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.

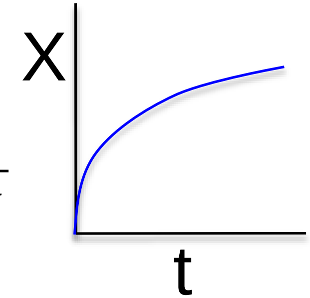
Lecture 5

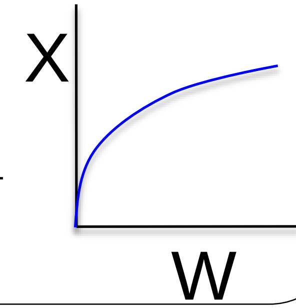
- Block 1: **Mole Balances**
- Block 2: **Rate Laws**
- Block 3: **Stoichiometry**
  - Stoichiometric Table: Flow
  - Definitions of Concentration: Flow
  - Gas Phase Volumetric Flow Rate
  - Calculate the Equilibrium Conversion X_e

Reactor Mole Balances Summary

in terms of conversion, X

Reactor	Differential	Algebraic	Integral
Batch	$N_{A0}\dfrac{dX}{dt} = -r_A V$		$t = N_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A V}$
CSTR		$V = \dfrac{F_{A0}X}{-r_A}$	
PFR	$F_{A0}\dfrac{dX}{dV} = -r_A$		$V = F_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A}$
PBR	$F_{A0}\dfrac{dX}{dW} = -r_A'$		$W = F_{A0}\displaystyle\int_0^X \dfrac{dX}{-r_A'}$





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 $-r_A = f(X)$

Review Lecture 3

Reaction Engineering

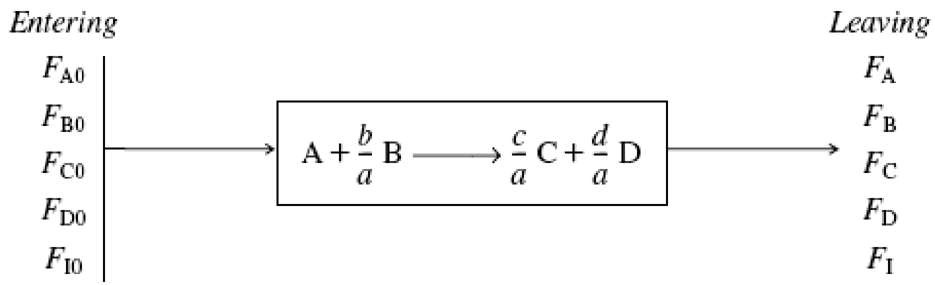
Mole Balance

Rate Laws

Stoichiometry

These topics build upon one another

Flow System Stoichiometric Table



Species	**Symbol**	**Reactor Feed**	**Change**	**Reactor Effluent**
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	$F_{I0}=F_{A0}\Theta_I$	----------	$F_I=F_{A0}\Theta_I$
		F_{T0}		$F_T=F_{T0}+\delta F_{A0}X$

Where: $\Theta_i = \frac{F_{i0}}{F_{A0}} = \frac{C_{i0}\upsilon_0}{C_{A0}\upsilon_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$ and $\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$

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

Stoichiometry

Concentration Flow System: $C_A = \dfrac{F_A}{\upsilon}$

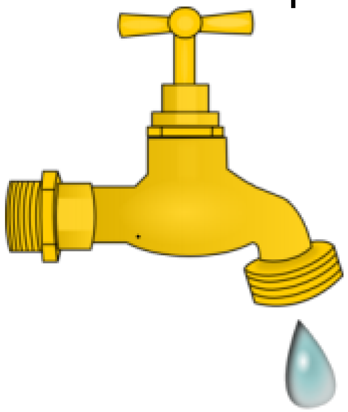
Liquid Phase Flow System: $\upsilon = \upsilon_0$

Liquid Systems

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1-X)}{\upsilon_0} = C_{A0}(1-X)$$ 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.

