

Lecture 5

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Lecture 5 – Thursday 1/24/2013

- Block 1: **Mole Balances**
- Block 2: **Rate Laws**
- Block 3: **Stoichiometry**
 - Stoichiometric Table: Flow
 - Definitions of Concentration: Flow
 - Gas Phase Volumetric Flow Rate
 - Calculate the Equilibrium Conversion X_e

Review Lecture 2

Reactor Mole Balances Summary

in terms of conversion, X

Reactor

Differential

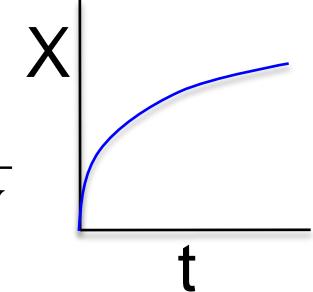
Algebraic

Integral

Batch

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

$$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$$



CSTR

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

PFR

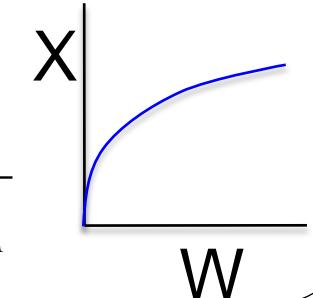
$$F_{A0} \frac{dX}{dV} = -r_A$$

$$V = F_{A0} \int_0^X \frac{dX}{-r_A}$$

PBR

$$F_{A0} \frac{dX}{dW} = -r'_A$$

$$W = F_{A0} \int_0^X \frac{dX}{-r'_A}$$



Algorithm

How to find $-r_A = f(X)$

Step 1: Rate Law $-r_A = g(C_i)$



Step 2: Stoichiometry $(C_i) = h(X)$

Step 3: Combine to get $-r_A = f(X)$

Reaction Engineering

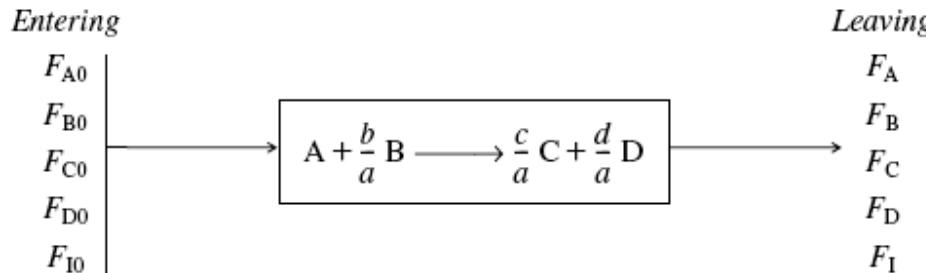
Mole Balance

Rate Laws

Stoichiometry

These topics build upon one another

Flow System Stoichiometric Table



<u>Species</u>	<u>Symbol</u>	<u>Reactor Feed</u>	<u>Change</u>	<u>Reactor Effluent</u>
A	A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	B	$F_{B0} = F_{A0}\Theta_B$	$-b/aF_{A0}X$	$F_B = F_{A0}(\Theta_B - b/aX)$
C	C	$F_{C0} = F_{A0}\Theta_C$	$+c/aF_{A0}X$	$F_C = F_{A0}(\Theta_C + c/aX)$
D	D	$F_{D0} = F_{A0}\Theta_D$	$+d/aF_{A0}X$	$F_D = F_{A0}(\Theta_D + d/aX)$
Inert	I	$F_{I0} = F_{A0}\Theta_I$	-----	$F_I = F_{A0}\Theta_I$
				<hr/>
		F_{T0}		$F_T = F_{T0} + \delta F_{A0}X$

Where: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}v_0}{C_{A0}v_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

6 Concentration – Flow System $C_A = \frac{F_A}{v}$

Stoichiometry

Concentration Flow System: $C_A = \frac{F_A}{v}$

Liquid Phase Flow System: $v = v_0$

Liquid Systems

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1-X)}{v_0} = C_{A0}(1-X) \quad \text{Flow Liquid Phase}$$

$$C_B = \frac{N_B}{V} = \frac{N_{A0}}{V_0} \left(\Theta_B - \frac{b}{a} X \right) = C_{A0} \left(\Theta_B - \frac{b}{a} X \right)$$

etc.

