

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

- 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

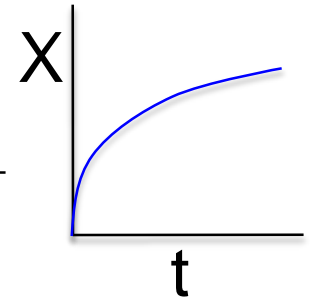
Algebraic

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

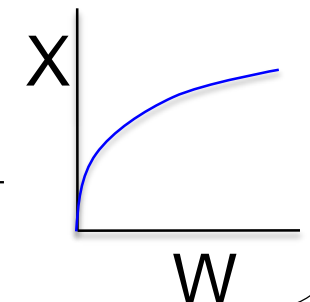
$$F_{A0} \frac{dX}{dV} = -r_A$$

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

PBR

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

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

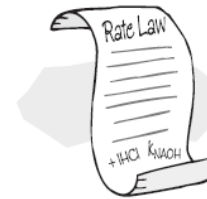


Review Lecture 3

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



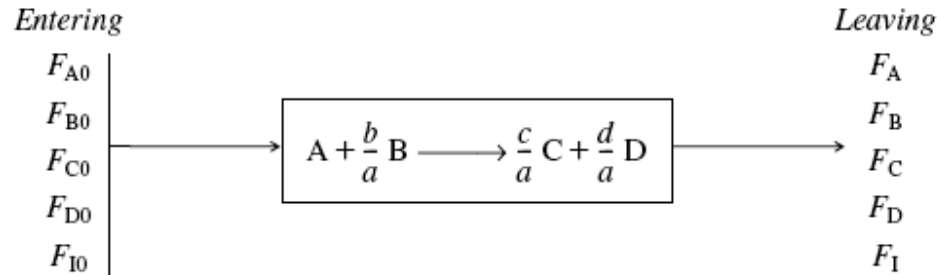
Rate Laws



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}		<hr/> $F_T = F_{T0} + \delta F_{A0}X$

Where: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}\nu_0}{C_{A0}\nu_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

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

Stoichiometry

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

Liquid Phase Flow System: $\nu = \nu_0$

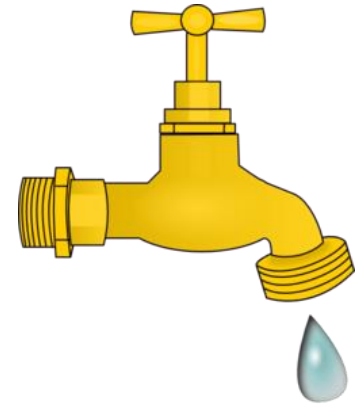
Liquid Systems

$$C_A = \frac{F_A}{\nu} = \frac{F_{A0}(1-X)}{\nu_0} = C_{A0}(1-X) \quad \text{Flow Liquid Phase}$$

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

etc.

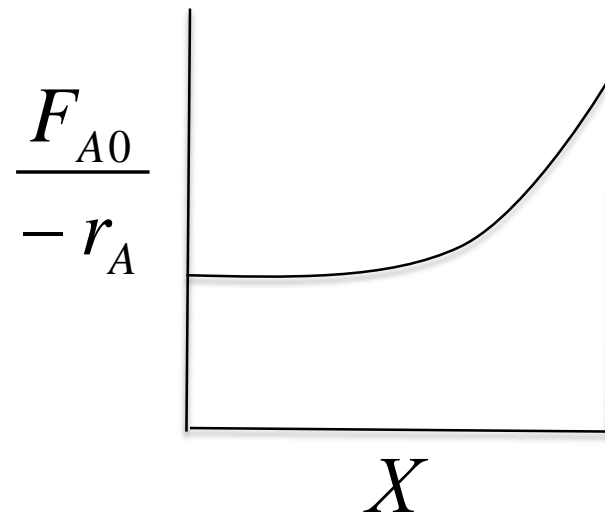
Liquid Systems



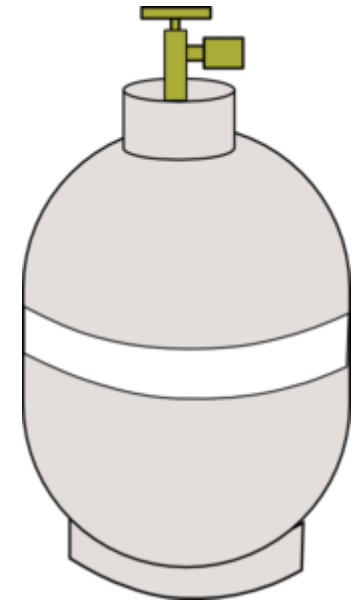
If the rate of reaction were $-r_A = kC_A C_B$

