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 4

- Block 1
  - **Mole Balances**
  - Size CSTRs and PFRs given \(-r_A = f(X)\)
- Block 2
  - **Rate Laws**
  - Reaction Orders
  - Arrhenius Equation
- Block 3
  - **Stoichiometry**
  - Stoichiometric Table
  - Definitions of Concentration
  - 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>$N_{A_0} \frac{dX}{dt} = -r_A V$</td>
<td>$t = N_{A_0} \int_0^X \frac{dX}{-r_A V}$</td>
<td></td>
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<tr>
<td>CSTR</td>
<td>$V = \frac{F_{A_0} X}{-r_A}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFR</td>
<td>$F_{A_0} \frac{dX}{dV} = -r_A$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBR</td>
<td>$F_{A_0} \frac{dX}{dW} = -r_A'$</td>
<td>$V = F_{A_0} \int_0^X \frac{dX}{-r_A}$</td>
<td>$W = F_{A_0} \int_0^X \frac{dX}{-r_A'}$</td>
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</table>
Levenspiel Plots

\[ \frac{F_A 0}{-r_A} \]

\[ X \]
Area = Volume of PFR

\[ V = \int_{0}^{X_1} \left( \frac{F_A 0}{-r_A} \right) dX \]
Reactors in Series

\[ X_i = \frac{\text{moles of } A \text{ reacted up to point } i}{\text{moles of } A \text{ fed to first reactor}} \]

Only valid if there are no side streams
Reactors in Series

\[ \frac{F_{AO}}{-r_A} \text{ (m}^3\text{)} \]

Conversion, \( X \)

- First CSTR Volume (188 dm\(^3\))
- PFR Volume (380 dm\(^3\))
- Second CSTR Volume (100 dm\(^3\))
Two steps to get $-r_A = f(X)$

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

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

Step 3: Combine to get $-r_A = f(X)$
Building Block 2: Rate Laws

Power Law Model:

\[ -r_A = kC_A^\alpha C_B^\beta \quad \alpha \text{ order in } A \]
\[ \beta \text{ order in } B \]

Overall Reaction Order = \( \alpha + \beta \)

2A + B → 3C

A reactor follows an elementary rate law if the reaction orders just happen to agree with the stoichiometric coefficients for the reaction as written.

e.g. If the above reaction follows an elementary rate law

\[ -r_A = k_A C_A^2 C_B \]

2nd order in A, 1st order in B, overall third order
Arrhenius Equation

\[ k = Ae^{-E/RT} \]

- \( E \) = Activation energy (cal/mol)
- \( R \) = Gas constant (cal/mol*K)
- \( T \) = Temperature (K)
- \( A \) = Frequency factor (same units as rate constant \( k \))

(units of \( A \), and \( k \), depend on overall reaction order)

\[ T \to \infty \quad k \to A \]
\[ T \to 0 \quad k \to 0 \]
\[ A \approx 10^{13} \]

\[ \ln k_A = \ln A - \frac{E}{R} \left( \frac{1}{T} \right) \]
These topics build upon one another
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 $-r_A = f(X)$
Building Block 3: **Stoichiometry**

We shall set up **Stoichiometry Tables** using species A as our basis of calculation in the following reaction. We will use the stoichiometric tables to express the concentration as a function of conversion. We will combine $C_i = f(X)$ with the appropriate rate law to obtain $-r_A = f(X)$.

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

A is the limiting reactant.
Stoichiometry

\[ N_A = N_{A0} - N_{A0}X \]

For every mole of A that reacts, \( \frac{b}{a} \) moles of B react. Therefore, moles of B remaining:

\[ N_B = N_{B0} - \frac{b}{a} N_{A0}X = N_{A0} \left( \frac{N_{B0}}{N_{A0}} - \frac{b}{a} X \right) \]

Let \( \Theta_B = \frac{N_{B0}}{N_{A0}} \)

Then:

\[ N_B = N_{A0} \left( \Theta_B - \frac{b}{a} X \right) \]

\[ N_C = N_{C0} + \frac{c}{a} N_{A0}X = N_{A0} \left( \Theta_C + \frac{c}{a} X \right) \]
# Batch System - Stoichiometry Table

<table>
<thead>
<tr>
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<th>Symbol</th>
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<th>Change</th>
<th>Remaining</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>A</td>
<td>$N_{A0}$</td>
<td>$-N_{A0}X$</td>
<td>$N_A = N_{A0}(1 - X)$</td>
</tr>
<tr>
<td>B</td>
<td>B</td>
<td>$N_{B0} = N_{A0}\Theta_B$</td>
<td>$-\frac{b}{a}N_{A0}X$</td>
<td>$N_B = N_{A0}(\Theta_B - \frac{b}{a}X)$</td>
</tr>
<tr>
<td>C</td>
<td>C</td>
<td>$N_{C0} = N_{A0}\Theta_C$</td>
<td>$+\frac{c}{a}N_{A0}X$</td>
<td>$N_C = N_{A0}(\Theta_C + \frac{c}{a}X)$</td>
</tr>
<tr>
<td>D</td>
<td>D</td>
<td>$N_{D0} = N_{A0}\Theta_D$</td>
<td>$+\frac{d}{a}N_{A0}X$</td>
<td>$N_D = N_{A0}(\Theta_D + \frac{d}{a}X)$</td>
</tr>
<tr>
<td>Inert</td>
<td>I</td>
<td>$N_{I0} = N_{A0}\Theta_I$</td>
<td>--------</td>
<td>$N_I = N_{A0}\Theta_I$</td>
</tr>
</tbody>
</table>

\[ F_{T0} = N_T = N_{T0} + \delta N_{A0}X \]

