

① Design eqs. for Ideal Isothermal Reactors

- The bread and butter tools for a chemical engineer are the material and energy balances. Chemical Reactor Design is a classical application of these fundamental principles. In the design of chemical reactors we are concerned with:

- Design eqs.
 - Material, energy, and momentum balances
 - These depend on the type of reactor but are independent of chemical kinetics
 - Basic form: $IN - OUT + GENERATION = ACCUMULATION$
- Rate functions
 - for heat and mass transfer (e.g.: rate of heat transfer = $hA(T_w - T)$)
 - for chemical rxns are a function of T and C
 - are independent of the reactor type

- First we consider the simplest case: Ideal, Isothermal Reactors

- Isothermal
 - constant T
 - No energy balance needed, No heat transfer rate function
- Ideal
 - constant P (No momentum balance)
 - Degree of mixing specified (No mass transfer rate functions)
- Needed eqs. & functionalities
 - Design eqs. (through material balance)
 - Rate functions (" rates of chemical rxns)

1.1 Nomenclature & subscripts

- Nomenclature
 - Symbol \triangleq definition [unit]
 - E_i or C_i \triangleq concentration of component i [mol/m³]
 - F_i \triangleq molar flow rate of " " [mol/s]
 - N_i \triangleq moles of component i in a batch reactor [mol]
 - v_i \triangleq volumetric flowrate [m³/s]
 - r_i \triangleq rate of formation of i [mol/m³.s] or [mol/kg.cat.s] (positive for ~~reactants~~ products)
 - $-r_i$ \triangleq rate of disappearance of i ["] or ["] (positive for reactants)
 - t \triangleq time of operation for batch reactors [s]
 - V \triangleq reactor volume [m³]
 - X or f \triangleq fractional conversion [-] (X is used in Fogler & f in Hill)

- Subscripts
 - 0 \triangleq conditions at reactor flow inlet or t=0 for batch reactors.
 - E \triangleq " " " " exit or final t " " "
 - i \triangleq component i
 - t \triangleq total

• for example F_{t0} \equiv total molar flowrate into the reactor

1.2 Some basic functions

- Fractional conversion of component i, X_i
 - definition: $X_{iE} = \frac{\text{moles of component i that has reacted}}{\text{total moles of i fed to or placed in the reactor}}$ - X_i is constant for CSTRs only
 - specifications:
 - batch system $\leftarrow X_{iE} = \frac{N_{i0} - N_{iE}}{N_{i0}}$
 - flow system $\leftarrow X_{iE} = \frac{F_{i0} - F_{iE}}{F_{i0}}$
- Space time, τ
 - definition: $\tau = \frac{V}{v_0}$ (holding time, or mean residence time)
 - it is the time necessary to process one reactor volume of fluid based on entrance
- Space velocity, SV
 - definition: $SV = \frac{v_0}{V} = \frac{1}{\tau}$, (volumetric flow was taken at entrance conditions)
 - other commonly used SVs
 - LHSV \equiv liquid hourly (typically at 60 or 75 °F)
 - GHSV \equiv gas " (" " STP conditions)

- mean or average residence time, \bar{t} → definition:

$$\bar{t} = \int_0^V \frac{dV}{v}$$

for tubular reactor

$$\bar{t} = \int_0^L \frac{dx}{u}$$

→ x : position along the reactor

→ u : fluid velocity

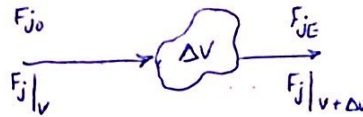
volumetric flowrate can change due to change in moles

- v, u change as $T, P, \#$ of moles change as rxn progresses

② General Mole balance eq.

→ for component j
→ Ideal, Isothermal

- consider a volume element ΔV over the time Δt



IN - OUT + GENERATION = ACCUMULATION

$$\left[\text{molar flow of } j \text{ into } \Delta V \text{ in } \Delta t \right] - \left[\text{molar flow of } j \text{ out of } \Delta V \text{ in } \Delta t \right] + \left[\text{molar formation of } j \text{ in } \Delta V \text{ in } \Delta t \right] = \left[\text{molar accumulation of } j \text{ in } \Delta V \text{ in } \Delta t \right]$$

$$\Rightarrow F_{j0} \cdot \Delta t - F_{jE} \cdot \Delta t + r_j \cdot \Delta V \Delta t = (C_j \Delta V)_{t+\Delta t} - (C_j \Delta V)_t$$

$$\Rightarrow F_{j|v} \cdot \Delta t - F_{j|v+\Delta V} \cdot \Delta t + r_j \cdot \Delta V \Delta t = (C_j \Delta V) \Big|_{t+\Delta t} - (C_j \Delta V) \Big|_t \rightarrow \text{General mole balance eq. for comp. } j$$