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

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

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

$$F_T = C_T \nu$$

$$F_{T0} = C_{T0} \nu_0$$

We obtain:

$$\nu = \nu_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

Stoichiometry

for Gas Phase Flow Systems

$$C_A = F_A/\nu = \frac{F_A}{\nu_0 \left(\frac{F_T}{F_0} \right)} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right) = \frac{F_{T0}}{\nu_0} \frac{F_A}{F_T} \left(\frac{P}{P_0} \right) \left(\frac{T_0}{T} \right)$$

Since $C_{T0} = F_{T0}/\nu_0$,

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

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:

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

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

For Gas Phase Flow Systems

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

$$\text{Gas Phase Flow System: } \nu = \nu_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}$$

$$C_A = \frac{F_A}{\nu} = \frac{F_{A0}(1-X)}{\nu_0(1+\varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{C_{A0}(1-X) T_0 P}{(1+\varepsilon X) T P_0}$$

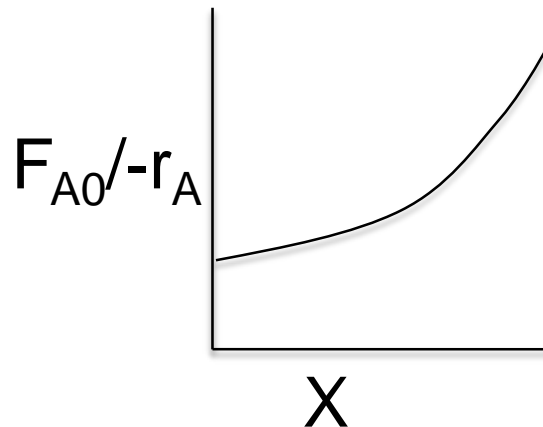
$$C_B = \frac{F_B}{\nu} = \frac{F_{A0} \left(\Theta_B - \frac{b}{a} X \right)}{\nu_0(1+\varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{C_{A0} \left(\Theta_B - \frac{b}{a} X \right) T_0 P}{(1+\varepsilon X) T P_0}$$

For Gas Phase Flow Systems

If $-r_A = kC_A C_B$

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

This gives us



For Gas Phase Flow Systems

where

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

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

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

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

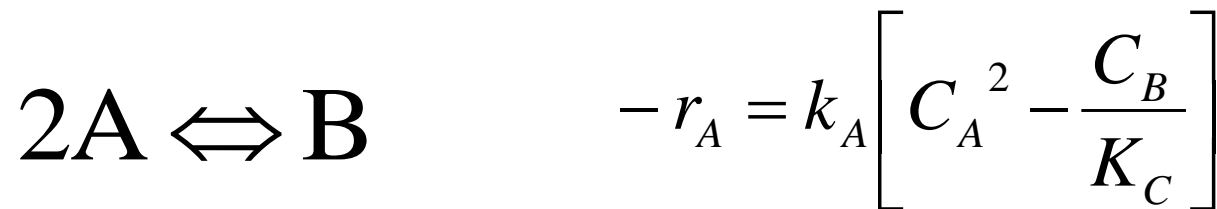
$$\varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$$

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

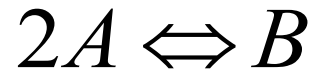
Consider the following elementary reaction where

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

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



Gas Flow Example (X_{ef})



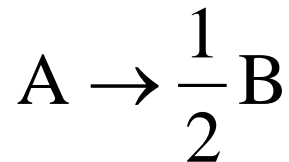
$$X_{eb} = 0.703$$

$$X_{ef} = ?$$

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	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1-X)$
B	0	$F_{A0}X/2$	$F_B = F_{A0}X/2$

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})