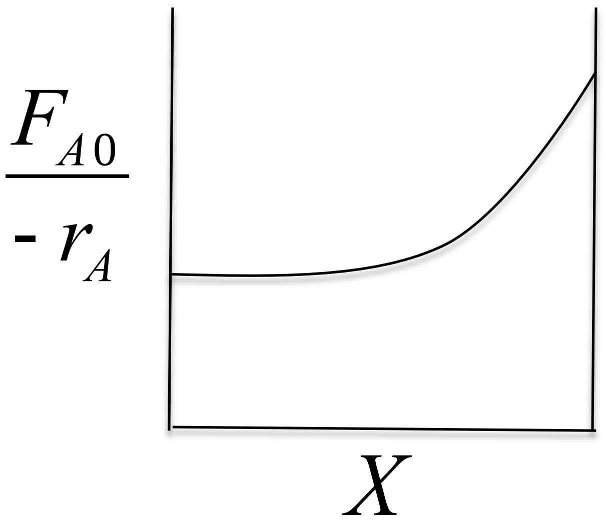


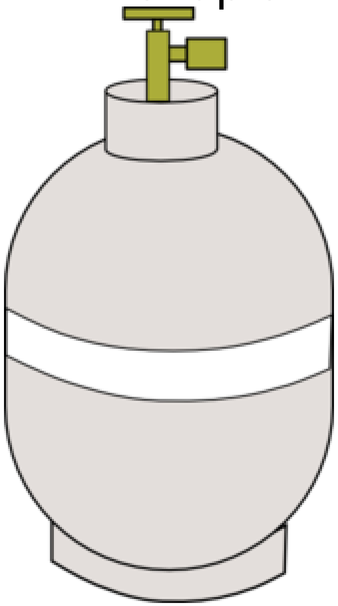
Liquid Systems

If the rate of reaction were $-r_A = kC_AC_B$

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

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:

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

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

$$F_T = C_T \upsilon$$

$$F_{T0} = C_{T0} \upsilon_0$$

We obtain:

$$\boxed{\upsilon = \upsilon_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}}$$

Stoichiometry for Gas Phase Flow Systems

$$C_A = F_A/\upsilon = \frac{F_A}{\upsilon_0\left(\frac{F_T}{F_0}\right)}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right) = \frac{F_{T0}}{\upsilon_0}\frac{F_A}{F_T}\left(\frac{P}{P_0}\right)\left(\frac{T_0}{T}\right)$$

Since $C_{T0} = F_{T0}/\upsilon_0$,

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

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:

$$\upsilon = \upsilon_0 \left(\frac{F_{T0} + F_{A0}\delta X}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P} = \upsilon_0 \left(1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{T}{T_0} \frac{P_0}{P}$$

$$= \upsilon_0 \left(1 + y_{A0}\delta X \right) \frac{T}{T_0} \frac{P_0}{P} = \upsilon_0 \left(1 + \varepsilon X \right) \frac{T}{T_0} \frac{P_0}{P}$$

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

For Gas Phase Flow Systems

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

Gas Phase Flow System: $\upsilon = \upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}$

$$C_A = \frac{F_A}{\upsilon} = \frac{F_{A0}(1 - X)}{\upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

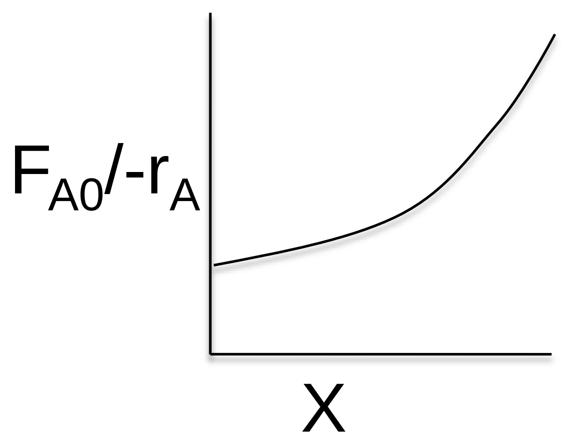
$$C_B = \frac{F_B}{\upsilon} = \frac{F_{A0}\left(\Theta_B - \frac{b}{a} X\right)}{\upsilon_0 (1 + \varepsilon X) \frac{T}{T_0} \frac{P_0}{P}} = \frac{C_{A0}\left(\Theta_B - \frac{b}{a} X\right)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

For Gas Phase Flow Systems

If $-r_A = kC_AC_B$

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

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 dm^3/mol and C_{A0}=0.2 mol/dm^3.

