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 6 – Tuesday 1/29/2013

- Block 1: Mole Balances
- Block 2: Rate Laws
- Block 3: Stoichiometry
- Block 4: Combine

Review of Blocks 1, 2 and 3
Examples: Undergraduate Reactor Experiments
CSTR
PFR
BR

Gas Phase Reaction with Change in
the Total Number of Moles
# Building Block 1: Mole Balances

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>( V = \frac{F_{A0}X}{-r_A} )</td>
<td>( t = N_{A0} \int_{0}^{X} \frac{dX}{-r_A} )</td>
</tr>
<tr>
<td>CSTR</td>
<td>( V = F_{A0}X )</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
Building Block 2: Rate Laws

Power Law Model:

\[- r_A = k C_A^\alpha C_B^\beta \]

\(\alpha\) order in A

\(\beta\) order in B

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

\[2A + B \rightarrow 3C\]

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
Building Block 3: Stoichiometry
Review Lecture 5

Building Block 4: Combine

Le Cataliste Flambé
344 Champs Elysses

Menu à 220 F

Appétizer
Pate de Canard (supplément 15 FF)
Coquilles Saint-Jacques
Potage Crème de Cresson
Escargots à La Bourguignonne
(supplement 15 FF)

Mole Balance
Batch Reactor
CSTR
PFR/PBR
Semibatch Reactor

Entrée
Cassoulet
Ragons de Veau
Coq au Vin
Boeuf à la provençale
(Tous nos plats sont garnis)

Rate Law
Power Law (e.g.)
1st Order
2nd Order
Non-Integer Order

Dessert
Brie ou Crème Anglaise

Slochiometry
Gas or Liquid

Combine
Mix together and digest with
1/2 bouteille of POLYMATH

Service Compris
Review Lecture 5

Building Block 4: Combine

1. MOLE BALANCES
   - PFR:
     \[ \frac{dX}{dV} = -\frac{r_A}{F_{A0}} \]
   - CSTR:
     \[ V = \frac{F_{A0}X}{-r_A} \]
   - BATCH:
     \[ \frac{dX}{dt} = -\frac{r_AV}{N_{A0}} \]

2. RATE LAWS
   \[ \frac{dA}{dt} = -\frac{r_A}{1 + K_A C_A} \]
   \[ \frac{dA}{dt} = k \left( \frac{C_{eq} C}{K_b} \right) \]

3. STOICHIOMETRY
   - FLOW
     \[ C_A = \frac{F_A}{V} \]
   - BATCH
     \[ C_A = \frac{N_A}{V} \]
   - LIQUID:
     Constant flow rate
     \[ V = v_0 \]
   - IDEAL GAS:
     Variable flow rate
     \[ V = v_0 (1 + \varepsilon X) \frac{P_0 T}{P T_0} \]
   - IDEAL GAS:
     Variable volume
     \[ V = V_0 (1 + \varepsilon X) \frac{P_0 T}{P T_0} \]
   - LIQUID OR GAS:
     Constant volume
     \[ V = V_0 \]

   - From mole balance
   - From rate law
   - From stoichiometry

4. COMBINE (First Order Gas-Phase Reaction in a PFR)
   \[ \frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{k C_A}{F_{A0}} = \frac{k}{F_{A0}} \left( \frac{C_{A0} (1 - X)}{1 + \varepsilon X} \right) \frac{P T_0}{P_0 T} \]
   \[ \frac{dX}{dV} = \frac{k (1 - X)}{v_0 (1 + \varepsilon X)} y \frac{T_0}{T} \]

Integrating for the case of constant temperature and pressure gives
\[ V = \frac{v_0}{k} \left( 1 + \varepsilon \ln \left( \frac{1}{1 - X} \right) - \varepsilon X \right) \]
Today’s lecture

- Example for Liquid Phase Undergraduate Laboratory Experiment

\[(\text{CH}_2\text{CO})_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{COOH}\]

Entering

Volumetric flow rate \(v_0 = 0.0033 \text{ dm}^3/\text{s}\)

Acetic Anhydride 7.8% (1M)

Water 92.2% (51.2M)