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

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

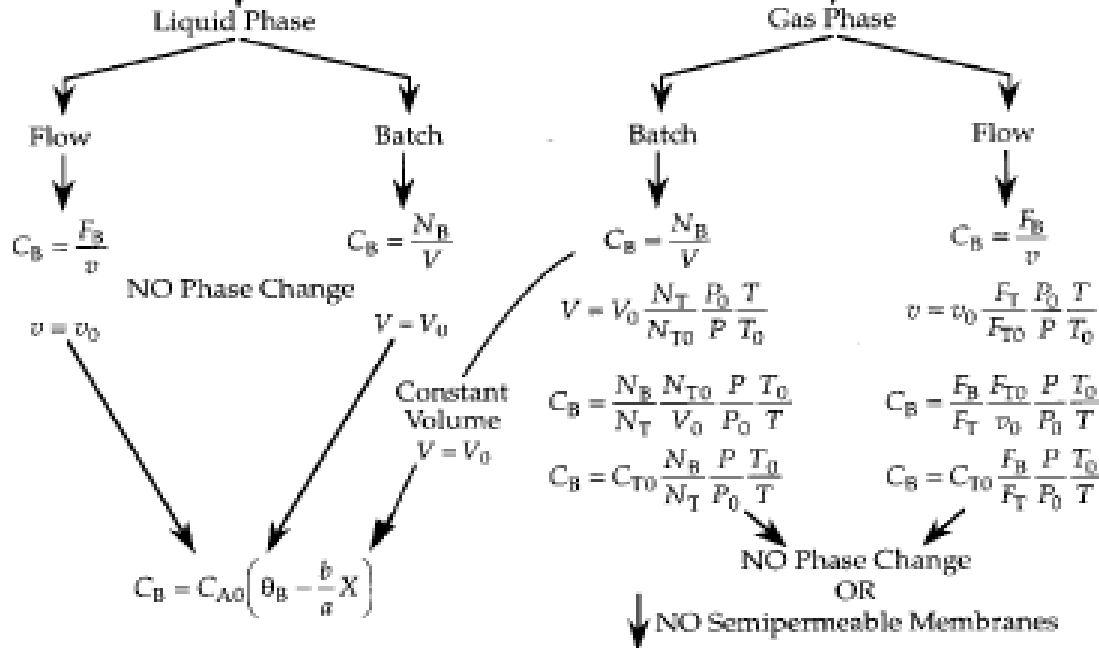
$$8 = \frac{X_e - 0.5X_e^2}{(1 - 2X_e + X_e^2)}$$

