq$

x must be fraction of x_{eq}

$\uparrow x$ $\uparrow$ volume $\rightarrow$ flow reactor is better for eq. rxn
 $\downarrow$ approach x_{eq}

2.97×10^3
 2.63×10^3

Dec 9

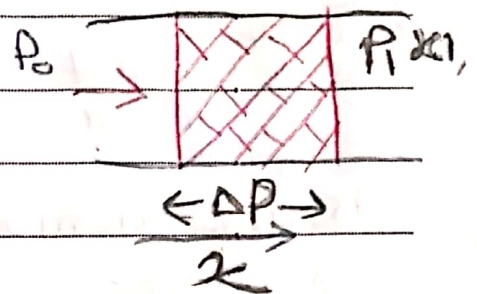
For Isothermal Rxr design $T = T_0$

For Isothermal Rxr design $C_i = C_{A_0} \left(\frac{\theta_i + \nu_i x}{1 + \epsilon x} \right) \frac{P}{P_0}$

variables ↓
 $\theta_i = \frac{C_{A_0}}{C_{A_0} - C_{A_i}}$
 $\nu_i = \frac{C_{A_0}}{C_{A_0} - C_{A_i}}$

Design of PFR (Isothermal), [Packed bed]

$$F_{A_0} \frac{dx}{dw} = -r_A^*$$

Assume $2A \rightarrow B$

$$r_A = -k C_A^2$$

$$r_A^* = -k \left[\frac{C_{A_0} (1-x)}{(1+\epsilon x)} \frac{P}{P_0} \frac{T_0}{T} \right]^2$$

$$F_{A_0} \frac{dx}{dw} = k \left[\frac{C_{A_0} (1-x)}{(1+\epsilon x)} \frac{P}{P_0} \right]^2 \Rightarrow F(x, P) \rightarrow \text{Can't solve alone}$$

Ergun equation:

$$\frac{dP}{dz} = - \frac{G}{\rho_g D_p} \left(\frac{1-\phi}{\phi^3} \right) \left[\frac{150 (1-\phi) \mu}{D_p} + 1.75 G \right]$$

superficial velocity
 void

$$G: \text{Superficial velocity} = \rho u = \left[\frac{g}{m^2 \cdot s} \right]$$

$$g: \frac{32.174 \text{ lbm} \cdot \text{ft}}{\text{s}^2 \cdot \text{lb}_f}$$

surface of catalyst

$$\phi: \text{porosity} = \frac{\text{void volume}}{\text{Total bed vol}}$$

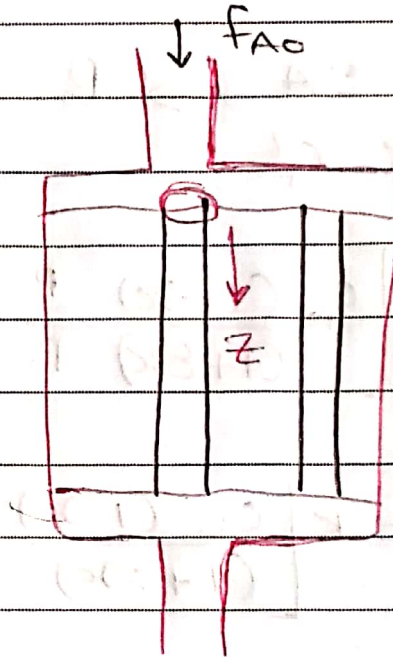
μ : viscosity $\rightarrow$ fluid that passing (Reactant product)
 D_p : particle diameter

$G = \rho u \rightarrow u = \frac{\text{volumetric flow rate}}{\text{cross-sectional area of rxr (pipe)}}$
 indirect related to cross section of that reactor
 tube diameter is πd

Assume number of tubes
 $N = 500$

$$u_{\text{tube}} = U_T / N$$

Assume A_o per tube



$$u = \frac{u_{\text{tube}}}{A_o \text{ tube}}$$

$$G = \rho u$$

μ ✓

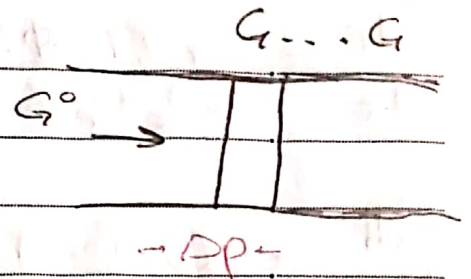
ϕ = each catalyst has its voidage
 $[0.25 \rightarrow 0.55] \approx 0.45$

(given)

$$D_p = \checkmark$$

$\frac{dP}{dz}$ is a fn of G

$$G = G(z) \approx G(w)$$



back to design equation:

$$\frac{dx}{dw} = K \left[\frac{C}{A^*} \frac{(1-x)}{(1+\epsilon x)} \frac{P}{P_0} \right]^2$$

$$\frac{dP}{dz} = \text{Ergun equation} = f(G)$$

Two dependant variable (x, P)

Two independent variable (w, z)

Two equations.

Dof = 1!

$$(w \stackrel{?}{=} z)$$

two equation $\rightarrow$ 2 independent 1 dependent

$z \rightarrow w$ or $w \rightarrow z \rightarrow 2$ eq.

x, P w) fxn - f w or z

To do that as follow:

$$m = \dot{m}_0, \quad \underset{\substack{\uparrow \\ \text{constant} \\ \text{initially}}}{P_0} \underset{\substack{\downarrow \\ \text{variable}}}{U} = P U$$

$$\frac{U}{U_0} = \frac{P_0}{P} \frac{T}{T_0} \frac{F}{F_0} \quad \left[\frac{U}{U_0} = \frac{P_0}{P} \frac{T}{T_0} \frac{F}{F_0} \right]$$

$$\text{at any distance} \quad P = \frac{P_0 U_0}{U} = P_0 \frac{P}{P_0} \frac{T_0}{T} \frac{F_0}{F}$$

$$\frac{dp}{dz} = - \frac{G (1-\phi)}{\rho_0 g_c D_p \phi^3} \left[\frac{150 (1-\phi) \mu}{D_p} + 1.75 G \right] \frac{p_0}{p} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$\frac{dp}{dz} = - \beta \frac{p_0}{p} \frac{T}{T_0} \frac{F_T}{F_{T0}} \Rightarrow f(p, x, T) \quad \text{--- } \textcircled{*}$$

$$F_T = F(x)$$

$$w = (1-\phi) A_c z \times \rho_c$$

$\uparrow$ weight of catalyst
 $\underbrace{(1-\phi) A_c z}_{\text{solid vol.}} \times \underbrace{\rho_c}_{\text{density of catalyst}}$
 $\phi A_c z$: void volume
 z : length of tube

$$V_s (\text{solid volume}) = V_b (1-\phi)$$

$\downarrow$ bulk volume
 $(1-\phi)$ fraction of solid into that bed

$$\frac{1}{V_b} = \frac{1}{V_s} (1-\phi)$$

$$\frac{m_s \text{ mass of solid}}{V_b} = \frac{m_s \text{ mass of solid}}{V_s} (1-\phi)$$

$$\rho_b = \rho_c (1-\phi)$$

$\frac{m_s}{V_b}$
 mass of solid / volume of bulk

$$dw = (1-\phi) A_c \rho_c dz \quad \text{derivative of } \textcircled{*} \textcircled{*}$$

$$\frac{dp}{dz} = - \rho_0 \left(\frac{p_0}{p} \right) \left(\frac{T}{T_0} \right) \left(\frac{F_T}{F_{T0}} \right)$$

$$\frac{dp}{dz} = \frac{dw}{(1-\phi) A_c \rho_c}$$

Substitute in

ask, solve & relieve

$$\frac{dP}{dw/(1-\phi)A_c \rho_c} = -\beta_0 \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$\frac{dP}{dw} = \frac{-\beta_0}{A_c (1-\phi) \rho_c} \frac{P_0}{P} \frac{T}{T_0} \frac{F_T}{F_{T0}}$$

$$= -\frac{\alpha}{2} \frac{T}{T_0} \frac{P_0}{(P/P_0)} \frac{F_T}{F_{T0}} ; \boxed{\alpha = \frac{2\beta_0}{A_c \rho_c (1-\phi) P_0}}$$

rationale b.c.

$$F_T = F_{T0} + \frac{F_T}{T_0} \delta T = \frac{F_T}{T_0} \left(1 + \frac{F_{T0}}{F_T} \delta T \right)$$

$$= F_{T0} \left(1 + y_{A0} \delta x \right) = \frac{F_T}{T_0} (1 + \epsilon x)$$

$$\frac{F_T}{F_{T0}} = \frac{F_{T0} (1 + \epsilon x)}{F_{T0}} = (1 + \epsilon x)$$

= 1 isothermal

$$\frac{dP}{dw} = \frac{-\alpha}{2} \frac{T}{T_0} \frac{P_0}{P} \frac{P_0}{(P/P_0)} (1 + \epsilon x) \rightarrow F(P, T, x)$$

To solve this equation;

Assume $1 \gg \epsilon x$

$$\frac{dP}{dw} = \frac{-\alpha}{2} \frac{P_0}{(P/P_0)} (1 + \epsilon x)$$

$$\epsilon = y_{A0} \delta = y_0 (1 - 1)$$

Fraction (-1/2)