Elementary with \(k'\) 1.95x10^{-4} \text{ dm}^3/(\text{mol.s})

Case I CSTR \(V = 1\text{ dm}^3\)

Case II PFR \(V = 0.311 \text{ dm}^3\)
Today’s lecture

- Example for Gas Phase: PFR and Batch Calculation

\[ 2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2 \]
\[ 2\text{A} \rightarrow 2\text{B} + \text{C} \]

Pure NOCl fed with \( C_{\text{NOCl},0} = 0.2 \text{ mol/dm}^3 \) follows an elementary rate law with \( k = 0.29 \text{ dm}^3/\text{(mol.s)} \)

Case I PFR with \( v_0 = 10 \text{ dm}^3/\text{s} \)
Find space time, \( \tau \) with \( X = 0.9 \)
Find reactor volume, \( V \) for \( X = 0.9 \)

Case II Batch constant volume
Find the time, \( t \), necessary to achieve 90% conversion. Compare \( \tau \) and \( t \).
Part 1: **Mole Balances in terms of Conversion**

Algorithm for Isothermal Reactor Design

1. **Mole Balances** and Design Equation
2. Rate Laws
3. Stoichiometry
4. Combine
5. Evaluate
   
   A. Graphically (Chapter 2 plots)
   B. Numerical (Quadrature Formulas Chapter 2 and appendices)
   C. Analytical (Integral Tables in Appendix)
   D. Software Packages (Appendix- Polymath)
**CSTR Laboratory Experiment**

Example: \( \text{CH}_3\text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OOH} \)

\[
C_{A0} = 1 M \\
C_{B0} = 51.2 M
\]

\[
V = 1 \text{ dm}^3 \\
\nu_0 = 3.3 \cdot 10^{-3} \frac{\text{dm}^3}{s}
\]

\[ A + B \rightarrow 2C \]

1) Mole Balance: \[ V = \frac{F_{A0} X}{-r_A} \]

\[ X = ? \]
CSTR Laboratory Experiment

2) Rate Law:

\[-r_A = k_A C_A C_B\]

3) Stoichiometry:

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>F_{A0}</td>
<td>-F_{A0}X</td>
<td>F_A = F_{A0}(1-X)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>F_{A0} \Theta_B</td>
<td>-F_{A0}X</td>
<td>F_B = F_{A0}(\Theta_B - X)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>2F_{A0}X</td>
<td>F_C = 2F_{A0}X</td>
<td></td>
</tr>
</tbody>
</table>
CSTR Laboratory Experiment

\[ C_A = \frac{F_A}{\nu} = \frac{F_{A0}(1-X)}{\nu_0} = C_{A0}(1-X) \]

\[ C_B = \frac{F_{A0}(\Theta_B - X)}{\nu_0} = C_{A0}(\Theta_B - X) \]

\[ \Theta_B = \frac{51.2}{1} = 51.2 \]

\[ C_B = C_{A0}(51.2 - X) \approx C_{A0}(51.2) \approx C_{B0} \]
CSTR Laboratory Experiment

\[-r_A = k' C_{B0} C_{A0} (1 - X) = k C_{A0} (1 - X)\]

\[V = \frac{\nu_0 k C_{A0} X}{C_{A0} (1 - X)} \Rightarrow \frac{V}{\nu_0} = \frac{k X}{(1 - X)} \Rightarrow \tau = \frac{V}{\nu_0} = \frac{k X}{(1 - X)}\]

\[X = \frac{\tau k}{1 + \tau k}\]

\[X = \frac{3.03}{4.03} = 0.75\]
**PFR Laboratory Experiment**

\[ A + B \rightarrow 2C \]

\[ \frac{0.00324 \, dm^3}{s} \quad \rightarrow \quad 0.311 \, dm^3 \quad \rightarrow \quad X = ? \]

1) **Mole Balance:**

\[ \frac{dX}{dV} = \frac{-r_A}{F_{A0}} \]

2) **Rate Law:**

\[ -r_A = kC_A C_B \]