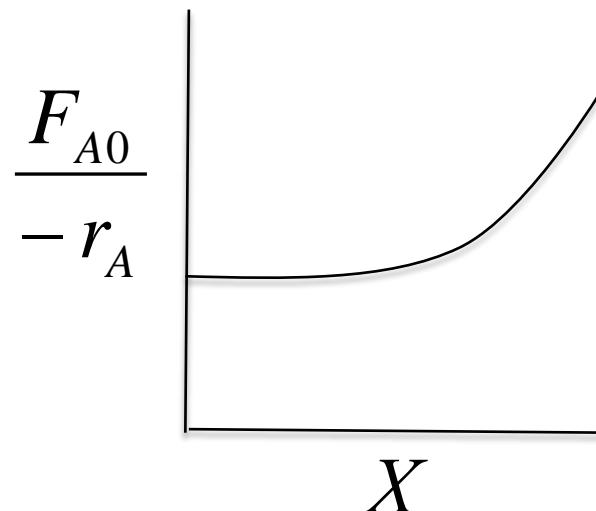
Liquid Systems



If the rate of reaction were $-r_A = kC_A C_B$

then we would have $-r_A = C_{A0}^2 \left(1 - X\right) \left(\Theta_B - \frac{b}{a} X\right)$

This gives us $-r_A = f(X)$



Stoichiometry for Gas Phase Flow Systems

Combining the compressibility factor equation of state with $Z = Z_0$

Stoichiometry: $C_T = \frac{P}{ZRT}$

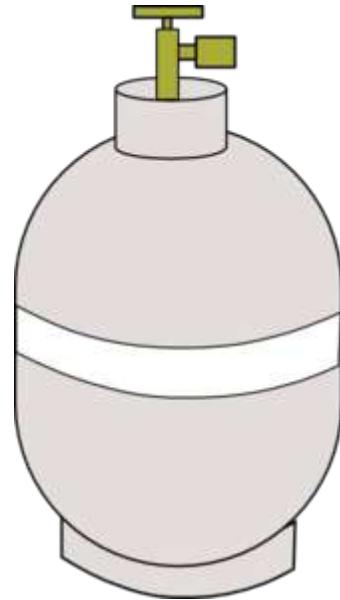
$$C_{T0} = \frac{P_0}{Z_0 R_0 T_0}$$

$$F_T = C_T v$$

$$F_{T0} = C_{T0} v_0$$

We obtain:

$$v = v_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$



Stoichiometry for Gas Phase Flow Systems

$$C_A = F_A/v = \frac{F_A}{v_0 \left(\frac{F_T}{F_0} \right)} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right) = \frac{F_{T0}}{v_0} \frac{F_A}{F_T} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

Since $C_{T0} = F_{T0}/v_0$,

$$C_A = F_A/v = C_{T0} \frac{F_A}{F_T} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

Using the same method,

$$C_B = C_{T0} \left(\frac{F_B}{F_T} \right) \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

Stoichiometry for Gas Phase Flow Systems

The total molar flow rate is: $F_T = F_{T0} + F_{A0}\delta X$

Substituting F_T gives:

$$\begin{aligned} v &= v_0 \left(\frac{F_{T0} + F_{A0}\delta X}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P} = v_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{T}{T_0} \frac{P_0}{P} \\ &= v_0 \left(1 + y_{A0} \delta X \right) \frac{T}{T_0} \frac{P_0}{P} = v_0 \left(1 + \varepsilon X \right) \frac{T}{T_0} \frac{P_0}{P} \end{aligned}$$

Where $\varepsilon = y_{A0}\delta$

For Gas Phase Flow Systems

Concentration Flow System: $C_A = \frac{F_A}{v}$

Gas Phase Flow System: $v = v_0(1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}$

$$C_A = \frac{F_A}{v} = \frac{F_{A0}(1 - X)}{v_0(1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

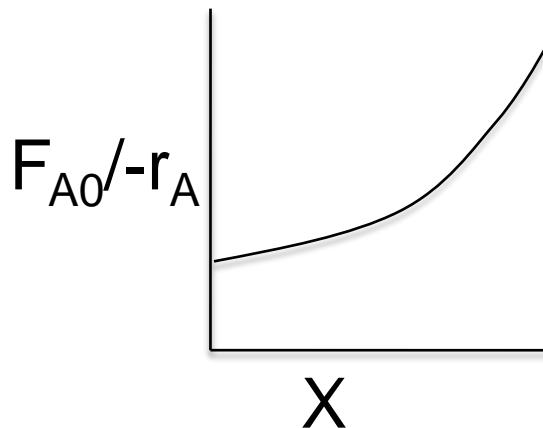
$$C_B = \frac{F_B}{v} = \frac{F_{A0} \left(\Theta_B - \frac{b}{a} X \right)}{v_0(1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{C_{A0} \left(\Theta_B - \frac{b}{a} X \right)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