- We will apply this general eq. for the following reactors

- CVBRs and VVBRs
- PFRs
- CSTRs

2.1 Batch Reactors

- Assumptions

- Ideal (well mixed), Isothermal batch reactors
- Uniform composition ($C_i \neq f(\text{position in reactor})$)
- Start of rxn at: $t=0, T=T_0, P=P_0, C_j=C_{j0}$
- End ~ ~ ~ : $t=t, T=T_0, P=P_E, C_j=C_{jE}$
- Reactant was charged at $t=0$ and discharged at the end.

- Starting from the general mole balance eq. \Rightarrow

$$F_{j0} \Big|_0 \Delta t - F_{jE} \Big|_0 \Delta t + r_j \Delta V \Delta t = (C_j \Delta V)_{t+\Delta t} - (C_j \Delta V)_t$$

(no flowrate into or out of the batch reactor)

- Volume element ΔV can be replaced by the reactor volume since the reactor is well-mixed with uniform composition

$$\Rightarrow r_j V \Delta t = C_j V \Big|_{t+\Delta t} - C_j V \Big|_t \Rightarrow r_j V = \frac{C_j V \Big|_{t+\Delta t} - C_j V \Big|_t}{\Delta t}$$

- Limit as $\Delta t \rightarrow 0$

$$\Rightarrow r_j = \frac{1}{V} \cdot \frac{d(C_j V)}{dt} \quad \text{where } r_j \text{ is the rate of formation of } j$$

- If j is a reactant, then it is usual to write the eq. as:

$$-r_j = \frac{-1}{V} \frac{d(C_j V)}{dt} \quad (-r_j) \text{ is positive for rate of disappearance of reactant } j$$

→ The general design eq. for batch reactor,

- For a Constant Volume Batch Reactor (CVBR):

$$V = \text{cte} \Rightarrow -r_j = -\frac{dC_j}{dt}$$

- For a Variable Volume Batch Reactor (VVBR):

$$-r_j = \frac{1}{V} \left(V \frac{dC_j}{dt} + C_j \frac{dV}{dt} \right) = -\frac{dC_j}{dt} - \frac{C_j}{V} \frac{dV}{dt}$$

- The general design eq. can be ~~used~~ expressed in terms of N_j or X_j :

$$N_j = C_j V \Rightarrow -r_j = \frac{-1}{V} \frac{dN_j}{dt}$$

$$N_j = N_{j0} (1 - X_j) \Leftrightarrow -r_j = \frac{-1}{V} \frac{d[N_{j0} (1 - X_j)]}{dt} = \frac{N_{j0}}{V} \frac{dX_j}{dt}$$

- alternate expressions for the design eq. of batch reactors are:

$$\underline{-r_j = \frac{-1}{V} \cdot \frac{d(C_j V)}{dt}} \quad , \quad \underline{-r_j = \frac{-1}{V} \cdot \frac{dN_j}{dt}} \quad , \quad \underline{-r_j = \frac{N_{j0}}{V} \cdot \frac{dX_j}{dt}}$$

- to obtain $C_j, N_j,$ or X_j as a function of time, we must integrate the above expression. To do that we need to know

- V_j as a function of $C_j, N_j,$ or X_j • and in the case of VVBRs we have to express V as a function of $X_j, C_j, N_j,$ or t .

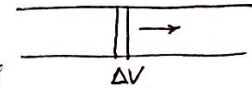
2.2 Plug Flow Reactors → PFRs

- also referred to as a tubular or piston flow reactor since the rxn takes place in a cylindrical tube or pipe.

- In a PFR, the composition of the liquid changes along the path of flow

- a PFR is normally operated at Steady-State → ~~steady~~ Conditions at any point of the reactor is time invariant
 → changes in composition occur in spatial dimension

- Consider a volume element ΔV which moves along the length of the reactor. In an ideal PFR, the following assumptions are made:



1. Perfect Radial Mixing → i.e. within the ΔV , composition is not a function of radial position.

2. No Axial Mixing → i.e. volume elements are separated from one another by a hypothetical piston which prevents axial mixing

• Composition within each ΔV , however, changes as it moves along the reactor.