Fraction

$$\text{ex: } 0.1 \times 0.1 = 0.01$$

$$1 \gg 0.01$$

Then:

$$\frac{dP}{dw} = \frac{-\alpha P_0}{2(P/P_0)} \rightarrow 2 \frac{P}{P_0} \frac{dP}{P_0} \bigg|_{P_0} = -\alpha \frac{P_0}{P_0} dw \bigg|_{P_0}$$

ask : & recieve

$$P = P_0(1 - \alpha w)^{1/2} \rightarrow \frac{P}{P_0} = \left(1 - \frac{2B_0 z}{P_0}\right)^{1/2}$$

$$\frac{P}{P_0} = (1 - \alpha w)^{1/2}$$

design equation

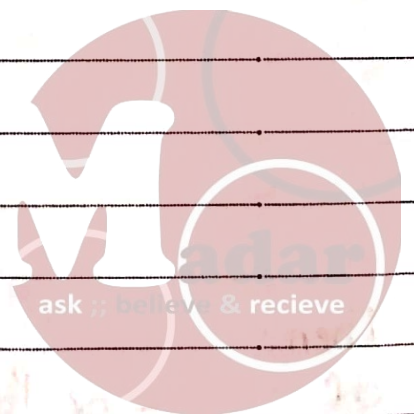
$$\frac{dx}{dw} = K \left[\frac{CA_0 (1-x)^2}{(1+\epsilon x)} \right] \left[\frac{P}{P_0} \right]^2$$

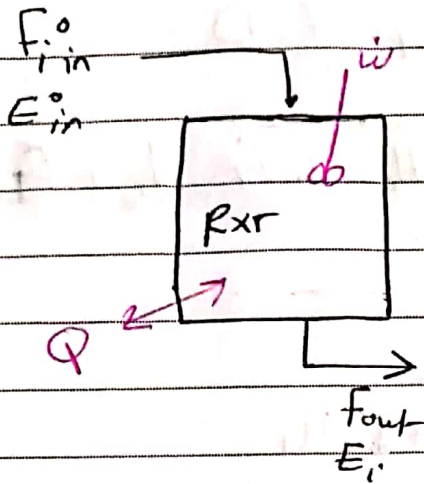
$$\frac{dx}{dw} = K \left[\frac{CA_0 (1-x)^2}{(1+\epsilon x)} \right] (1 - \alpha w)$$

$$\frac{dx}{\left[\frac{(1-x)^2}{(1+\epsilon x)} \right]^2} = \int K C_{A_0}^2 (1 - \alpha w) dw$$

$$x = f(w)$$

$$P = f(w)$$





Energy Balance ... the rxr

Energy IN - Energy out + Energy added - ^{shaft} work done = Rate of accumulation

(Flow work + work of stirrer)

$$F_i^0 E_i^0 - F_i E_i + \dot{Q} - \dot{w} = \frac{dE_{sys}}{dt}$$

$\dot{w}$ = flow work + shaft work

$$= - \sum F_i P V_i + F_i^0 P V_o + \dot{w}_s$$

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{w}_s + \sum F_i (E_i + P V_i) - \sum F_i^0 (E_i^0 + P V_i^0)$$

$$E_i = \underbrace{U_i}_{\text{internal}} + \underbrace{\frac{V_i^2}{2}}_{\text{kinetic}} + \underbrace{g z_i}_{\text{potential}} + \underbrace{h_L}_{\text{friction loss}}$$

negligible (flow under st. st condition)

$$E_i \approx U_i$$

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{w}_s + \sum_{in} F_i (U_i + P V_i) - \sum_{out} (U_i + P V_i) F_i$$

$$H_i = U_i + P V_i$$

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{w}_s + \sum_{in} F_i H_i - \sum_{out} F_i H_i$$

$$\frac{dE_{sys}}{dt} = \sum_{i=1}^n F_{i0} H_{i0} - \sum_{i=1}^n F_i H_i + \dot{Q} - \dot{w}_s$$

ask : balance & relieve

0 for steady state system

Consider $A + \frac{b}{a} B \rightarrow \frac{c}{a} C + \frac{d}{a} D$
 Species $\rightarrow$ $+ I$ (inert)

$$\sum_{i=1}^n H_i^\circ F_i^\circ = F_A H_{A^\circ} + F_B H_{B^\circ} + F_C H_{C^\circ} + F_D H_{D^\circ} + F_I H_{I^\circ}$$

out let (liquid phase)

$$\begin{aligned} \sum_{i=1}^n F_i H_i &= F_A H_A + F_B H_B + F_C H_C + F_D H_D + F_I H_I \\ &= F_{A_0} (1-x) H_A + F_{A_0} (\theta_B - \frac{b}{a} x) H_B + F_{A_0} (\theta_C + \frac{c}{a} x) H_C \\ &\quad F_{A_0} (\theta_D + \frac{d}{a} x) H_D + F_{A_0} (\theta_I + \phi) \end{aligned}$$

$$\sum F_{i_0} H_{i_0} - \sum F_i H_i = F_{A_0} \left[\underbrace{(H_{A_0} - H_A)}_{\text{reactant}} + \underbrace{(H_{B_0} - H_B) \theta_B}_{\text{reactant}} + \underbrace{(H_{C_0} - H_C) \theta_C}_{\text{product}} + \underbrace{(H_{D_0} - H_D) \theta_D}_{\text{product}} + \underbrace{(\theta_I + \phi)}_{\text{inert}} \right]$$

exist Temp

$$- \left(\frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A \right) F_{A_0} x$$

$$\Delta H_R(T) = \frac{d}{a} H_D(T) + \frac{c}{a} H_C(T) - \frac{b}{a} H_B(T) - H_A(T)$$

Heat of rxn.

$$\sum F_{i_0} H_{i_0} - \sum F_i H_i = F_{A_0} \sum_{i=1}^n (H_{i_0} - H_i) \theta_i - \Delta H_R(T) F_{A_0} x + \dot{Q} - \dot{W}_s$$

gas phase
 $H_i(T) = H_i^\circ(T_R) + \int_{T_R}^T C_{p,i} dT$

gas phase change as fcn of T

$$C_{p,i}(T) = \alpha + \beta T + \gamma T^2$$

$$C_{p_i}(T) \sim \text{constant}$$

$$H_i - H_{i0} = \left[\cancel{H_{i0}^\circ(T_R)} + \int_{T_R}^T C_{p_i} dT \right] - \left[\cancel{H_{i0}^\circ(T_R)} + \int_{T_R}^{T_0} C_{p_i} dT \right]$$

↑ the sample
↑ standard

$$H_i - H_{i0} = \int_{T_R}^T C_{p_i} dT + \int_{T_0}^{T_R} C_{p_i} dT = \int_{T_0}^T C_{p_i} dT$$

$$\frac{dE_{cys}}{dt} = \dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^n \int_{T_0}^T \theta_i C_{p_i} dT - \Delta H_R(T) F_{A0} X$$

$$\Delta H_R(T) = \frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A$$

$$H_i = H_{i0}^\circ(T_R) + \int_{T_R}^T C_{p_i} dT$$

$$\Delta H_R(T) = \left[\frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \right] + \int_{T_R}^T \left[\frac{d}{a} C_{pD} + \frac{c}{a} C_{pC} - \frac{b}{a} C_{pB} - C_{pA} \right] dT$$

heat of rxn $\rightarrow$ standard Temp
 $\rightarrow$ @ given Temp

$$= \overset{\text{st}}{\Delta H_R^\circ(T_R)} + \int_{T_R}^T \Delta C_p dT$$

$$\Delta H_R^\circ(T_R) = \frac{d}{a} H_D^\circ(T_R) + \frac{c}{a} H_C^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R)$$

$$\Delta C_p = \frac{d}{a} C_{pD} + \frac{c}{a} C_{pC} - \frac{b}{a} C_{pB} - C_{pA}$$

$$\Delta H_R(T) = \Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT$$

$$C_{p,i} = \alpha_i + \beta_i T + \gamma_i T^2$$

$$\Delta C_p = \left[\left(\frac{d}{a} \alpha_D + \frac{c}{a} \alpha_C - \frac{b}{a} \alpha_B - \alpha_A \right) + \left(\frac{d}{a} \beta_D + \frac{c}{a} \beta_C - \frac{b}{a} \beta_B - \beta_A \right) \right. \\ \left. * T + \left(\frac{d}{a} \gamma_D + \frac{c}{a} \gamma_C - \frac{b}{a} \gamma_B - \gamma_A \right) T^2 + \dots \right]$$

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{T_0}^T \Theta_i C_{p,i} dT - \Delta H_R(T) F_{A0} X = 0$$

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{T_0}^T \Theta_i C_{p,i} dT - \left[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] F_{A0} X = 0$$

⊗ ⊗

Case I : CSTR

$$F_{A0} X = -r_A V$$

$$r_A = -k C_A \quad k = A e^{-E_A/RT}$$

Consider $A \rightarrow B$

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

$$V = \frac{F_{A0} X}{-r_A} = \frac{U_0 C_{A0} X}{A e^{-E_A/RT} C_{A0} (1 - X)}$$

$$V = \frac{U_0 X}{A e^{-E_A/RT} (1 - X)} \rightarrow T, X \text{ main Parameters}$$

Assume:

* U_0, C_{A0}, F_{A0}, X are given

* Adiabatic condition $\dot{Q} = 0$

* No stirring, $\dot{W}_s = 0$

* $C_{pA} = C_{pB}$ (assumption) (constant, not vary with T)

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Calculate T.

$$-x \left[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] = \sum \theta_i C_{p,i} (T - T_0)$$

integral $\rightarrow$
constant ΔC_p not vary with T

if $C_{p,A} = C_{p,B}$ $\rightarrow$ $\Delta C_p = 0$ Special case if $A \rightarrow B$

$$T = T_0 + \frac{x (-\Delta H_R^\circ(T_R))}{\bar{C}_p} \quad \text{eq (1)}$$

$$\Delta C_p = \frac{b}{a} C_{p,B} - C_{p,A}$$

$\Delta C_p = 0$

$$-x [\Delta H_R^\circ] = \sum \theta_i C_{p,i} (T - T_0) - (T - T_0) \sum \theta_i C_{p,i}$$

$$T - T_0 = \frac{-x \Delta H_R^\circ(T_R)}{\sum \theta_i C_{p,i}} \rightarrow T = T_0 + \frac{x (-\Delta H_R^\circ(T_R))}{\bar{C}_p}$$

$$\text{that} \rightarrow \bar{C}_p = \sum \theta_i C_{p,i}$$

$\theta_i = \frac{f_{i0}}{F_{A0}}$

$$V = \frac{V_0 x}{A e^{-EA/RT} (1-x)} \quad \text{eq (2)}$$

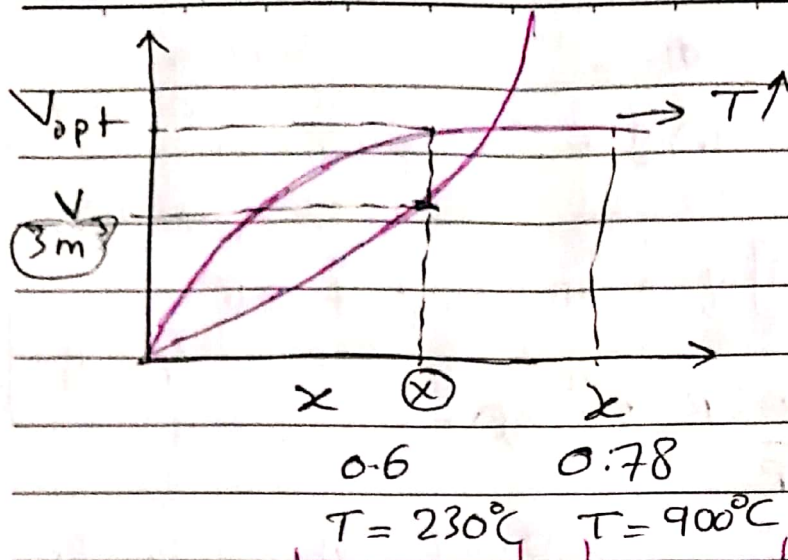
for isothermal T fixed $T(x)$

for non isothermal $\rightarrow$ T change with $\Delta H, x, C_p(\text{const})$
 $\bar{C}_p$ (fxn of molar flow rate)

to solve eq (1) and eq (2)

Assume x, T as function of $x \rightarrow V$ x, T V_{new}

V vs x (T hidden changing)



volume the same almost

Case II :

U_0, C_{A0}, V, F_0

T and $x \rightarrow$ needed

Solve Energy equation for $x = f(T)$

Solve $V = \frac{U_0}{A e^{-E/RT}} \left(\frac{x}{1-x} \right)$ as $x = f(T)$ — (1)

given

$\hookrightarrow x, T$ unknown

eq(2) energy equation as fn of $T \rightarrow$ eq (2)

solve!

$$T = T_0 + \frac{x(-\Delta H_R^\circ(T_R))}{\bar{C}_p}$$

$$V = \frac{U_0}{A \exp \left[\frac{E_a}{R \left(T_0 + \frac{x(-\Delta H_R^\circ(T_R))}{\bar{C}_p} \right)} \right]} \cdot \frac{x}{(1-x)}$$

given

fn of x

ask : balance & recieve

trial & error $x \rightarrow T \rightarrow C_p \rightarrow \dots$

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x_v v
 $v_{new} \rightarrow x_{new}$

$\vdots$



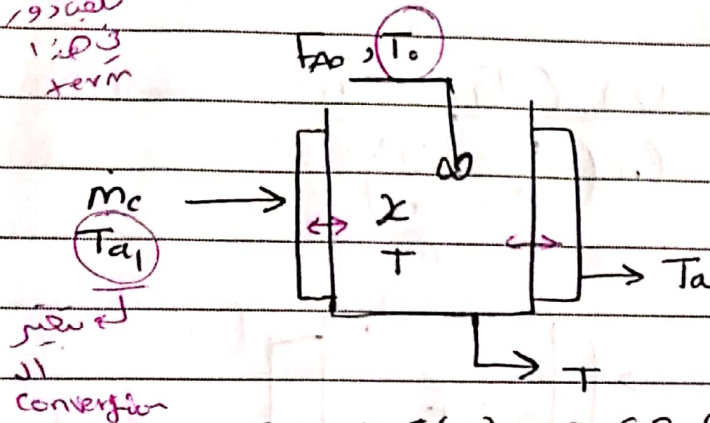
CSTR w/ heat effect

$$\dot{Q} - \dot{w}_s + F_{A0} \sum_{i=1}^N \int_{T_0}^T \theta_i C_{p,i} dT - \left[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] F_{A0} x = 0$$

not constant

↓
 T_a
 920 cal
 1.253
 term

110, 120, 130, 140
 terms



$Q \rightarrow$ environment around the jacket

$C_p \neq f(T) \therefore C_p$ constant

$$\dot{Q} - \dot{w}_s - F_{A0} \sum \theta_i C_{p,i} (T - T_0) - [\Delta H_R^\circ(T_R) + \Delta C_p (T - T_R)] F_{A0} x = 0$$

Design equation $V = \frac{F_{A0} x}{-r_A} \leftrightarrow \underline{F_{A0} x} = -r_A V$

$$\dot{Q} - \dot{w}_s - F_{A0} \sum \theta_i C_{p,i} (T - T_0) - \Delta H_R(T) [-r_A V] = 0$$

where

→ standard

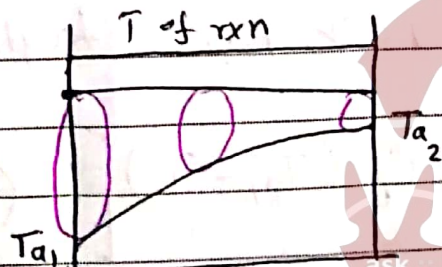
$$\Delta H_R(T) = \Delta H_R^\circ(T_R) + \Delta C_p (T - T_R)$$

$T_R x$
 K's 0.230 L/mol

* $Q \rightarrow$ function of temperature:

$$Q = UA \Delta T_{LMTD}$$

$$LMTD = \frac{(T - T_{a1}) - (T - T_{a2})}{\ln \left(\frac{T - T_{a1}}{T - T_{a2}} \right)}$$



$$INTD = \frac{T_{a2} - T_{a1}}{\ln \left(\frac{T - T_{a1}}{T - T_{a2}} \right)}$$

Energy balance across CSTR:

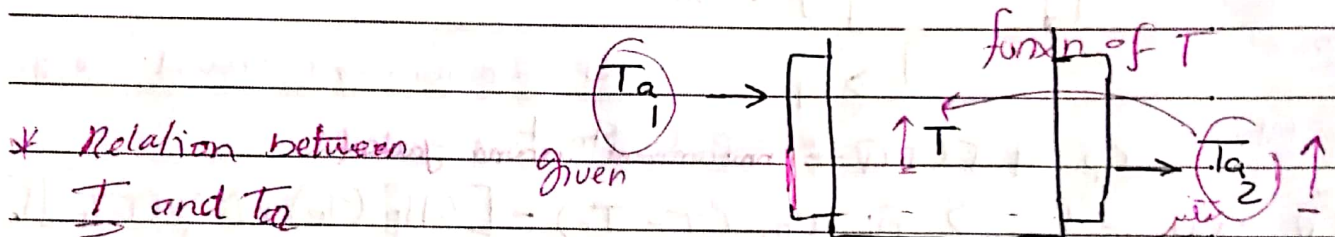
$$\text{Rate}_{\text{in}} - \text{Rate}_{\text{out}} - \text{Rate}_{\text{transfer}} = 0$$

$$\dot{m} c_p (T_{a1} - T_r) - \dot{m} c_p (T_{a2} - T_r) - \frac{UA (T_{a1} - T_{a2})}{\ln \left(\frac{T - T_{a1}}{T - T_{a2}} \right)}$$

$$\dot{m} c_p (T_{a1} - T_{a2}) = \dot{Q} = \frac{UA (T_{a2} - T_{a1})}{\ln \left(\frac{T - T_{a1}}{T - T_{a2}} \right)} \quad \text{--- (8)}$$

$\downarrow$
 heat convection across the wall

$\ln \left(\frac{T - T_{a1}}{T - T_{a2}} \right)$
 given T_{a1} unknown T_{a2} unknown