For Gas Phase Flow Systems

If $-r_A = k C_A C_B$

$$-r_A = k_A C_{A0}^2 \left[\frac{(1-X)}{(1+\varepsilon X)} \frac{\left(\Theta_B - \frac{b}{a} X \right)}{(1+\varepsilon X)} \left(\frac{P}{P_0} \frac{T_0}{T} \right)^2 \right]$$

This gives us



For Gas Phase Flow Systems

where

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

$$\delta = \frac{\text{change in total number of moles}}{\text{mole of A reacted}}$$

$$\varepsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{F_{A0}}{F_{T0}} = y_{A0} \delta$$

$$\boxed{\varepsilon = y_{A0} \delta}$$

$$\varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$$

Example: Calculating the equilibrium conversion (X_{ef}) for **gas phase** reaction in a flow reactor

Consider the following elementary reaction where

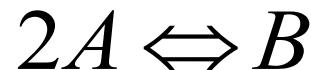
$K_C = 20 \text{ dm}^3/\text{mol}$ and $C_{A0} = 0.2 \text{ mol/dm}^3$.

Calculate Equilibrium Conversion or both a batch reactor (X_{eb}) and a flow reactor (X_{ef}).



$$-r_A = k_A \left[C_A^2 - \frac{C_B}{K_C} \right]$$

Gas Flow Example (X_{ef})



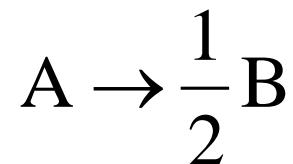
$$X_{eb} = 0.703$$

$$X_{ef} = ?$$

Solution:

Rate Law:

$$-r_A = k_A \left[C_A^2 - \frac{C_B}{K_C} \right]$$



Gas Flow Example (X_{ef})

<u>Species</u>	<u>Fed</u>	<u>Change</u>	<u>Remaining</u>
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	0	$+F_{A0}X/2$	$F_B = F_{A0}X/2$
	$F_{T0} = F_{A0}$		$F_T = F_{A0} - F_{A0}X/2$

Gas Flow Example (X_{ef})

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

$$B \quad 0 \quad F_{A0}X/2 \quad F_B = F_{A0}X/2$$

Stoichiometry:

Gas isothermal
Gas isobaric

$T = T_0$
 $P = P_0$

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

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

$$C_B = \frac{F_{A0}X/2}{v_0(1+\varepsilon X)} = \frac{C_{A0}(1-X)}{2(1+\varepsilon X)}$$

Gas Flow Example (X_{ef})

$$-r_A = k_A \left[\left(\frac{C_{A0}(1-X)}{(1+\varepsilon X)} \right)^2 - \frac{C_{A0}X}{2(1+\varepsilon X)K_C} \right]$$

Pure A $\rightarrow y_{A0}=1$, $C_{A0}=y_{A0}P_0/RT_0$, $C_{A0}=P_0/RT_0$

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

At equilibrium: $-r_A=0$

$$2K_C C_{A0} = \frac{X_e(1+\varepsilon X_e)}{(1-X_e)^2}$$

Gas Flow Example (X_{ef})

$$2K_C C_{A0} = 2 \left(20 \frac{dm^3}{mol} \right) \left(0.2 \frac{mol}{dm^3} \right) = 8$$