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

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

Gas Flow Example (X_{ef})

$$2A \Leftrightarrow B$$

$$X_{eb} = 0.703$$

$$X_{ef} = ?$$

Solution:

Rate Law:

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

$$\mathrm{A} \rightarrow \frac{1}{2}\mathrm{B}$$

Gas Flow Example (X_{ef})

Species	Fed	Change	Remaining
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 $T=T_0$

Gas isobaric $P=P_0$

$$\upsilon=\upsilon_0\left(1+\varepsilon X\right)$$

$$C_A=\frac{F_{A0}\left(1-X\right)}{\upsilon_0\left(1+\varepsilon X\right)}=\frac{C_{A0}\left(1-X\right)}{\left(1+\varepsilon X\right)}$$

$$C_B=\frac{F_{A0}X/2}{\upsilon_0\left(1+\varepsilon X\right)}=\frac{C_{A0}\left(1-X\right)}{2\left(1+\varepsilon X\right)}$$

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 → $y_{A0}=1$, $C_{A0}=y_{A0}P_0/RT_0$, $C_{A0}=P_0/RT_0$

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

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})

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

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

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

$$8.5X_e^{\ 2} - 17X_e + 8 = 0$$

Flow: $X_{ef} = 0.757$ Recall Batch: $X_{eb} = 0.70$

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

Liquid Phase

Flow

$$C_B = \frac{F_B}{v}$$

Batch

$$C_B = \frac{N_B}{V}$$

NO Phase Change

$$v = v_0 \qquad V = V_0$$

Constant Volume $V = V_0$

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

Gas Phase

Batch

$$C_B = \frac{N_B}{V}$$

$$V = V_0 \frac{N_T}{N_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$

$$C_B = \frac{N_B}{N_T} \frac{N_{T0}}{V_0} \frac{P}{P_0} \frac{T_0}{T}$$

$$C_B = C_{T0} \frac{N_B}{N_T} \frac{P}{P_0} \frac{T_0}{T}$$

Flow

$$C_B = \frac{F_B}{v}$$

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

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

$$C_B = C_{T0} \frac{F_B}{F_T} \frac{P}{P_0} \frac{T_0}{T}$$

NO Phase Change
OR
NO Semipermeable Membranes

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

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

Isothermal

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

Neglect Pressure Drop

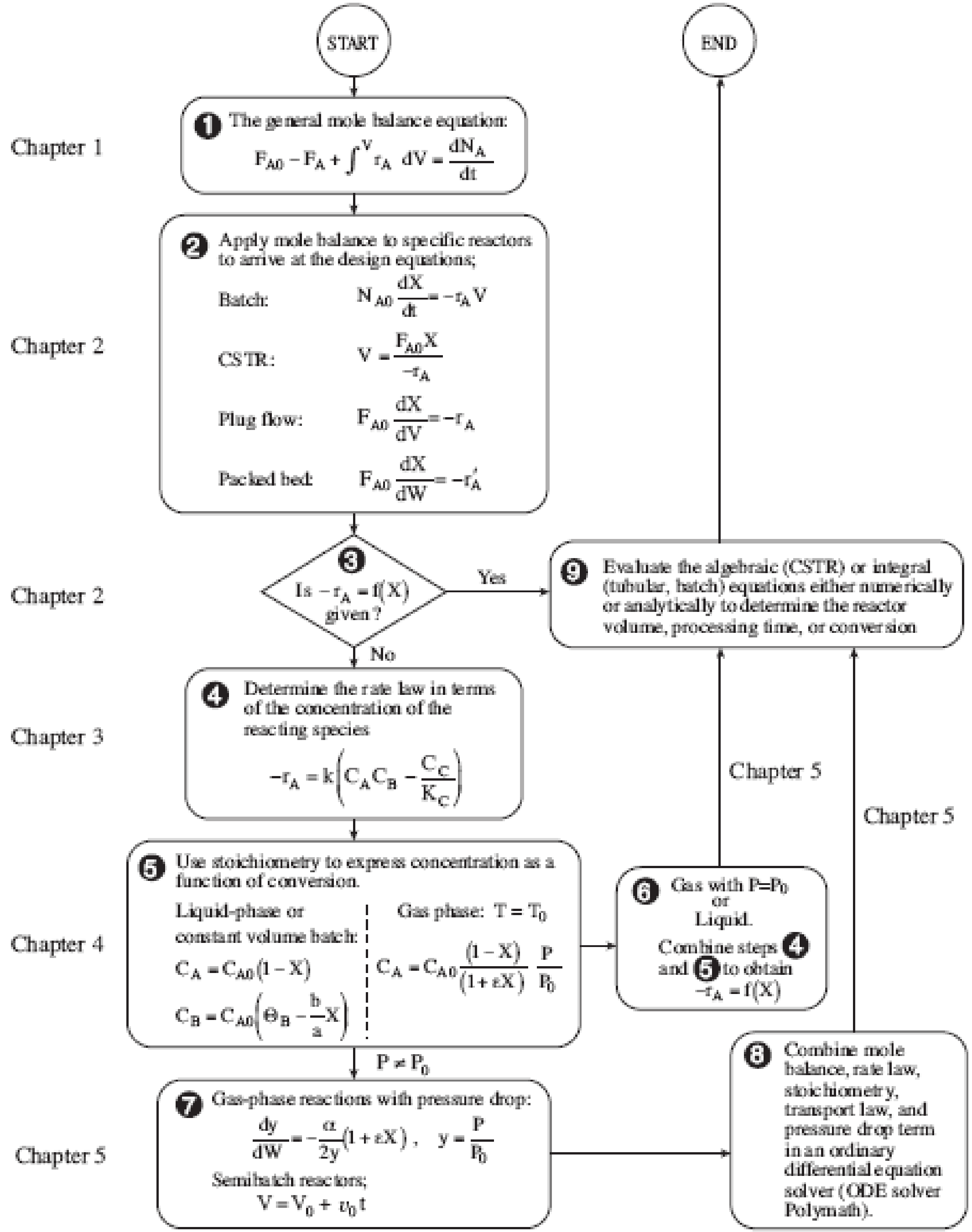
$$C_B = \frac{C_{A0}\left(\theta_B - \frac{b}{a}X\right)}{1+\varepsilon X}$$