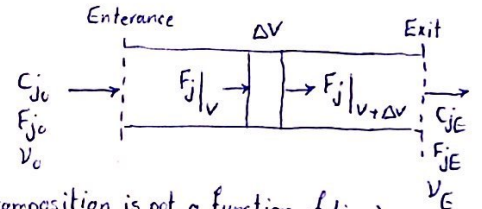
• We can think about each ΔV as a small batch reactor moving along the tubular reactor.

- Let's now develop the design eq. for the PFR:

• starting from the general mole balance eq.:

$$F_j|_V \cdot \Delta t - F_j|_{V+\Delta V} \cdot \Delta t + r_j \cdot \Delta V \cdot \Delta t = C_j \cdot \Delta V \Big|_{t+\Delta t} - C_j \cdot \Delta V \Big|_t$$

↳ = 0 (for a SS operation, composition is not a function of time)



• Hence $F_j|_V - F_j|_{V+\Delta V} + r_j \cdot \Delta V = 0$

$$\Rightarrow \frac{F_j|_{V+\Delta V} - F_j|_V}{\Delta V} = r_j \xrightarrow{\Delta V \rightarrow 0} \frac{dF_j}{dV} = r_j \quad \text{where } r_j \text{ is the rate of formation of species } j$$

- If j is a reactant, then we usually write the design eq. as:

$$\boxed{-\frac{dF_j}{dV} = -r_j} \quad \text{"Basic design eq. for a PFR"}$$

- Using $F_j = F_{j0}(1 - X_j) \Rightarrow F_{j0} \frac{dX_j}{dV} = -r_j$

- To obtain X_j (or F_j) as a function of V → We must integrate the design eq.

→ To do that, it is necessary to express $(-r_j)$ in terms of X_j (or F_j)

2.3 Continuous Stirred Tank Reactor → CSTRs

- also known as Backmix Reactor

- Normally operated at SS (compositions are time invariant)

- Fluid phase is well-mixed, composition is the same throughout the reactor.

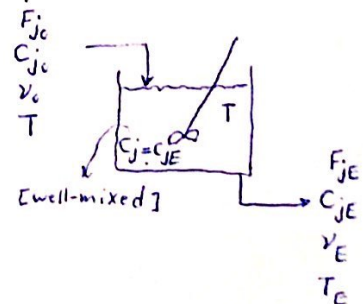
- Well-mixed behavior is for liquid phase rxns, and is harder to achieve for gas phase rxns.

- No spatial variation in concentration, rate, or T inside the reactor.

- To develop the design eq. for a CSTR, we start again with the general mole balance eq.:

$$F_j|_V \cdot \Delta t - F_j|_{V+\Delta V} \cdot \Delta t + r_j \cdot \Delta V \cdot \Delta t = C_j \Delta V \Big|_{t+\Delta t} - C_j \Delta V \Big|_t$$

= 0 (steady-state)



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

Because there is no variation in concentration or T with position inside a CSTR, the entire reactor volume has the properties of a differential volume. thus, replacing ΔV with V, we get:

$$F_{j0} - F_{jE} + r_j V = 0 \implies \frac{F_{jE} - F_{j0}}{V} = r_j \quad \text{where } r_j \text{ is the rate of formation of comp. } j$$

If j is a reactant, then we usually write the above eq. as:

$$\frac{F_{j0} - F_{jE}}{V} = -r_{jE} \quad \text{"General design eq. for a CSTR"}$$

Some alternate forms are:

$$-r_{jE} = \frac{X_{jE} F_{j0}}{V} \quad F_{j0} = v_0 C_{j0} \implies -r_{jE} = \frac{X_{jE} v_0 C_{j0}}{V} \quad \tau = \frac{V}{v_0} \implies -r_{jE} = \frac{X_{jE} C_{j0}}{\tau}$$

- Ex. 01 → CVBR, VVBR [V = f(t)]

- Consider the gas phase rxn: $A + B \rightarrow C$ which follows 2nd order kinetics with $-r_A = k C_A C_B$
- the value of k at 100°C is $1.0 \times 10^{-5} \text{ m}^3/\text{mol}\cdot\text{s}$ [Note that A is the limiting reactant]
- 0.05 moles of A and 0.2 moles of B are charged to a batch reactor. What is the fractional conversion of A if the rxn is carried out at 100°C for 500 s
- a) in a CVBR with $V = 0.001 \text{ m}^3$
- b) in a VVBR with $V = V_0(1 + 0.002t) \text{ m}^3$, $V_0 = 0.001 \text{ m}^3$