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

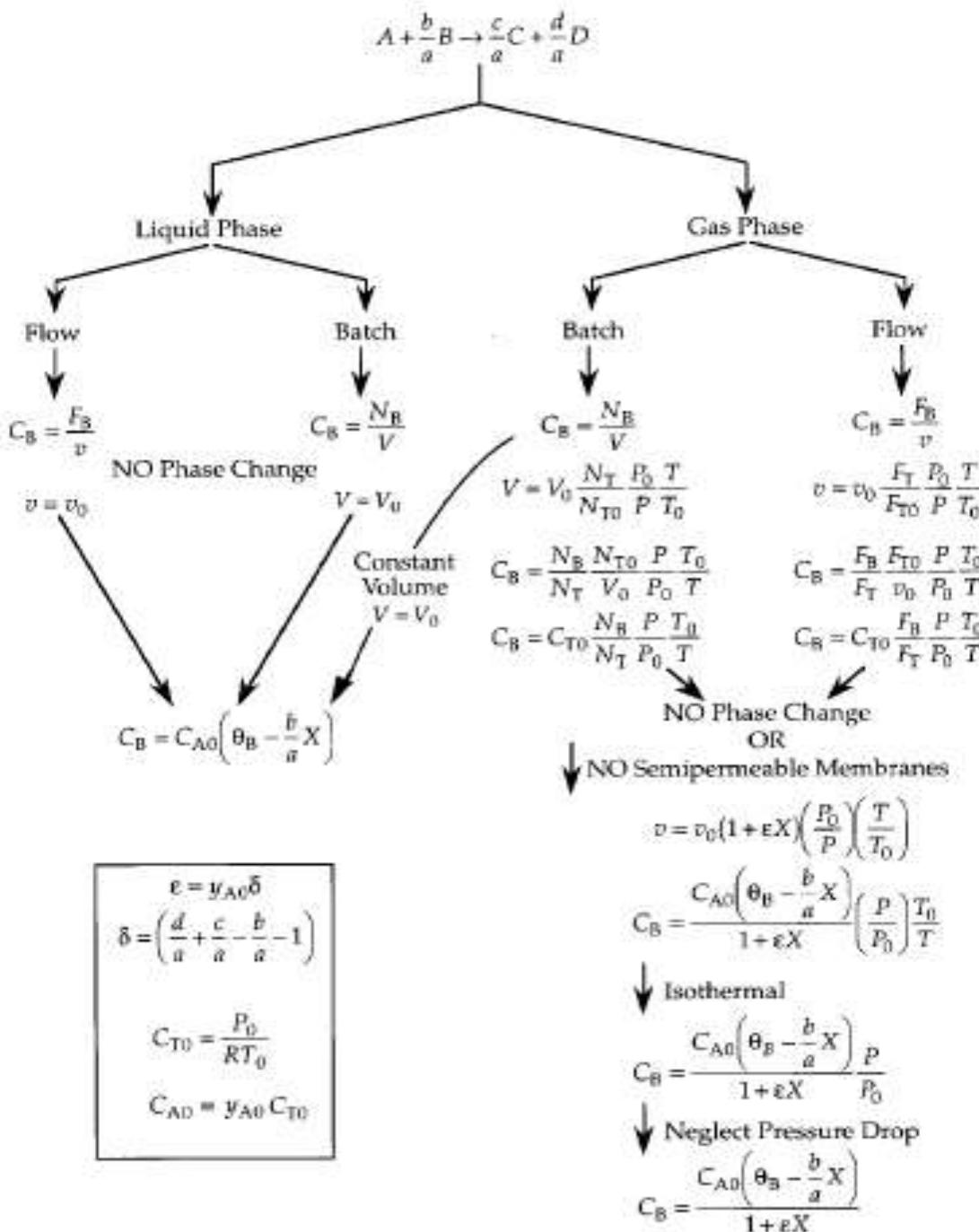
$$8 = \frac{X_e - 0.5X_e^2}{(1 - 2X_e + X_e^2)}$$