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

\( \delta \) = change in total number of mol per mol A reacted
Stoichiometry Constant Volume Batch

Note: If the reaction occurs in the liquid phase or if a gas phase reaction occurs in a rigid (e.g. steel) batch reactor

Then $V = V_0$

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X)}{V_0} = C_{A0}(1 - X)$$

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

etc.
Stoichiometry Constant Volume Batch

Suppose \(-r_A = k_A C_A^2 C_B\)

Batch: \(V = V_0\)

\[ r_A = k_A C_A^3 \left(1 - X\right)^2 \]

Equimolar feed: \(\Theta_B = 1\)

Stoichiometric feed: \(\Theta_B = \frac{b}{a}\)
Stoichiometry Constant Volume Batch

If \(- r_A = k_A C_A^2 C_B \), then

\[- r_A = C_{A0}^3 (1 - X)^2 \left( \Theta_B - \frac{b}{a} X \right) \]

and we have \(- r_A = f(X)\)
Batch Reactor - Example

Calculate the equilibrium conversion for gas phase reaction, $X_e$.

Consider the following elementary reaction with $K_C=20 \text{ dm}^3/\text{mol}$ and $C_{A0}=0.2 \text{ mol/dm}^3$.

Find $X_e$ for both a batch reactor and a flow reactor.

\[
2A \rightleftharpoons B
\]

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

Calculate $X_e$

$C_{A0} = 0.2 \text{ mol/dm}^3$

$K_C = 20 \text{ dm}^3/\text{mol}$

Step 1: \[
\frac{dX}{dt} = -\frac{r_A V}{N_{A0}}
\]

Step 2: rate law: \[
-r_A = k_A C_A^2 - k_B C_B
\]

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

$K_C = \frac{k_A}{k_B}$
Batch Reactor - Example

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<td>(N_{A0})</td>
<td>(-N_{A0}X)</td>
<td>(N_{A0}(1-X))</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>(\frac{1}{2}N_{A0}X)</td>
<td>(N_{A0} \times \frac{X}{2})</td>
</tr>
</tbody>
</table>

Totals: \(N_{T0}=N_{A0}\) \(N_T=N_{A0} - N_{A0} \times \frac{X}{2}\)

@ equilibrium: \(-r_A=0\)

\[0 = C_{Ae}^2 - \frac{C_{Be}}{K_C}\]

\[K_e = \frac{C_{Be}}{C_{Ae}^2}\]

\[C_{Ae} = \frac{N_{Ae}}{V} = C_{A0}(1 - X_e)\]

\[C_{Be} = C_{A0} \times \frac{X_e}{2}\]
Batch Reactor - Example

**Solution:**
At equilibrium \(-r_A = 0 = k_A \left[ C_{Ae}^2 - \frac{C_{Be}}{K_C} \right]\)

Stoichiometry: \(A \rightarrow B/2\)
Constant Volume: \(V = V_0\)

**Batch**

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<tr>
<td>B</td>
<td>0</td>
<td>(+N_{A0}X/2)</td>
<td>(N_B = N_{A0}X/2)</td>
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<td></td>
<td>(N_{T0}=N_{A0})</td>
<td></td>
<td>(N_T = N_{A0}-N_{A0}X/2)</td>
</tr>
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\[K_C = \frac{C_{Be}}{C_{Ae}^2}\]
Batch Reactor - Example

\[ K_e = \frac{C_{A0} \frac{X_e}{2}}{\left[ C_{A0} (1 - X_e) \right]^2} = \frac{X_e}{2C_{A0} (1 - X_e)^2} \]

\[ 2K_e C_{A0} = \frac{X_e}{(1 - X_e)^2} = 2(20)(0.2) = 8 \]

\[ X_{eb} = 0.703 \]
Flow System – Stoichiometry Table

<table>
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<tr>
<th>Entering</th>
<th>Reactor Feed</th>
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<th>Reactor Effluent</th>
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<tr>
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Species | Symbol | Reactor Feed | Change | Reactor Effluent
---|--------|--------------|--------|------------------
A | A | $F_{A0}$ | -$F_{A0}X$ | $F_A = F_{A0}(1-X)$ |
B | B | $F_{B0} = F_{A0} \Theta_B$ | -$b/aF_{A0}X$ | $F_B = F_{A0}(\Theta_B - b/aX)$ |

Where: \( \Theta_i = \frac{F_i}{F_{A0}} = \frac{C_{i0}v_0}{C_{A0}v_0} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}} \)
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$F_T=F_{T0}+\delta F_{A0}X$

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Concentration – Flow System $C_A = \frac{F_A}{v}$
# Flow System – Stoichiometry Table

## Concentration – Flow System

![Flow System Diagram](flow_system_diagram.png)

### Table: Stoichiometry

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Stoichiometry

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

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

\[ C_A = \frac{F_A}{\nu} = \frac{F_A 0 (1 - X)}{\nu_0} = C_A 0 (1 - X) \quad \text{Flow Liquid Phase} \]

\[ C_B = \frac{N_B}{\nu} = \frac{N_A 0}{\nu_0} \left( \Theta_B - \frac{b}{a} X \right) = C_A 0 \left( \Theta_B - \frac{b}{a} X \right) \]

etc.

We will consider \( C_A \) and \( C_B \) for gas phase reactions in the next lecture.
End of Lecture 4