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

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Differential</th>
<th>Algebraic</th>
<th>Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>$N_{A0} \frac{dX}{dt} = -r_A V$</td>
<td>$t = N_{A0} \int_0^X \frac{dX}{-r_A V}$</td>
<td>$V = \frac{F_{A0}X}{-r_A}$</td>
</tr>
<tr>
<td>CSTR</td>
<td>$V = \frac{F_{A0}X}{-r_A}$</td>
<td>$V = F_{A0} \int_0^X \frac{dX}{-r_A}$</td>
<td></td>
</tr>
<tr>
<td>PFR</td>
<td>$F_{A0} \frac{dX}{dV} = -r_A$</td>
<td>$V = F_{A0} \int_0^X \frac{dX}{-r_A}$</td>
<td></td>
</tr>
<tr>
<td>PBR</td>
<td>$F_{A0} \frac{dX}{dW} = -r'_A$</td>
<td>$W = F_{A0} \int_0^X \frac{dX}{-r'_A}$</td>
<td></td>
</tr>
</tbody>
</table>

Review Lecture 2
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

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

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

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

Liquid Phase Flow System: \[ \nu = \nu_0 \]

Liquid Systems

\[ C_A = \frac{F_A}{\nu} = \frac{F_{A0}(1 - X)}{\nu_0} = C_{A0}(1 - X) \] 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.
If the rate of reaction were

\[ r_A = kC_A C_B \]

then we would have

\[ r_A = kC_A^2 (1 - X) B \frac{b}{a} X \]

This gives us

\[ r_A = f(X) \]
Combining the compressibility factor equation of state with $Z = Z_0$

Stoichiometry:

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

$$C_{T0} = \frac{P_0}{Z_0R_0T_0}$$

$$F_T = C_T\nu$$

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

We obtain:

$$\nu = \nu_0 \frac{F_T}{F_{T0}} \frac{P_0}{P} \frac{T}{T_0}$$
Stoichiometry
for Gas Phase Flow Systems

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

Since \( C_{T0} = \frac{F_{T0}}{\nu_0} \),

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

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:

\[
\nu = \nu_0 \left( \frac{F_{T0} + F_{A0} \delta X}{F_{T0}} \right) \frac{T}{T_0} \frac{P_0}{P} = \nu_0 \left( 1 + \frac{F_{A0}}{F_{T0}} \delta X \right) \frac{T}{T_0} \frac{P_0}{P}
\]

\[
= \nu_0 \left( 1 + y_{A0} \delta X \right) \frac{T}{T_0} \frac{P_0}{P} = \nu_0 \left( 1 + \varepsilon X \right) \frac{T}{T_0} \frac{P_0}{P}
\]

Where \( \varepsilon = y_{A0} \delta \)
For **Gas Phase** Flow Systems

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

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

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

\[ C_B = \frac{F_B}{\nu} = \frac{F_{A0} \left( \Theta_B - \frac{b}{a} X \right)}{\nu_0 (1 + \varepsilon X) T \frac{P_0}{T_0} P} = \frac{C_{A0} \left( \Theta_B - \frac{b}{a} X \right) T_0}{(1 + \varepsilon X)} \frac{P}{T} \frac{P_0}{P} \]
For **Gas Phase Flow Systems**

If \(-r_A = kC_AC_B\)

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

This gives us

\[F_{A0}/-r_A\]
where

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

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

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

\[ \varepsilon = y_{A0} \delta \]

\[ \varepsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}} \]
Example: Calculating the equilibrium conversion \( X_{ef} \) for gas phase reaction in a flow reactor

Consider the following elementary reaction where

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

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

\[
2A \leftrightarrow B \quad -r_A = k_A \left[ C_A^2 - \frac{C_B}{K_C} \right]
\]
Gas Flow Example ($X_{ef}$)

$$2A \leftrightarrow B$$

$$X_{eb} = 0.703$$

$$X_{ef} = ?$$

**Solution:**

Rate Law:

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

$$A \rightarrow \frac{1}{2} B$$
## Gas Flow Example \((X_{ef})\)

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<tr>
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<th>Change</th>
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<tr>
<td>A</td>
<td>(F_{A0})</td>
<td>(-F_{A0}X)</td>
<td>(F_A = F_{A0}(1-X))</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>(+F_{A0}X/2)</td>
<td>(F_B = F_{A0}X/2)</td>
</tr>
<tr>
<td></td>
<td>(F_{T0} = F_{A0})</td>
<td></td>
<td>(F_T = F_{A0} - F_{A0}X/2)</td>
</tr>
</tbody>
</table>
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 \quad T=T_0
Gas isobaric \quad P=P_0