- Deriving the specific design eq.

start with the design eq. : $-r_A = \frac{-1}{V} \frac{d(C_A V)}{dt} = \frac{-1}{V} \frac{dN_A}{dt}$, $N_A = N_{A0}(1 - X_A)$

substituting N_A we would get: $-r_A = \frac{N_{A0}}{V} \frac{dX_A}{dt}$ (I)

express $(-r_A)$ in terms of X_A : $-r_A = k C_A C_B = k \frac{N_A}{V} \frac{N_B}{V} = k \frac{N_{A0}(1 - X_A)}{V} \frac{N_B}{V}$ (II)

now we have to express N_A & N_B in terms of X_A . This can be done by setting up a stoichiometric table:

Comp.	initially	at time t	in terms of X_A	# of moles of A reacted = $N_{A0} - N_A = N_{A0} X_A$
A	N_{A0}	N_A	$N_{A0}(1 - X_A)$	
B	N_{B0}	$N_{B0} - (N_{A0} - N_A)$	$N_{B0} - N_{A0} X_A$	$N_B = N_{B0} - N_{A0} X_A = N_{A0} (\frac{N_{B0}}{N_{A0}} - X_A)$ (III)
C	0	$N_{A0} - N_A$	$N_{A0} X_A$	
total	$N_{A0} + N_{B0}$	$N_{B0} + N_A$	$N_{B0} + N_{A0}(1 - X_A)$	

(II), (III) $\implies -r_A = k \frac{N_{A0}^2}{V^2} (1 - X_A) (\frac{N_{B0}}{N_{A0}} - X_A)$ (IV)

(I) = (IV) $\implies \frac{k}{V} N_{A0} (1 - X_A) (\frac{N_{B0}}{N_{A0}} - X_A) = \frac{dX_A}{dt}$ "Design eq. for our system"

- a) CVBR

$v = cte \implies \int \frac{k N_{A0}}{V} \int_0^t dt = \int_0^{X_{AE}} \frac{dX_A}{(1 - X_A) (\frac{N_{B0}}{N_{A0}} - X_A)}$

NOTE: $\int \frac{dx}{(ax+b)(px+q)} = \frac{1}{bp-aq} \ln \left(\frac{px+q}{ax+b} \right)$

integrating: $(\frac{N_{B0}}{N_{A0}} - 1) \frac{N_{A0}}{V} kt = \ln \left(\frac{1 - \frac{N_{A0}}{N_{B0}} X_{AE}}{1 - X_{AE}} \right)$

using given data: $0.75 = \ln \left(\frac{1 - 0.25 X_{AE}}{1 - X_{AE}} \right) \implies (1 - X_{AE}) e^{0.75} = 1 - 0.25 X_{AE}$
 $\implies e^{0.75} - 1 = (e^{0.75} - 0.25) X_{AE} \implies X_{AE} = \frac{e^{0.75} - 1}{e^{0.75} - 0.25} \implies X_{AE} = 0.598$

- b) VVBR

$V = V_0(1 + 0.002t) \implies \int \frac{k N_{A0}}{V_0(1 + 0.002t)} dt = \int_0^{X_{AE}} \frac{dX_A}{(1 - X_A) (\frac{N_{B0}}{N_{A0}} - X_A)}$

$\implies \frac{k N_{A0}}{V_0} (\frac{N_{B0}}{N_{A0}} - 1) \frac{1}{0.002} \ln(1 + 0.002t) = \ln \left(\frac{1 - \frac{N_{A0}}{N_{B0}} X_A}{1 - X_A} \right)$

solving for X_{AE} : $X_{AE} = 0.476$

- Note for VVBR:

- as v increases with time, concentrations of A and B are decreased.
- hence, the rxn rate is decreased as we get a smaller fractional conversion
- V varies by external means

- Ex. 02 → Reactor volume gas phase [Levenspiel p. 113]
 → gas phase decomposition of phosphine $4\text{PH}_3^A \rightarrow \text{P}_4^B + 6\text{H}_2^C$, $T=925\text{K}$, $P=4.6\text{ atm}$
 follows 1st-order kinetics: $-r_{\text{PH}_3} = kC_{\text{PH}_3}$, $k=2.8 \times 10^{-3}\text{ (1/s)}$
 → What volume of a PFR is required to obtain 80% conversion of a feed containing $1.2 \times 10^{-3}\text{ mol/s}$ of pure phosphine? [assume ideal gas and constant pressure]

