CHAPTER 3: STOICHIOMETRY

Part 2-
3.5 Batch Systems
3.6 Flow Systems

What do we already know?

How to size CSTR’s, PFRs, and PBRs using the design equations on pg 99:

\[-r_A = g(X)\]

How to express the rate law as a function of concentration:

\[-r_A = k(T)fn(C_A, C_B, \ldots)\]

What do we need?

\[C_j = h_j(X)\]  Concentration as a function of conversion!
Stoichiometric Tables: *Used to express concentration as a function of conversion.*

Presents the stoichiometric relationship between molecules for a single reaction.

**Must be written in terms of the limiting reactant.**

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

Divide thru by \(a\)

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

Develop the stoichiometric relationship on a basis of “per mole of A.”
**Batch Systems**

The number of moles of A in the reactor after a conversion X has been achieved?

\[ N_A = N_{A0} - N_{A0}X = N_{A0}(1-X) \]

To determine the number of moles of each species remaining after \( N_{A0}X \) moles of A have been reacted we make the stoichiometric table.

**How do we write the change for each of the species in terms of \( N_{A0} \)?**

\[ \text{moles } B \text{ reacted} = \frac{\text{moles } B \text{ reacted}}{\text{moles } A \text{ reacted}} \cdot \text{moles } A \text{ reacted} \]

\[ \text{moles } B \text{ reacted} = -\frac{b}{a} \cdot N_{A0}X \]
What about C and D?

\[
\text{moles } C \text{ formed } = \frac{c}{a} \cdot N_{A0} X
\]

\[
\text{moles } D \text{ formed } = \frac{d}{a} \cdot N_{A0} X
\]

**Components of the Stoichiometric Table**

Column 1: the particular species

Column 2: the number of moles of each species initially present

Column 3: the change in the number of moles brought about by the reaction

Column 4: the number of moles remaining in the system at time t.
### Stoichiometric Table Example

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Initially (mol)</th>
<th>Change (mol)</th>
<th>Remaining (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( N_{A0} )</td>
<td>-(( N_{A0}X ))</td>
<td>( N_A = N_{A0} - N_{A0}X )</td>
</tr>
<tr>
<td>B</td>
<td>( N_{B0} )</td>
<td>-(( b/a )( N_{A0}X ))</td>
<td>( N_B = N_{B0} - (b/a)N_{A0}X )</td>
</tr>
<tr>
<td>C</td>
<td>( N_{C0} )</td>
<td>+(( c/a )( N_{A0}X ))</td>
<td>( N_C = N_{C0} + (c/a)N_{A0}X )</td>
</tr>
<tr>
<td>D</td>
<td>( N_{D0} )</td>
<td>+(( d/a )( N_{A0}X ))</td>
<td>( N_D = N_{D0} + (d/a)N_{A0}X )</td>
</tr>
<tr>
<td>I (inerts)</td>
<td>( N_{I0} )</td>
<td></td>
<td>( N_I = N_{I0} )</td>
</tr>
<tr>
<td>Totals</td>
<td>( N_{T0} )</td>
<td></td>
<td>( N_I = N_{T0} + (d/a + c/a - b/a - 1)N_{A0}X )</td>
</tr>
</tbody>
</table>
EXAMPLE: CLASS EXCERCISE

\[ 2A \rightarrow B \]

<table>
<thead>
<tr>
<th>Species</th>
<th>Initially (mol)</th>
<th>Change (mol)</th>
<th>Remaining (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td>(N_A=)</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td>(N_B=)</td>
</tr>
<tr>
<td>Totals</td>
<td>(N_{T0}=N_{A0})</td>
<td></td>
<td>(N_T=)</td>
</tr>
</tbody>
</table>
\[ N_T = N_{T0} + \left( \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) N_{A0} X \]

Represents the increase in total number of moles per mole A reacted.

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

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

What do we need?

Cj = hj(X)  Concentration as a function of conversion!
**EQUATIONS FOR BATCH CONCENTRATIONS**

**Concentration of A:**

\[ C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X)}{V} \]

Number of moles of A \((N_A)\) per unit volume, \(V\).