* Rearranging --- (8)

$$T_{a2} = T - (T - T_{a1}) e^{\left(-\frac{UA}{\dot{m} c_p} \right)}$$

$$\dot{Q} = \dot{m} c_p (T_{a1} - T_{a2})$$

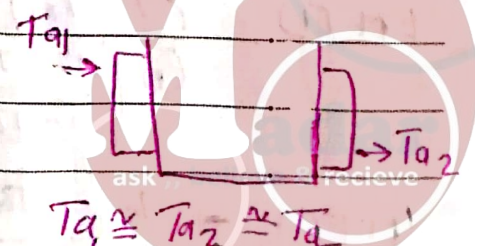
$$= \dot{m} c_p \left(T_{a1} - \left(T - (T - T_{a1}) e^{\left(-\frac{UA}{\dot{m} c_p} \right)} \right) \right)$$

* From math:

$$e^{-x} = 1 - x + \dots \quad \text{Taylor series}$$

$$\dot{Q} = \dot{m} c_p (T_{a1} - T) \left[1 - \left(1 - \frac{UA}{\dot{m} c_p} \right) \right]$$

$$\dot{Q} = UA (T_{a1} - T)$$



$T_{a1} \approx T_{a2} \approx T_a$
 @ high flow rate

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$$\dot{Q} - \dot{Q}_s - F_{A0} \sum \Theta_i C_{p_i} (T - T_0) - \Delta H_R (T) F_{A0} X = 0$$

$$UA(T_a - T) - F_{A0} \sum \Theta_i C_{p_i} (T - T_0) - \Delta H_R (T) F_{A0} X = 0$$

$$[T_a = T_{a1} = T_{a2}]$$

$$\frac{UA}{F_{A0}} (T_a - T) - \sum \Theta_i C_{p_i} (T - T_0) - \Delta H_R (T) X = 0$$

$$X = \frac{\left(\frac{UA}{F_{A0}}\right) (T_a - T) - \sum \Theta_i C_{p_i} (T - T_0)}{\Delta H_R^\circ(T_R) + \Delta C_p (T - T_R)}$$

(linear)

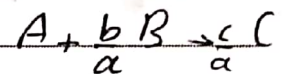
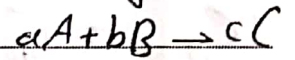
important equation

$$\Delta H_R^\circ(T_R) + \Delta C_p (T - T_R)$$

constant

conversion from energy balance equation

for design (x, T):



$$r_A = -K C_A^a C_B^b$$

$$= -K e^{-E/RT} C_{A0} (1-X)^a C_{B0} \left(\theta_B - \frac{b}{a} X \right)^b$$

$$C_{A0} \left(\theta_B - \frac{b}{a} X \right)^b$$

$$V = \frac{F_{A0} X}{-r_A}$$

(*) (*)

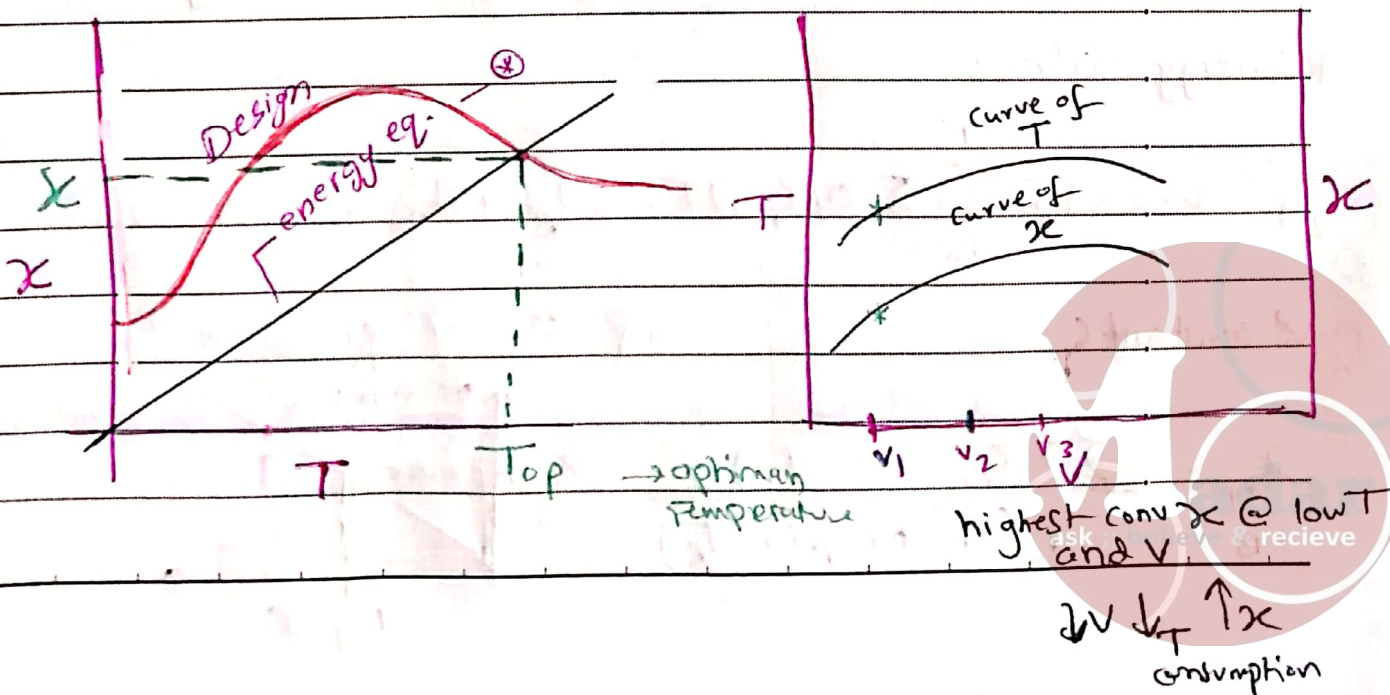
(non-linear)

$$F(X, T)$$

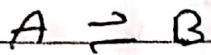
$$F(X, T)$$

two eqs, three variable
(V, X, T)

make one variable constant, solve for the rest variables



* Equilibrium conversion:



$$-r_A = k_f \left(C_A - \frac{C_B}{K_{eq}} \right) = 0 \text{ @ eq.}$$

$$C_{Aeq} = \frac{C_{Beq}}{K_{eq}}$$

$$C_{A0} (1 - x_{eq}) = C_{Aeq}$$

$$C_{Beq} = C_{A0} \left(\cancel{0}^0 + \frac{b}{a} x_{eq} \right)$$

$$\cancel{C_{A0}} (1 - x_{eq}) = \frac{\cancel{C_{A0}} x_{eq}}{K_{eq}}$$

$$x_{eq} = \frac{K_{eq}}{1 + K_{eq}} = \frac{A \exp \left[\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]}{1 + A \exp \left[\frac{-\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]}$$

activation energy based on given Temp

* Energy balance

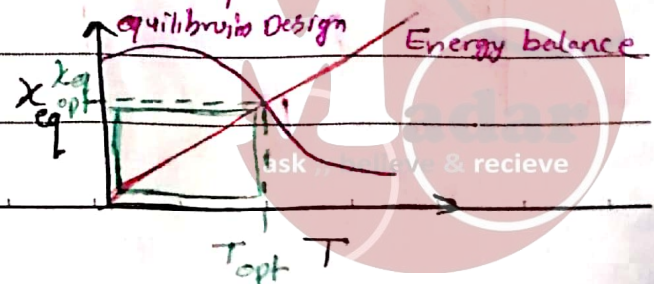
$$\dot{Q} - \dot{W} - F_{A0} \int_{T_0}^T \sum \Theta_i C_p dT - \Delta H_R(T) F_{A0} x = 0$$

@ constant C_p

$Q = 0$ at equilibrium !!

$$x_{eq} = \frac{\sum \Theta_i \tilde{C}_{p_i} (T - T_0)}{\Delta H_R(T_R) + \Delta \tilde{C}_p (T - T_R)}$$

average



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example $A \rightleftharpoons B$ Pure A is fed @ $T = 300\text{K}$

$$H_A^\circ(298\text{K}) = -40,000 \text{ cal/mol}$$

$$H_B^\circ(298\text{K}) = -60,000 \text{ cal/mol}$$

$$C_{pA} = C_{pB} = 50 \text{ cal/mol}\cdot\text{K}$$

$$K_{eq} = 100,000 e^{\frac{-20,000}{1.987} \left(\frac{1}{298} - \frac{1}{T} \right)}$$

what is the opt. Temp to obtain max x_{eq} ?