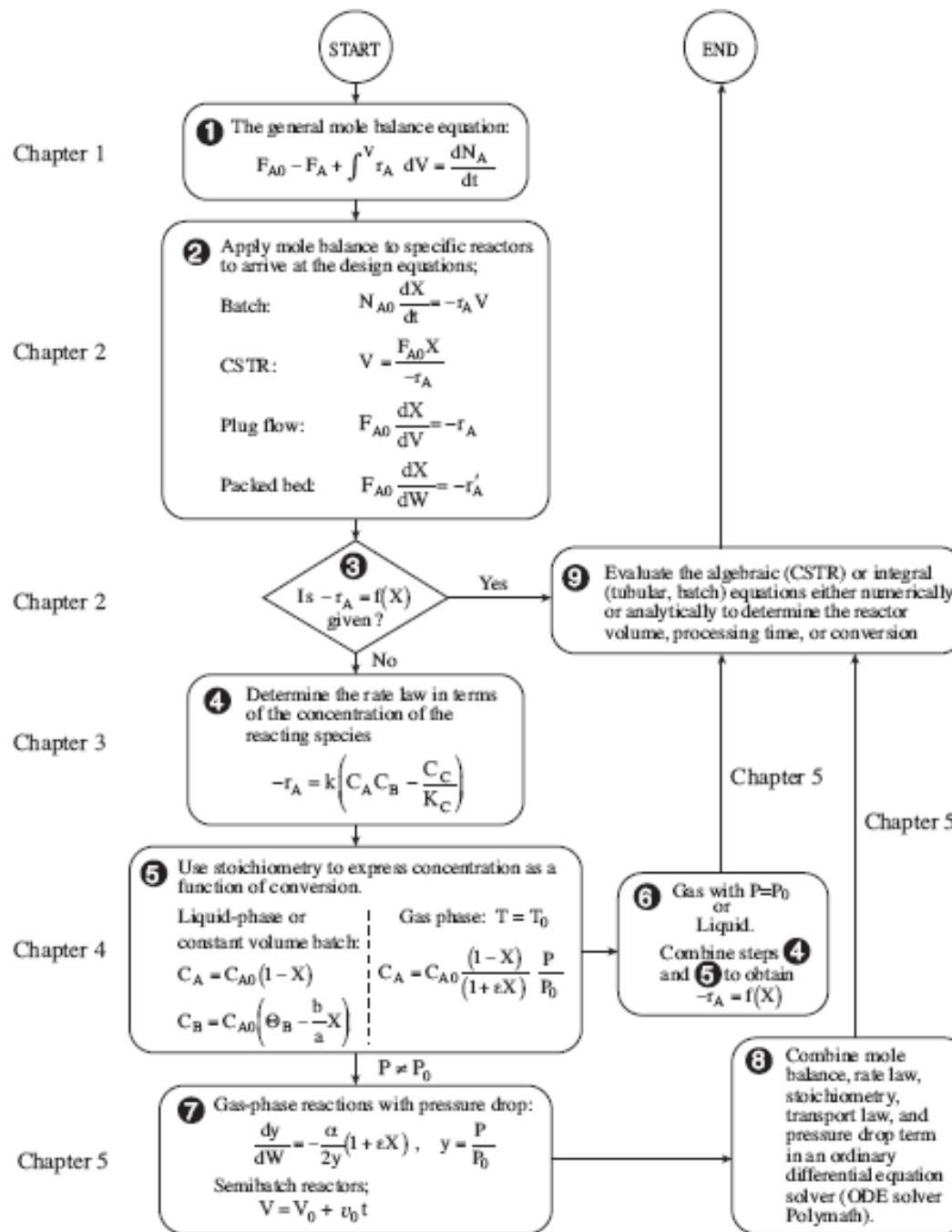
$$8.5X_e^2 - 17X_e + 8 = 0$$

Flow: $X_{ef} = 0.757$

Recall

Batch: $X_{eb} = 0.70$





Choices



1. MOLE BALANCES

$$\text{PFR} \quad \frac{dX}{dV} = -\frac{-r_A}{F_{A0}}$$

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

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

2. RATE LAWS

$$-\dot{r}_A = k C_A$$

$$-\dot{r}_A = \frac{k C_A}{1 + K_A C_A}$$

$$-\dot{r}_A = k \left[C_A - \frac{C_B C_C}{K_e} \right]$$

3. STOICHIOMETRY

$$\text{FLOW} \quad C_A = \frac{F_A}{V}$$

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

$$\text{BATCH} \quad C_A = \frac{N_A}{V}$$

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

LIQUID $\xrightarrow{\text{Constant flow rate}}$ IDEAL GAS $\xrightarrow{\text{Variable flow rate}}$

IDEAL GAS $\xrightarrow{\text{Variable volume}}$ LIQUID OR GAS $\xrightarrow{\text{Constant volume}}$

$$v = v_0$$

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

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

$$V = V_0$$

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

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

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

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

4. COMBINE (First Order Gas-Phase Reaction in a PFR)

From mole balance

From rate law

From stoichiometry

$$\frac{dX}{dV} = -\frac{-r_A}{F_{A0}} = \frac{k C_A}{F_{A0}} = \frac{k}{F_{A0}} \left(C_{A0} \frac{(1-X)}{(1+\epsilon X)} \frac{P_0 T_0}{P_0 T} \right)$$

$$\frac{dX}{dV} = \frac{k (1-X)}{v_0 (1+\epsilon X)} y \frac{T_0}{T}, \text{ where } y = \frac{P}{P_0} \quad (\text{A})$$

Integrating for the case of constant temperature and pressure gives

$$V = \frac{v_0}{k} \left[(1+\epsilon) \ln \left(\frac{1}{1-X} \right) - \epsilon X \right] \quad (\text{B})$$

End of Lecture 5