3) **Stoichiometry:**

\[ C_A = C_{A0} (1 - X) \]

\[ C_B \approx C_{B0} \]
PFR Laboratory Experiment

4) Combine: \(-r_A = k' C_{B0} C_{A0} (1 - X) = k C_{A0} (1 - X)\)

\[
\frac{dX}{dV} = k C_{A0} (1 - X) / C_{A0} \nu_0
\]

\[
\frac{dX}{(1 - X)} = \frac{k}{\nu_0} dV = k d\tau
\]

\[
\ln \frac{1}{1 - X} = k \tau
\]

\[
X = 1 - e^{-k\tau}
\]

\[
\tau = \frac{V}{\nu_0} = \frac{0.311 \text{dm}^3}{0.00324 \text{dm}^3/\text{sec}} = 96.0 \text{ sec}
\]

\[
k = 0.01 \text{ s}^{-1}
\]

\[
X = 0.61
\]
Gas Flow PFR Example

2 NOCl $\rightarrow$ 2 NO + Cl$_2$

2A $\rightarrow$ 2B + C

$\nu_0 = 10 \frac{dm^3}{s}$  \hspace{1cm} k = 0.29 \frac{dm^3}{mol \cdot s}$  \hspace{1cm} C_{A0} = 0.2 \frac{mol}{L}$

$T = T_0$  \hspace{1cm} P = P_0$  \hspace{1cm} X = 0.9$  \hspace{1cm} V = ?$

1) Mole Balance:

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

2) Rate Law:

$$-r_A = kC_A^2$$
Gas Flow PFR Example

3) Stoichiometry: (Gas Flow)
\[
\nu = \nu_0 (1 + \varepsilon X)
\]
\[
C_A = \frac{C_{A0} (1 - X)}{(1 + \varepsilon X)}
\]
\[
A \rightarrow B + \frac{1}{2}C
\]

4) Combine:
\[
-r_A = \frac{k C_{A0}^2 (1 - X)^2}{(1 + \varepsilon X)^2}
\]
\[
\frac{dX}{dV} = \frac{k C_{A0}^2 (1 - X)^2}{C_{A0} \nu_0 (1 + \varepsilon X)^2}
\]
\[
\Rightarrow \int_0^X \frac{(1 + \varepsilon X)^2}{(1 - X)^2} dX = \int_0^V \frac{k C_{A0}}{\nu_0} dV = \frac{k C_{A0} V}{\nu_0} = Da \frac{Da}{k C_{A0} \tau}
\]
Gas Flow PFR Example

\[ kC_{A0} \tau = 2\varepsilon (1 + \varepsilon) \ln(1 - X) + \varepsilon^2 X + \frac{(1 + \varepsilon)^2 X}{1 - X} \]

\[ \varepsilon = y_{A0} \delta = (1) \left( \frac{1}{2} \right) = \frac{1}{2} \]

\[ kC_{A0} \tau = 17.02 \]

\[ \tau = \frac{17.02}{kC_{A0}} = 294 \text{ sec} \]

\[ V = V_0 \tau = 2940 \text{ L} \]
Constant Volume **Batch Example**

**Gas Phase** \(2A \rightarrow 2B + C\) \(t=?\)

1) **Mole Balance:**

\[
\frac{dX}{dt} = -\frac{r_A V_0}{N_{A0}} = -\frac{r_A}{N_{A0}/V_0} = -\frac{r_A}{C_{A0}}
\]

2) **Rate Law:**

\[-r_A = k C_A^2\]

3) **Stoichiometry:**

**(Gas Flow)**

\[V = V_0\]

\[C_A = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)\]

\[-r_A = k C_{A0}^2 (1-X)^2\]
Constant Volume **Batch** Example

4) Combine: 

\[
\frac{dX}{dt} = \frac{kC_A^2 (1 - X)^2}{C_A} = kC_A (1 - X)^2
\]

\[
\frac{dX}{dt} = kC_A (1 - X)^2
\]

\[
\frac{dX}{(1 - X)^2} = kC_A dt
\]

\[
\frac{1}{1 - X} = kC_A t
\]

\[
t = 155 \text{ sec}
\]
End of Lecture 6