- Ex. 02 solution

→ starting from the design eq. for a PFR: $F_{A0} \frac{dX_A}{dV} = -r_A = kC_A \Rightarrow F_{A0} \frac{dX_A}{kC_A} = dV$
 → integrate: $V = \int_0^{X_{AE}} dV = F_{A0} \int_0^{X_{AE}} \frac{dX_A}{kC_A}$
 → to perform integration, we need to express C_A in terms of X_A ; construct the stoichiometric table.

comp.	initial	at any point	in terms of X_A	mole fraction
A	F_{A0}	F_A	$F_{A0}(1-X_A)$	F_A/F_t
B	0	$\frac{1}{4}(F_{A0}-F_A)$	$\frac{1}{4}F_{A0}X_A$	F_B/F_t
C	0	$\frac{3}{2}(F_{A0}-F_A)$	$\frac{3}{2}F_{A0}X_A$	F_C/F_t
total	F_{A0}	$F_{A0}(1+\frac{3}{4}X_A)$	$F_{A0}(1+\frac{3}{4}X_A)$	1

$C_A = \frac{F_A}{F_t} C_t$, $C_t = \frac{P}{RT}$ (ideal gas)
 $\Rightarrow C_A = \frac{F_{A0}(1-X_A)}{F_{A0}(1+\frac{3}{4}X_A)} \left(\frac{P}{RT}\right)$

$V = F_{A0} \int_0^{X_{AE}} \frac{dX_A}{\frac{kP}{RT} \frac{(1-X_A)}{1+\frac{3}{4}X_A}} = \frac{F_{A0}RT}{kP} \int_0^{X_{AE}} \frac{1+\frac{3}{4}X_A}{1-X_A} dX_A$
 $\Rightarrow V = \frac{F_{A0}}{k} \frac{RT}{P} \left[-\frac{3}{4}X_A - (1+\frac{3}{4}) \ln(1-X_A) \right]_0^{X_{AE}}$
 $\Rightarrow V = 1.5673 \times 10^{-2} \text{ m}^3$

- Ex. 03 → Fractional Conversion, gas phase
 → gas phase rxn: $3A \rightarrow B$, $-r_A = kC_A^2$, $k=9.045 \times 10^{-6}\text{ m}^3/\text{mol s}$, ideal gas, constant P
 → Feed: $8 \times 10^{-4}\text{ mol/s}$, pure A, $C_{A0}=50\text{ mol/m}^3$, $V_R=5\text{ m}^3$
 → What is the fractional conversion of A?

- Ex. 03 solution

→ Design eq.: $-r_A = \frac{X_{AE} v_0 C_{A0}}{V} = kC_A^2$
 → use the stoichiometric table to express C_A in terms of X_{AE} :
 → for a constant P, ideal gas: $C_{tE} = \frac{P}{RT} = C_{t0} = C_{A0}$

comp.	inlet	Exit	in terms of X_{AE}
A	F_{A0}	$F_A = F_{A0}(1-X_{AE})$	$F_{A0}(1-X_{AE})$
B	0	$\frac{1}{3}(F_{A0}-F_A)$	$\frac{1}{3}F_{A0}X_{AE}$
total	F_{A0}	$F_{A0}(1-\frac{2}{3}X_{AE})$	$F_{A0}(1-\frac{2}{3}X_{AE})$

$C_{AE} = \frac{F_{AE}}{F_{tE}} C_{tE} = \frac{F_{AE}}{F_{tE}} C_{A0} = \frac{F_{A0}(1-X_{AE})}{F_{A0}(1-\frac{2}{3}X_{AE})} C_{A0}$
 $C_{AE} = \left(\frac{1-X_{AE}}{1-\frac{2}{3}X_{AE}} \right) C_{A0}$
 → substituting in the design eq.: $\frac{X_{AE} v_0 C_{A0}}{V} = k C_{A0}^2 \left(\frac{1-X_{AE}}{1-\frac{2}{3}X_{AE}} \right)^2 \Rightarrow \frac{v_0}{k C_{A0} V} = \frac{(1-X_{AE})^2}{X_{AE} (1-\frac{2}{3}X_{AE})^2}$
 → solving method: Gauss Seidel with relaxation [initial guess: 0 (?), relaxation factor: 0.7]
 → solving for X_{AE} : $X_{AE} = 0.585$