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

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

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

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


START
END
Chapter 1
1 The general mole balance equation:
$F_{A0} - F_A + \int^V r_A \, dV = \frac{dN_A}{dt}$
Chapter 2
2 Apply mole balance to specific reactors to arrive at the design equations;
Batch: $N_{A0}\frac{dX}{dt} = -r_A V$
CSTR: $V = \frac{F_{A0}X}{-r_A}$
Plug flow: $F_{A0}\frac{dX}{dV} = -r_A$
Packed bed: $F_{A0}\frac{dX}{dW} = -r_A'$
Chapter 2
3 Is $-r_A = f(X)$ given?
Yes
No
9 Evaluate the algebraic (CSTR) or integral (tubular, batch) equations either numerically or analytically to determine the reactor volume, processing time, or conversion
Chapter 3
4 Determine the rate law in terms of the concentration of the reacting species
$-r_A = k\left(C_A C_B - \frac{C_C}{K_C}\right)$
Chapter 5
Chapter 5
Chapter 4
5 Use stoichiometry to express concentration as a function of conversion.
Liquid-phase or constant volume batch:
$C_A = C_{A0}(1-X)$
$C_B = C_{A0}\left(\Theta_B - \frac{b}{a}X\right)$
Gas phase: $T = T_0$
$C_A = C_{A0}\frac{(1-X)}{(1+\varepsilon X)}\frac{P}{P_0}$
6 Gas with $P=P_0$ or Liquid.
Combine steps 4 and 5 to obtain $-r_A = f(X)$
$P \neq P_0$
Chapter 5
7 Gas-phase reactions with pressure drop:
$\frac{dy}{dW} = -\frac{\alpha}{2y}(1+\varepsilon X)$, $y = \frac{P}{P_0}$
Semibatch reactors;
$V = V_0 + \upsilon_0 t$
8 Combine mole balance, rate law, stoichiometry, transport law, and pressure drop term in an ordinary differential equation solver (ODE solver Polymath).

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
$$C_A = \frac{F_A}{v}$$

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

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

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

LIQUID
Constant flow rate
$$v = v_0$$
$$C_A = C_{A0}(1 - X)$$

IDEAL GAS
Variable flow rate
$$v = v_0(1 + \varepsilon X)\frac{P_0}{P}\frac{T}{T_0}$$
$$C_A = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)}\frac{P}{P_0}\frac{T_0}{T}$$

IDEAL GAS
Variable volume
$$V = V_0(1 + \varepsilon X)\frac{P_0}{P}\frac{T}{T_0}$$
$$C_A = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)}\frac{P}{P_0}\frac{T_0}{T}$$

LIQUID OR GAS
Constant volume
$$V = V_0$$
$$C_A = C_{A0}(1 - X)$$

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

From mole balance | From rate law | From stoichiometry

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

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

Integrating for the case of constant temperature and pressure gives

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

End of Lecture 5