Design Equation $x_{eq} = \frac{K_{eq}}{1+K_{eq}}$

$$x_{eq} = \frac{10,000 \exp \left[\frac{-33.78(T-298)}{T} \right]}{1 + 10,000 \exp \left[\frac{-33.78(T-298)}{T} \right]}$$

Energy balance equation:

$$x_{eq} = \frac{\sum \theta_i \bar{C}_{pi} (T - T_0)}{-[\Delta H_R^\circ(T_R) + \Delta \bar{C}_p (T - T_R)]}$$

$$\Delta \bar{C}_p = C_{pB} - C_{pA} = 50 - 50 = 0$$

$$x_{eq} = \frac{[C_{pA} + \theta_B C_{pB}](T - 300)}{-\Delta H_R^\circ(T_R)} = \frac{50(T - 300)}{20,000} = 2.5(T - 300)$$

Note

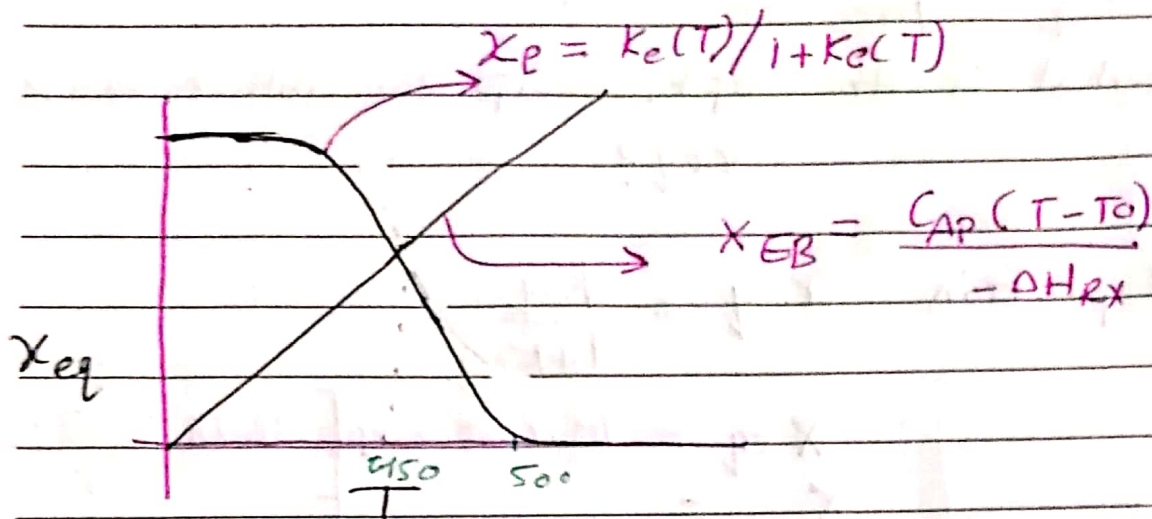
$$\theta_B = \frac{C_B^\circ}{C_A^\circ} = \frac{F_B^\circ}{F_A^\circ} = 0, \text{ No B exist initially}$$

T	K_{eq}	$X_{eq}(\text{mass})$	$X_{eq}(\text{energy})$
---	----------	-----------------------	-------------------------

298	100,000	1	—
-----	---------	---	---

460	18.17	0.95	0.25
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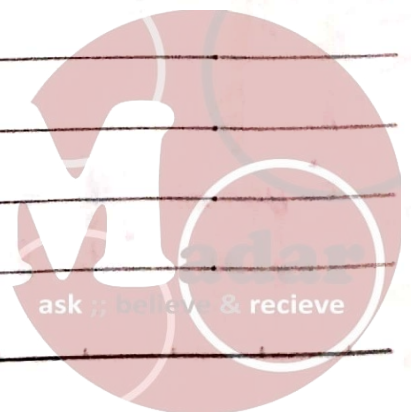
500	0.12	0.11	0.5
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So $T_{opt} = 465K$

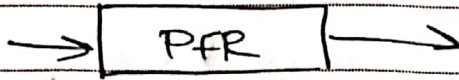
$X_{eq} = 0.41$

Note This example from ch 8, Voglar 3rd edition
example 8.8.
Calculating the adiabatic Equilibrium
Temperature



Non-Isothermal PFR

Dec 21



163 kmol/hr

adiabatic cond

99% butane

10% iso pentane

inert

$$C_{A0} = 9.3 \text{ kg mol/m}^3$$

* Condition:

$$T_0 = 330 \text{ K}$$

Rxn takes place @ $T = 360 \text{ K}$

Given $\Delta H_{Rxn}^\circ = -6900 \text{ J/mol butane}$

$$C_p = 141 \text{ J/mol}\cdot\text{K}$$

$$C_{p\text{-butane}} = 161 \text{ J/mol}\cdot\text{K}$$

$$C_{p\text{-pentane}}$$

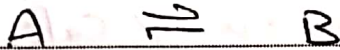
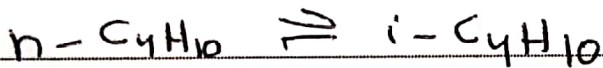
$$E = 65700 \text{ kJ/mol}$$

k_f = takes place. $T = 360 \text{ K}$

k_c = " " $T = 333 \text{ K}$

$V = ?$ to achieve the desired Conversion.

Soln:



Design equation

$$F_{A0} \frac{dx}{dv} = -r_A = k_f \left[\frac{C_A}{K_{eq}} - C_B \right]$$

mole balance

Rate law

given that

$$k_f = 31.1 \text{ e}^{E/R(\frac{1}{T_1} - \frac{1}{T})}$$

$$C_A = C_{A0}(1-x), \quad C_B = C_{A0}x$$

(liquid phase, $v = 0$)

ask & recieve

$$-r_A = k_f C_{A_0} \left[1 - \left(1 + \frac{1}{K_{eq}} \right) X \right] \quad \begin{matrix} k_f = f(T) \\ r_A = f(X, T) \end{matrix}$$

$$V = \int_0^X \frac{F_{A_0}}{-r_A} dx = \int_0^X \frac{F_{A_0}}{C_{A_0} k_f \left[1 - \left(1 + \frac{1}{K_{eq}} \right) X \right]} dx$$

$$V = \int_0^X \frac{F_{A_0}}{C_{A_0}} \cdot \frac{dx}{31.1 e^{\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right)} \left[1 - \left(1 + \frac{1}{3.03 e^{\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right)}} \right) X \right]}$$

we need energy balance

$$\dot{Q} - \dot{W}_s - F_{A_0} \sum \theta_i \bar{C}_{p_i} (T - T_0) - F_{A_0} X \left[\Delta H_R^\circ (T_R) + \Delta \bar{C}_p (T - T_R) \right] = 0$$

Adiabatic $\dot{Q} = 0$

No work $\dot{W}_s = 0$

$\Delta \bar{C}_p = C_{p_B} - C_{p_A} = 141 - 141 = 0$ (to ease calculation)

$$-F_{A_0} \sum \theta_i C_{p_i} (T - T_0) = -F_{A_0} X \left[\Delta H_R^\circ (T_R) \right]$$

$$T - T_0 = \frac{-\Delta H_R^\circ (T_R) X}{\sum \theta_i C_{p_i}}$$

$$\sum \theta_i C_{p_i} = \theta_A C_{p_A} + \theta_B C_{p_B} + \theta_I C_{p_I} = (1)(141) + (0)(141) + \frac{0.1}{0.9}(16)$$

$$= 159 \text{ J/mol}\cdot\text{K}$$

$$T = 330 - \frac{6900 X}{159} = 330 + 43.3 X$$

$$k_f = 31.1 \exp \left[\frac{65700}{8.314} \left(\frac{1}{360} - \frac{1}{T} \right) \right]$$

$$= 31.1 \exp \left[7902 \left(\frac{T - 360}{360T} \right) \right]$$

$$K_{eq} = 3.03 \exp \left[\frac{-6900}{8.314} \left(\frac{1}{333} - \frac{1}{T} \right) \right] =$$

$$= 3.03 \exp \left[-830.3 \left(\frac{T - 333}{333T} \right) \right]$$

$$X_{eq} = \frac{k_{eq}}{1 + K_{eq}}$$

$$T = 330 + 43.3 X$$

$$-r_A = k C_{A0} \left[1 - \left[1 + \frac{1}{K_{eq}} \right] X \right]$$

for example: $X = 0.2$

$$T = 330 + 43.3 \times 0.2 = 338.6 \text{ K}$$

$$k = 31.1 \exp \left[7902 \left(\frac{338.6 - 360}{360 \times 338.6} \right) \right] = 7.76 \text{ h}^{-1}$$

$$k_{eq} = 3.03 \exp \left[-830.3 \left(\frac{338.6 - 333}{333 (338.6)} \right) \right]$$

$$= 2.9$$

$$X_{eq} = \frac{2.9}{1 + 2.9} = 0.74$$

$$-r_A = (7.76)(9.3) \left[1 - \left[1 + \frac{1}{2.9} \right] (0.2) \right] = 52.8$$