\nu = \nu_0 \left( 1 + \varepsilon X \right)

\[ C_A = \frac{F_{A0} \left( 1 - X \right)}{\nu_0 \left( 1 + \varepsilon X \right)} = \frac{C_{A0} \left( 1 - X \right)}{\left( 1 + \varepsilon X \right)} \]

\[ C_B = \frac{F_{A0} \frac{X}{2}}{\nu_0 \left( 1 + \varepsilon X \right)} = \frac{C_{A0} \left( 1 - X \right)}{2 \left( 1 + \varepsilon X \right)} \]
**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: \(-r_A = 0\)

\[2K_CC_{A0} = \frac{X_e \left(1 + \varepsilon X_e\right)}{(1 - X_e)^2} \]
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**
  - \( C_B = \frac{F_B}{v} \)
  - \( v = v_0 \)
  - \( C_B = C_{A0} \left( \frac{b}{a} X \right) \)

- **Batch**
  - \( C_B = \frac{N_B}{V} \)
  - \( V = V_0 \)
  - \( C_B = C_{T0} \left( \frac{P}{P_0} \right) \)

**Gas Phase**

- **Flow**
  - \( C_B = \frac{F_B}{v} \)
  - \( v = v_0 \frac{F_T}{P_0} \frac{P}{P_0} \frac{T}{T_0} \)

- **Batch**
  - \( C_B = \frac{N_B}{V} \frac{T}{T_0} \frac{P}{P_0} \frac{T_0}{T} \)
  - \( V = V_0 \frac{N_T}{N_{T0}} \frac{P}{P_0} \frac{T}{T_0} \)

\[ \epsilon = y_{A0} \delta \]
\[ \delta = \left( \frac{d}{a} + c - \frac{b}{a} - 1 \right) \]

\[ C_{T0} = \frac{P_0}{RT_0} \]

\[ C_{A0} = y_{A0} \cdot C_{T0} \]
Chapter 4

1. The general mole balance equation:
   \[ F_{A0} - F_A + \int_{V} \tau_A \, dV = \frac{dN_A}{dt} \]

2. Apply mole balance to specific reactors to arrive at the design equations:
   - Batch:
     \[ N_{A0} \frac{dX}{dt} = -\tau_A V \]
   - CSTR:
     \[ V = \frac{F_{A0}X}{-\tau_A} \]
   - Plug flow:
     \[ F_{A0} \frac{dX}{dV} = -\tau_A \]
   - Packed bed:
     \[ F_{A0} \frac{dX}{dW} = -\tau_A \]

3. Is \( -\tau_A = f(X) \) given? Yes

4. Determine the rate law in terms of the concentration of the reacting species:
   \[ -\tau_A = k_1 \left( C_A C_B - \frac{C_C}{K_C} \right) \]

5. Use stoichiometry to express concentration as a function of conversion.
   - Liquid-phase or constant volume batch:
     \[ C_A = C_{A0}(1 - X) \quad C_B = C_{A0} \left( \frac{b}{a} - \frac{X}{1 - X} \right) \]
     \[ C_A = \frac{C_{A0}(1 - X)}{(1 + \varepsilon X)} \quad \frac{P}{P_0} = 1 \]
   - Gas phase: \( T = T_0 \)

6. Gas with \( P = P_0 \) or Liquid. Combine steps 4 and 5 to obtain \(-\tau_A = f(X)\)

7. Gas-phase reactions with pressure drop:
   \[ \frac{dy}{dW} = -\frac{\alpha}{2y}(1 + \varepsilon X), \quad y = \frac{P}{P_0} \]
   Semibatch reactors:
   \[ V = V_0 + v_0 t \]


Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5
1. MOLE BALANCES

PFR
\[ \frac{dX}{dV} = -\frac{r_A}{F_{AD}} \]

CSTR
\[ V = \frac{F_{AD}X}{-r_A} \]

BATCH
\[ \frac{dX}{dt} = -\frac{r_AV}{N_{AD}} \]

2. RATE LAWS

\[ r_A = kC_A \]

\[ r_A = \frac{kC_A}{1 + K_A C_A} \]

\[ r_A = k \left( \frac{C_A - C_0 C_C}{K_c} \right) \]

3. STOICHIOMETRY

FLOW
\[ F_A = \frac{F_{AD} (1 - X)}{V} \]

BATCH
\[ N_A = N_{AD} (1 - X) \]

LIQUID
Constant flow rate

IDEAL GAS
Variable flow rate

IDEAL GAS
Variable volume

LIQUID OR GAS
Constant volume

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

From mole balance
\[ \frac{dX}{dV} = -\frac{r_A}{F_{AD}} \]

From rate law
\[ \frac{dX}{dV} = \frac{kC_A}{F_{AD}} \]

From stoichiometry
\[ \frac{dX}{dV} = \frac{k (1 - X) P T_0}{y (1 + \varepsilon X) P_0 T} \]

where \( y = \frac{P}{P_0} \)

Integrating for the case of constant temperature and pressure gives
\[ V = \frac{P_0}{k} \left( 1 + \varepsilon \ln \left( \frac{1}{1 - X} \right) - \varepsilon X \right) \]
End of Lecture 5