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

Flow: $X_{ef} = 0.757$

Recall

Batch: $X_{eb} = 0.70$



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

$$\delta = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right)$$

$$C_{T0} = \frac{P_0}{RT_0}$$

$$C_{A0} = y_{A0} C_{T0}$$

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

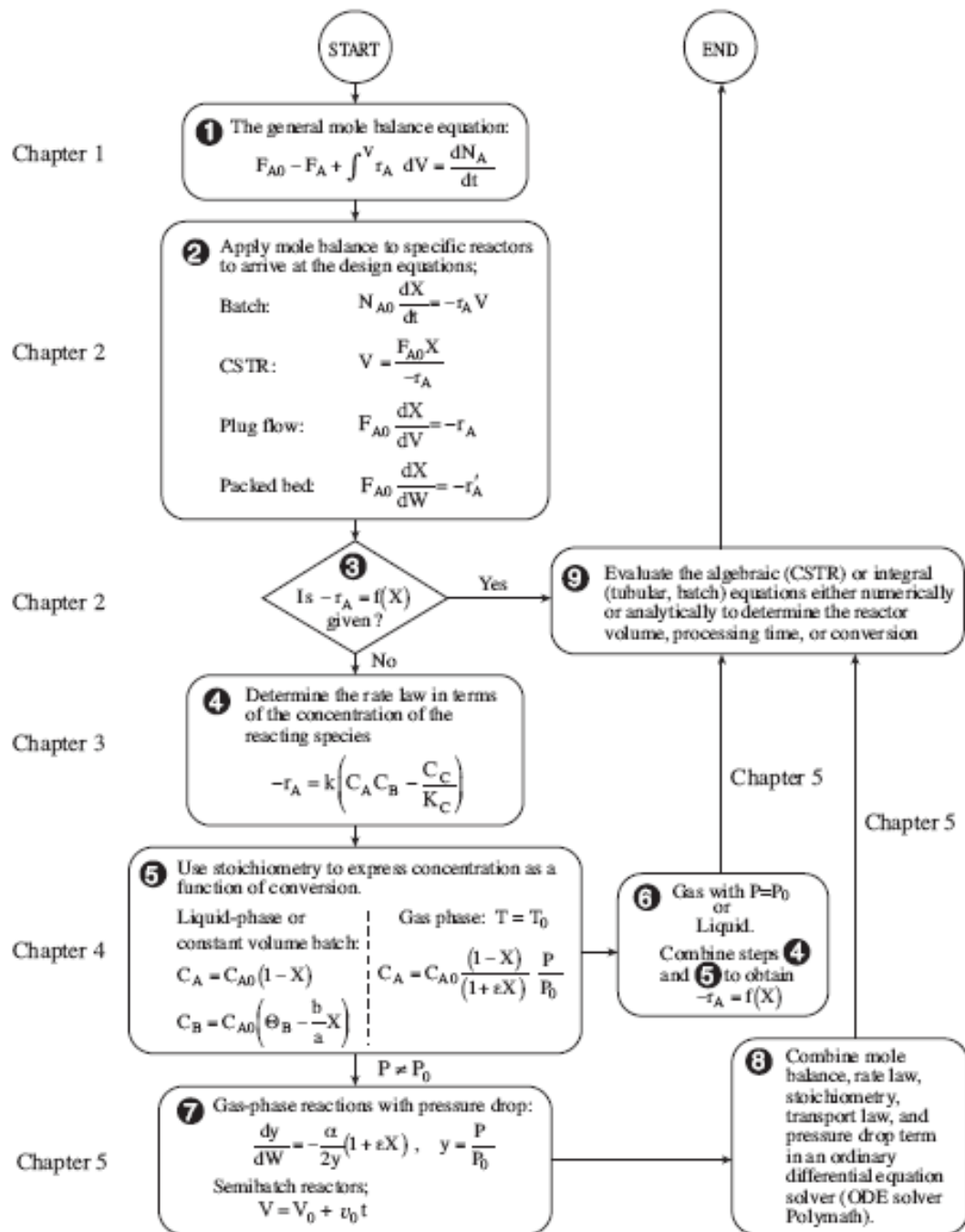
$$C_B = \frac{C_{A0} \left(\theta_B - \frac{b}{a} X \right)}{1 + \varepsilon X} \left(\frac{P}{P_0} \right) \frac{T_0}{T}$$

↓ Isothermal

$$C_B = \frac{C_{A0} \left(\theta_B - \frac{b}{a} X \right) P}{1 + \varepsilon X P_0}$$

↓ Neglect Pressure Drop

$$C_B = \frac{C_{A0} \left(\theta_B - \frac{b}{a} X \right)}{1 + \varepsilon X}$$



Choices



1. MOLE BALANCES

PFR $\frac{dX}{dV} = \frac{-r_A}{F_{A0}}$ CSTR $V = \frac{F_{A0}X}{-r_A}$ BATCH $\frac{dX}{dt} = \frac{-r_A V}{N_{A0}}$

2. RATE LAWS

$-r_A = kC_A$ $-r_A = \frac{kC_A}{1 + K_A C_A}$ $-r_A = k \left[C_A - \frac{C_B C_C}{K_e} \right]$

3. STOICHIOMETRY

FLOW $C_A = \frac{F_A}{V}$ BATCH $C_A = \frac{N_A}{V}$
 $F_A = F_{A0}(1 - X)$ $N_A = N_{A0}(1 - X)$

LIQUID Constant flow rate $v = v_0$ IDEAL GAS Variable flow rate $v = v_0(1 + \epsilon X) \frac{P_0 T}{P T_0}$ IDEAL GAS Variable volume $V = V_0(1 + \epsilon X) \frac{P_0 T}{P T_0}$ LIQUID OR GAS Constant volume $V = V_0$

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

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

From mole balance From rate law From stoichiometry

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

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

Integrating for the case of constant temperature and pressure gives

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

End of Lecture 5