$$\frac{F_{A0}}{-r_A} = \frac{0.9(163)}{52.8} = 2.778$$

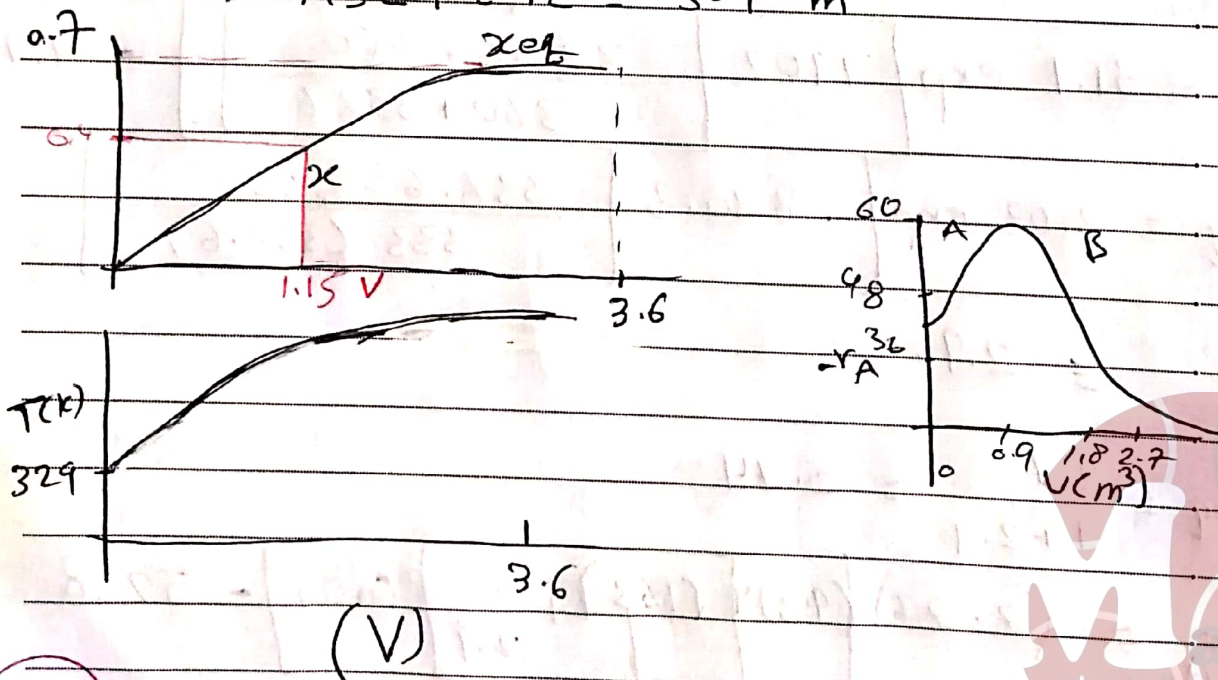
then

X	T(K)	k	k _{eq}	-r _A	F _{A0} /-r _A
0	330	4.22	3.1	39.2	3.74
0.2	338.7	7.76	2.9	52.8	2.78
0.4	347.3	13.93	2.73	58.6	2.50
0.6	356.0	24.27	2.57	37.7	3.89
0.7	360.3	31.67	2.5	4.1	35.8

$$V = \int_0^{0.6} \frac{F_{A0}}{-r_A} dx + \int_{0.6}^{0.7} \frac{F_{A0}}{-r_A} dx$$

$$V = \frac{3}{8} (0.2) \left[3.74 + 3(2.78) + 3(2.5) + 3.89 \right] + \frac{0.1}{3} \left[3.89 + 4(5.99) + 35.8 \right] =$$

$$= 1.32 + 2.12 = 3.4 \text{ m}^3$$



Note

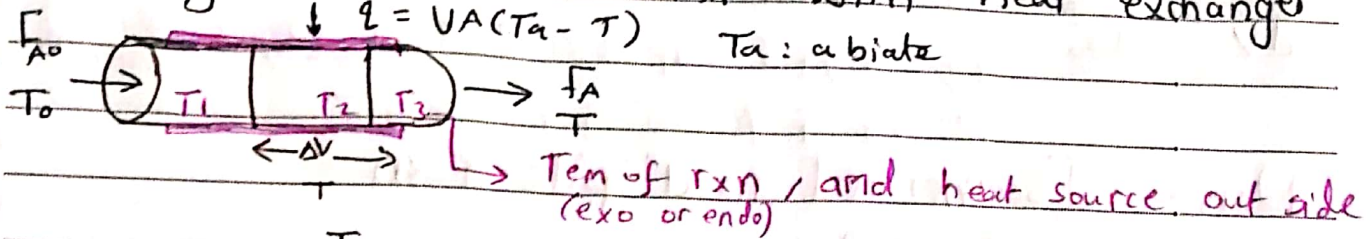
example No. 8-6 Ch 8 sec 8.3,

3rd Edition. Voglar

Steady state tubular Rxr

23rd Dec

steady state tubular Rxr with heat exchanger



$$\dot{Q} - \dot{W}_s - F_{A0} \int_{T_0}^T \sum \theta_i C_{p,i} dT - \left[\sum \Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] F_{A0} x = 0$$

$$\frac{d\dot{Q}}{dV} - F_{A0} \sum \theta_i C_{p,i} \frac{dT}{dV} - \left[\Delta H_R^\circ(T_R) F_{A0} x \frac{dx}{dV} + \frac{d}{dV} \left(\int_{T_R}^T \Delta C_p dT \right) F_{A0} x \right]$$

= 0

$$\frac{d}{dV} \left[\int_{T_R}^T \Delta C_p dT \right] F_{A0} x = F_{A0} x \Delta C_p \frac{dT}{dV}$$

$$\frac{d\dot{Q}}{dV} - F_{A0} \sum \theta_i C_{p,i} \frac{dT}{dV} - \left[\Delta H_R^\circ(T_R) F_{A0} x \frac{dx}{dV} + \left(\int_{T_R}^T C_p dT \right) F_{A0} \frac{dx}{dV} + F_{A0} x \Delta C_p \frac{dT}{dV} \right]$$

= 0

Rearrang.

$$\frac{d\dot{Q}}{dV} - \left[F_{A0} \left(\sum \theta_i C_{p,i} + x \Delta C_p \right) \right] \frac{dT}{dV} - \left[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] F_{A0} \frac{dx}{dV} = 0$$

* Conversion change with volume, T changes with volume for both (endo/exo) rxn

$$-r_A = F_{A0} \frac{dx}{dV} \rightarrow \frac{dx}{dV} = \frac{-r_A}{F_{A0}}$$

$$\frac{d\dot{Q}}{dV} - F_{A0} \left(\sum \theta_i C_{p,i} + \Delta C_p x \right) \frac{dT}{dV} - \left[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] (-r_A) = 0$$

$$\dot{Q} = UA(T_a - T)$$

$$\frac{d\dot{Q}}{dV} = Ua(T_a - T)$$

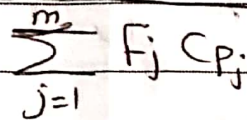
↓
area/volume unit

$$\text{but } a = \frac{\pi D L}{\frac{\pi D^2 L}{4}}$$

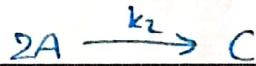
(2πrL)
Area of
contact
NOT
cross section

$\frac{T}{X} \rightarrow f(v)$
 $\uparrow \downarrow$ depend on $\rightarrow$ exo
 $\rightarrow$ endo fix

$A \rightarrow B$



$$A \xrightarrow{k_1} B$$



$$F_{A_0} = 100 \frac{\text{mol}}{\text{s}}$$

$$C_{A0} = 0.1 \frac{\text{mol}}{\text{L}}$$

$$\Delta H_{f1} = -20 \text{ kJ/mol} \cdot A$$

$$\Delta H_f = -60 \text{ kJ/mol}$$

$$C_{PA} = C_{PB} = 90 \text{ J/mol}\cdot\text{C}$$

$$C_p = 180 \text{ J/mol}\cdot\text{C}$$

$$E_i/r = 4000 \text{ k}$$

$$E_z/r = 9000 \text{ K}$$

$$k_1 = 10 e^{E_1/R(\frac{1}{300} - \frac{1}{T})}$$

$$k_2 = 0.09 e^{\frac{E_2}{R} \left(\frac{1}{300} - \frac{1}{T} \right)}$$

Ta

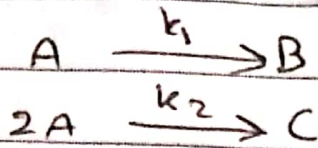
$$T_a = 100^\circ\text{C}$$

$$\overline{b} = 0$$

150°C

Determine T and Flowrate Profile across the reactor

Soln:



Design Equation $\frac{dF_A}{dV} = r_A = -k_1 C_A - k_2 C_A^2$

$$\frac{dF_B}{dV} = r_B = k_1 C_A$$

$$\frac{dF_C}{dV} = r_C = \frac{1}{2} k_2 C_A^2$$

NOTE

r_A	r_B
-1	1
r_C	
-2	1

Note: $C_j = C_{T_0} \frac{F_A}{F_T} \frac{T_0}{T} \frac{P}{P_0}$

$$C_A = C_{T_0} \frac{F_A}{F_T} \frac{T_0}{T}$$

$$C_B = C_{T_0} \left(\frac{F_B}{F_T} \right) \left(\frac{T_0}{T} \right) \quad C_C = C_{T_0} \left(\frac{F_C}{F_T} \right) \left(\frac{T_0}{T} \right)$$

$C_A = C_{A0} (1-x)$, fcn of x indirectly

Three eq $\rightarrow x$ hidden, T

3-equations with 4 variables (F_A, F_B, F_C, T)

$$\frac{dT}{dV} = \frac{U_a(T_a - T) + (-r_A)(-\Delta H_{Rx1A}) + (-r_C)(-\Delta H_{Rx2A})}{F_A C_{PA} + F_B C_{PB} + F_C C_{PC}}$$

$$\left. \begin{aligned} r_A &= -k_1 C_A \\ r_{A2} &= -k_2 C_A^2 \end{aligned} \right\} \text{gas phase } \Delta P = 0$$