**Batch Concentration**

\[ C_B = \frac{N_B}{V} = \frac{N_{B0} - \frac{b}{a}N_{A0}X}{V} \]

\[ C_C = \frac{N_C}{V} = \frac{N_{C0} + \frac{c}{a}N_{A0}X}{V} \]

\[ C_D = \frac{N_D}{V} = \frac{N_{D0} + \frac{d}{a}N_{A0}X}{V} \]
SIMPLIFY BY DEFINING NEW PARAMETER, $\Theta_i$

\[
\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}
\]

Now we can rewrite $C_B$, $C_C$, and $C_D$  

\[
C_B = \frac{N_{A0} \left[ \frac{N_{B0}}{N_{A0}} - \frac{b}{a} X \right]}{V} = \frac{N_{A0} \left[ \Theta_B - \frac{b}{a} X \right]}{V}
\]

\[
C_C = \frac{N_{A0} \left[ \frac{N_{C0}}{N_{A0}} + \frac{c}{a} X \right]}{V} = \frac{N_{A0} \left[ \Theta_C + \frac{c}{a} X \right]}{V}
\]

\[
C_D = \frac{N_{A0} \left[ \frac{N_{D0}}{N_{A0}} + \frac{d}{a} X \right]}{V} = \frac{N_{A0} \left[ \Theta_D + \frac{d}{a} X \right]}{V}
\]
WHAT'S LEFT?

Remember we want $C_j = h_j(X)$

We have number of moles in terms of conversion but we don't have volume as a function of conversion yet.

**TIME FOR SOME ASSUMPTIONS!**

Constant Volume or Constant Density

$$V = V_0$$
When can we use this assumption?

Gas phase – usually sealed, fixed volume

Number of moles of product = Number of moles of reactants

e.g. \[ CO + H_2O \rightleftharpoons CO_2 + H_2 \]

forms at the same pressure and temperature, volume will not change if ideal gas law is applicable or if the compressibility factors of reactants and products are approximately equal.

Liquid phase reactions solvent dominates, therefore the changes in the density of the solute do not affect the overall solution density (significantly).

Most liquid phase organic reactions do not change density during the reaction.
Now we can express \( C_j = h_j(X) \)

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

### Stoichiometric Table Example

<table>
<thead>
<tr>
<th>Species</th>
<th>Initially (mol)</th>
<th>Change (mol)</th>
<th>Remaining (mol)</th>
<th>Concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( N_{A_0} )</td>
<td>(-(N_{A_0}X))</td>
<td>( N_A = N_{A_0} - N_{A_0}X )</td>
<td>( C_A = C_{A_0} (1-X) )</td>
</tr>
<tr>
<td>B</td>
<td>( N_{B_0} )</td>
<td>(-(b/a)N_{A_0}X)</td>
<td>( N_B = N_{B_0} - (b/a)N_{A_0}X )</td>
<td>( C_B = C_{A_0} (\Theta_B - (b/a)X) )</td>
</tr>
<tr>
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<td>( N_{C_0} )</td>
<td>((c/a)N_{A_0}X)</td>
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</tr>
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<td>D</td>
<td>( N_{D_0} )</td>
<td>((d/a)N_{A_0}X)</td>
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<td>( C_D = C_{A_0} (\Theta_D + (d/a)X) )</td>
</tr>
<tr>
<td>I (inerts)</td>
<td>( N_{i0} )</td>
<td></td>
<td>( N_{i0} )</td>
<td>( C_{i0} )</td>
</tr>
<tr>
<td>Totals</td>
<td>( N_{T_0} )</td>
<td></td>
<td>( N_T = N_{T_0} + (d/a + c/a - b/a - 1)N_{A_0}X )</td>
<td></td>
</tr>
</tbody>
</table>
So how does this tie in with the rate expression?

How to size CSTR's, PFRs, and PBRs using the design equations on pg 99:

\[-r_A = g(X)\]

How to express the rate law as a function of concentration:

\[-r_A = k(T) \text{fn}(C_A, C_B, \ldots)\]

\[-r_A = kC_A C_B^2\]

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

\[-r_A = kC_{A0}^3 (1 - X) \cdot \left(\Theta_B - \frac{b}{a}X\right)^2\]
Write the rate law for the elementary liquid phase reaction

$$3A + 2B \rightarrow 4C$$

solely in terms of conversion. The feed to the batch reactor is equal molar A and B with $C_{A0} = 2 \text{ mol/dm}^3$ and $k_A = 0.01 \text{ (dm}^3/\text{mol})^4/\text{s}$. 

What is $-r_A = kC_A^3C_B^2$?

Choose basis – what is the limiting reactant?

$a = 1$, $b/a = 2/3$, $c/a = 4/3
HOMEWORK: DUE Monday February 5th, 2007

3-2_A : a, b,c,h, i
3-4_A
3-7_B
3-10_A
3-11_A : a