Substitute:

$$\frac{dT}{dV} = \frac{4000(373-T) + (-r_{A1})(20000) + (-r_{A2})(60000)}{90F_A + 90F_B + 180F_C}$$

using Polymath

equations

Initial Value

$$dF_b / d(V) = -r_{1a}$$

0

$$dF_a / d(V) = r_{1a} + r_{2a}$$

100

$$dF_c / d(V) = -r_{2a} / 2$$

0

$$d(T) / d(V) = (4000 * (373-T) + (-r_{1a}) * 20000 + (-r_{2a}) * 60000) / (90F_a + 90F_b + 180F_c) \quad 2/23$$

$$k_{1a} = 10 * \exp(4000 * (1/300 - 1/T))$$

$$k_{2a} = 0.09 * \exp(9000 * (1/300 - 1/T))$$

$$C_{T0} = 0.1$$

$$F_t = F_a + F_b + F_c$$

$$T_0 = 423$$

$$C_a = C_{T0} (F_a / F_t) * (T_0 / T)$$

$$C_b = C_{T0} * (F_b / F_t) * (T_0 / T)$$

$$C_c = C_{T0} * (F_c / F_t) * (T_0 / T)$$

$$r_{1a} = -k_{1a} * C_a$$

$$r_{2a} = -k_{2a} * C_a * 2$$

$$V_0 = 0, V_f = 1$$

NOTE

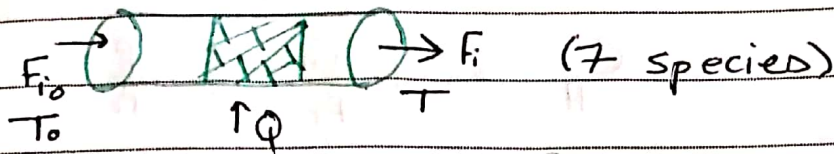
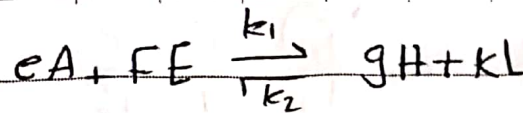
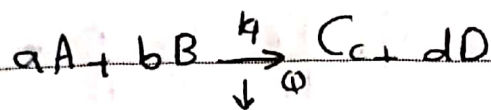
example in 3rd edition / Vogel / ch 8.7

Number example : 8-11

ask : before & receive

Design of Packed bed Rxr

28th - Dec



Packed bed:

- ① Design eq.
- ② Energy eq.
- ③ ΔP eq.

① Design eq.

$$\frac{dF_A}{dw} = -k_1 C_A^a C_B^b - k_2 C_A^e C_E^f + k_3 C_H^g C_L^k$$

$$\frac{dF_B}{dw} = -k_1 C_A^a C_B^b$$

$$\frac{dF_E}{dw} = k_1 C_A^a C_B^b$$

$$\frac{dF_D}{dw} = k_1 C_A^a C_B^b$$

$$\frac{dF_E}{dw} = -k_2 C_A^e C_E^f + k_3 C_H^g C_L^k$$

$$\frac{dF_H}{dw} = k_2 C_A^e C_E^f - k_3 C_H^g C_L^k$$

$$\frac{dF_L}{dw} = k_2 C_A^e C_E^f - k_3 C_H^g C_L^k$$

* Remember:

$$\rightarrow C_{A0} = y_{A0} C_{T0}$$

* Remember:

$$\rightarrow C_j = C_{T0} \frac{F_j}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$= C_{A0} \left(\frac{\theta_j + v_j X}{1 + \epsilon X} \right) \frac{P}{P_0} \frac{T_0}{T}$$

* Remember:

$$\rightarrow F_j = F_{A0} (\theta_j + v_j X)$$

v_j (-) Reactants

v_j (+) products

$$\rightarrow F_T = F_{T0} (1 + y_{A0} \delta X)$$

$$= F_{T0} (1 + \epsilon X)$$

$$\rightarrow y_{A0} = F_{A0} / F_{T0}$$

Needing 7 equation!

$$C_A = C_{T_0} \frac{F_A}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_E = C_{T_0} \frac{F_E}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_B = C_{T_0} \frac{F_B}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_H = C_{T_0} \frac{F_H}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_C = C_{T_0} \frac{F_C}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_L = C_{T_0} \frac{F_L}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$C_D = C_{T_0} \frac{F_D}{F_T} \frac{T_0}{T} \frac{P}{P_0}$$

$$F_T = \sum_{i=1}^n F_i$$

$\frac{P}{T}$
unknown

$F_A + F_B + F_C + F_D + F_E + F_H + F_L$
unknown

$$\begin{aligned} \Rightarrow \frac{dF_A}{dw} &= -K_1 \left[\frac{C}{T_0} \frac{F_A}{F_T} \frac{T_0}{T} \frac{P}{P_0} \right]^a \left[\frac{C}{T_0} \frac{F_B}{F_T} \frac{T_0}{T} \frac{P}{P_0} \right]^b \\ &\quad - K_2 \left[\frac{C}{T_0} \frac{F_A}{F_T} \frac{T_0}{T} \frac{P}{P_0} \right]^e \left[\frac{C}{T_0} \frac{F_E}{F_T} \frac{T_0}{T} \frac{P}{P_0} \right]^f \\ &\quad + K_3 \left[\frac{C}{T_0} \frac{F_H}{F_T} \frac{T_0}{T} \frac{P}{P_0} \right]^g \left[\frac{C}{T_0} \frac{F_L}{F_T} \frac{T_0}{T} \frac{P}{P_0} \right]^k \\ &= -K_1 \left[\frac{C}{T_0} \right]^{(a+b+e+f+g+k)} \left(\frac{F_j}{F_T} \right)^{\sum j} \left(\frac{T_0}{T} \frac{P}{P_0} \right)^{(a+b+\dots)} \end{aligned}$$

$$\frac{dF_A}{dw} = f(F_A, F_B, \dots, T, P) \quad 9 \text{ unknown}$$

$$\frac{dF_B}{dw} \rightarrow 9 \text{ unknown}$$

$$\frac{dF_L}{dw} \Rightarrow 9 \text{ unknown}$$

7 equations with
9-unknowns
 F_j^s, T, P

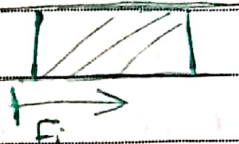
Energy equation $\rightarrow$

$$\dot{Q} - \dot{W} - F_{A0} \sum \theta_i c_{p,i} (T - T_0) - \sum_{i=1}^m \Delta H_{R,i}(T) (-r_i V) = 0$$

$\downarrow$ T $\downarrow$ $f(T)$ $\downarrow$ $F(F_i)$

Ergun equation:

$$\frac{dP}{dw} = f(F_i, T, P)$$



* Collection and Analysis of the Rate Data:

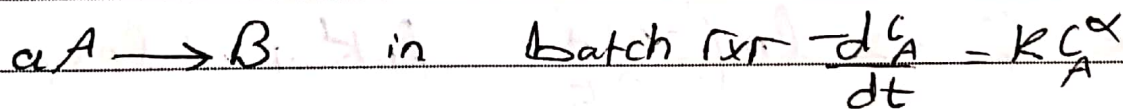
1. Differential Method

t C_i

$\vdots$ $\vdots$

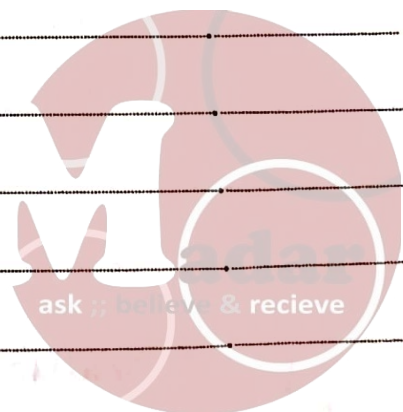
Order of Rxn

$K ??$



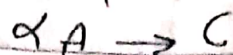
$$\ln\left(-\frac{dC_A}{dt}\right) = \ln K + \alpha \ln C_A$$

Plot $\ln\left(-\frac{dC_A}{dt}\right)$ vs $\ln C_A \Rightarrow$ Slope = α
Int = $\ln K$



28th Dec

example:



$C_{A0} = 0.05 \text{ mol/L}$

t :	0	50	100	150	200	300
$10^3 C_A$:	50	38	30.6	25.6	22.2	17.4

estimate rate constant

$\frac{C_{B0} - 0.5}{C_{A0} \cdot 0.05} = 10$

$C_{B0} \gg C_{A0}$

IN excess (Doesn't affect Rate of Rxn)

So the rate $-r_A = k C_A^\alpha C_B^\beta \rightarrow \text{excess} \rightarrow \text{constant}$

$= k' C_A^\alpha$

$k' = k C_B^\beta$

$-\frac{dC_A}{dt} = k' C_A^\alpha \rightarrow \ln\left(-\frac{\Delta C_A}{\Delta t}\right) = \ln k' + \alpha \ln C_A$

t	$C_A \times 10^3$	$\frac{\Delta C_A}{\Delta t} \times 10^3$	$\ln C_A$
0	50	$\frac{50 - 38}{0 - 50} = 2.4$	
50	38		
100	30.6		1.48

value = $\ln k'$

$k' = e^{\text{value}} \rightarrow k C_B^\beta = \text{value}$

$\rightarrow k = \frac{\text{value}}{C_B^\beta}$

$\rightarrow$ in excess, No effect

28th, Dec

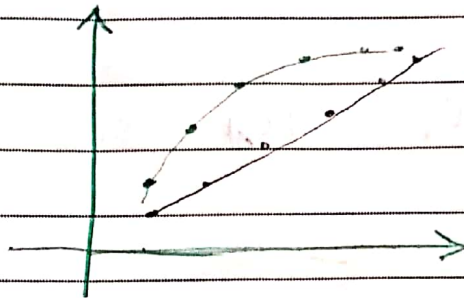
*Integral form:

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

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^\alpha} = \int_0^t k' dt$$

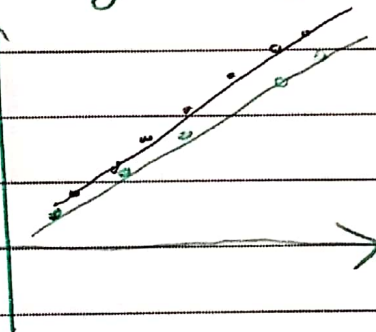
Assume $\alpha = 1$

t C_A
:
:
:



If not straight line
change the value ~~of~~ α

$\alpha = 2$
straight?
- yes, second order



change α if not straight

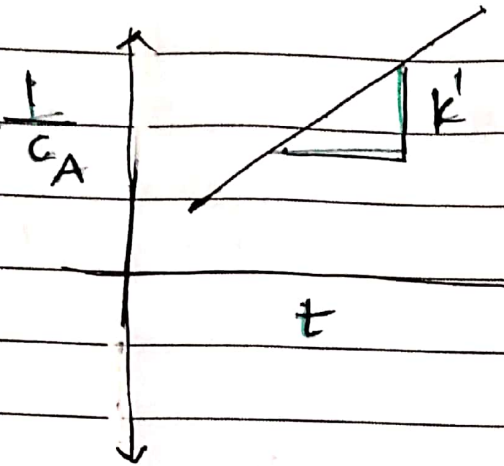
Assume $\alpha = 2$

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = \int_0^t k' dt$$

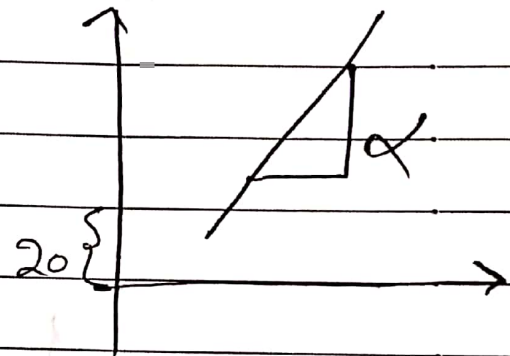
ask :: believe & recieve

28th Dec

$$\frac{1}{C_A} = \frac{1}{C_{A0}} + k' t$$



t	C_A	$1/C_A$
0	0.05	20
50	0.038	26.3
100	0.0306	32.7
⋮		



$$k' = 0.12 \frac{l}{mol \cdot min}$$

$$k - \frac{k'}{C_{B0}} = 0.12$$

$$= 0.24 l^2$$

$$mol^2 \cdot min$$

ask : believe & recieve

Desired and undesired Rxns Dec. 30



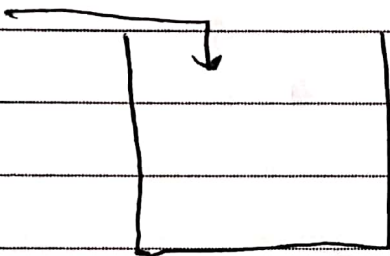
instantaneous $S_i = r_D / r_U = \frac{\text{rate of desired}}{\text{rate of undesired}}$

Overall $S_o = \frac{F_D}{F_U} = \frac{\text{exist molar flow rate of D}}{\text{" " " " " U}}$

Example: What will be the relation between instantaneous selectivity, and overall Sel.

$$S_o = \frac{F_D}{F_U} = \frac{F_D V}{r_U V} = \frac{r_D}{r_U} = S_i$$

batch rxr:



extent

$\downarrow$
 ξ_1

ξ_2

$$N_A = N_{A_0} - \xi_1 - \xi_2$$

$$N_B = \boxed{N_{B_0}} + \xi_1$$

$$N_D = \boxed{N_{D_0}} + \xi_1$$

$$N_C = \boxed{N_{C_0}} + \xi_2$$

$$N_U = \boxed{N_{U_0}} + \xi_2$$

Desired and undesired.

December 30

$$S_e = \frac{\varepsilon_1}{\varepsilon_2} = \frac{\text{desired}}{\text{undesired}} > 8 \quad \text{given}$$

$$X = \frac{N_{A0} - N_A}{N_{A0}}$$

2 eq.s, 2 unknowns.

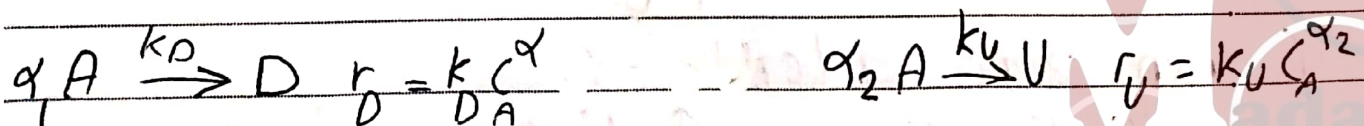
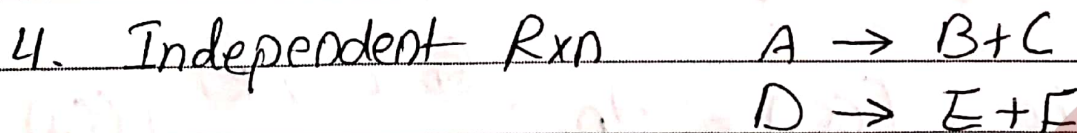
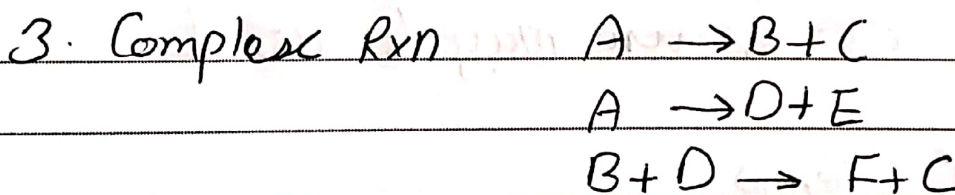
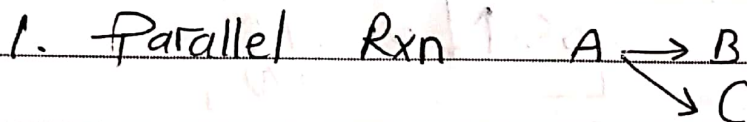
Reaction yield

$$Y_D = \frac{r_D}{-r_A} \quad \begin{matrix} \text{(desired)} \\ \text{(rate of reactant / consumption of A)} \end{matrix}$$

Overall yield

$$\bar{Y}_D = \frac{N_D}{N_{A0} - N_A} = \frac{F_D}{F_{A0} - F_A}$$

Multiple Rxns.



$$-r_A = r_D + r_U = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$$

Selectivity $S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{(\alpha_1 - \alpha_2)}$

Case I:

$$\alpha_1 > \alpha_2 \rightarrow \alpha_1 - \alpha_2 > 0$$

$$C_A \uparrow \quad S_{D/U} \uparrow$$

left from rxr at any given time

$$\uparrow C_A \quad \uparrow \text{Sel.}$$

- ① A batch rxr should be used,
A plug flow Rxr should be used.
CSTR should NOT be used?

Perfect mixing in CSTR

$$\textcircled{2} \alpha_2 > \alpha_1 ; \alpha_1 - \alpha_2 < 0$$

$$as C_A \downarrow \quad \text{Sel} \uparrow$$

How?
* So C_A must be diluted
CSTR may be used

③ effect of Temp.

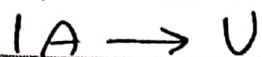
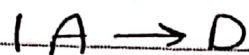
$$S_{D/U} = \frac{k_D}{k_U} f(C_A) = \frac{A_D}{A_U} e^{-(E_D - E_U)/RT} f(C_A)$$

if rxn zero-order

- if $E_D - E_U > 0$, $\uparrow \text{Temp} \rightarrow \uparrow \text{Sel D/U}$

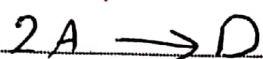
- if $E_D/E_U < 0$, $\downarrow T \rightarrow \uparrow \text{sel/D/U}$

Example:



$$\alpha_1 = \alpha_2 \rightarrow \alpha_1 - \alpha_2 = 0, \quad \text{Sel/D/U} = r_D/r_U = k_D/k_U C_A^0 \rightarrow \text{zero order} \\ = fCT, E_{is}$$

Example:



$$\text{SD/U} = \frac{k_D}{k_U} C_A^{2-1} = \frac{k_D}{k_U} C_A = \frac{A_D}{A_U} e^{-(E_D/E_U)/RT} \cdot C_A$$

gas phase
 $\downarrow$
 (T, P, X)

rxn $\leftarrow$ Jl Group $\rightarrow$

max. Sel. $\leftarrow T_{opt}$

(maximizing the selectivity of the rxn) example 6-2

checking

