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 1 – Thursday 1/10/2013

- Introduction
- Definitions
- General Mole Balance Equation
  - Batch (BR)
  - Continuously Stirred Tank Reactor (CSTR)
  - Plug Flow Reactor (PFR)
  - Packed Bed Reactor (PBR)
Chemical Reaction Engineering

- Chemical reaction engineering is at the heart of virtually every chemical process. It separates the chemical engineer from other engineers.

Industries that Draw Heavily on Chemical Reaction Engineering (CRE) are:
CPI (Chemical Process Industries)
Examples like Dow, DuPont, Amoco, Chevron
Dimersol G (an organometallic catalyst) unit (two CSTRs and one tubular reactor in series) to dimerize propylene into isohexanes. Institut Français du Pétrole process. [Photo courtesy of Editions Technip (Institut Français du Pétrole).]
Materials on the Web and CD-ROM

http://www.umich.edu/~essen/
Let’s Begin CRE

- **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.
Chemical Identity

- A chemical species is said to have reacted when it has lost its chemical identity.
- The identity of a chemical species is determined by the kind, number, and configuration of that species’ atoms.
Chemical Identity

- A chemical species is said to have reacted when it has lost its chemical identity.
- There are three ways for a species to lose its identity:

1. Decomposition \[ CH_3CH_3 \rightarrow H_2 + H_2C=CH_2 \]
2. Combination \[ N_2 + O_2 \rightarrow 2 \text{ NO} \]
3. Isomerization \[ C_2H_5CH=CH_2 \rightarrow CH_2=C(CH_3)_2 \]
Reaction Rate

- The reaction rate is the rate at which a species loses its chemical identity per unit volume.

- The rate of a reaction (mol/dm$^3$/s) can be expressed as either:
  - The rate of Disappearance of reactant: $-r_A$
    or as
  - The rate of Formation (Generation) of product: $r_P$
Reaction Rate

Consider the isomerization

\[ A \rightarrow B \]

\[ r_A = \text{the rate of formation of species A per unit volume} \]

\[ -r_A = \text{the rate of a disappearance of species A per unit volume} \]

\[ r_B = \text{the rate of formation of species B per unit volume} \]
Reaction Rate

EXAMPLE:  A → B

If Species B is being formed at a rate of 0.2 moles per decimeter cubed per second, i.e.,
\( r_B = 0.2 \text{ mole/dm}^3/\text{s} \)

Then A is disappearing at the same rate:
\( -r_A = 0.2 \text{ mole/dm}^3/\text{s} \)

The rate of formation (generation of A) is:
\( r_A = -0.2 \text{ mole/dm}^3/\text{s} \)
Reaction Rate

- For a catalytic reaction we refer to $-r_A'$, which is the rate of disappearance of species A on a per mass of catalyst basis. (mol/gcat/s)

**NOTE:** $dC_A/dt$ is not the rate of reaction
Reaction Rate

Consider species j:

1. \( r_j \) is the rate of formation of species j per unit volume [e.g. mol/dm\(^3\)/s]

2. \( r_j \) is a function of concentration, temperature, pressure, and the type of catalyst (if any)

3. \( r_j \) is independent of the type of reaction system (batch, plug flow, etc.)

4. \( r_j \) is an algebraic equation, not a differential equation (e.g. \( -r_A = kC_A \) or \( -r_A = kC_A^2 \))
Building Block 1:

**General Mole Balances**

![Diagram of mole balances]

\[
\begin{bmatrix}
\text{Molar Flow Rate of Species } j \text{ in} \\
\text{Species } j \text{ in}
\end{bmatrix} -
\begin{bmatrix}
\text{Molar Flow Rate of Species } j \text{ out} \\
\text{Species } j \text{ out}
\end{bmatrix} +
\begin{bmatrix}
\text{Molar Rate of Generation of Species } j \\
\text{Generation of Species } j
\end{bmatrix} =
\begin{bmatrix}
\text{Molar Rate Accumulation of Species } j \\
\text{Accumulation of Species } j
\end{bmatrix}
\]

\[
F_{j0} - F_j + G_j = \frac{dN_j}{dt}
\]

\[
\left( \frac{\text{mole}}{\text{time}} \right) - \left( \frac{\text{mole}}{\text{time}} \right) + \left( \frac{\text{mole}}{\text{time}} \right) = \left( \frac{\text{mole}}{\text{time}} \right)
\]
Building Block 1:

General Mole Balances

If spatially uniform:

\[ G_j = r_j V \]

If NOT spatially uniform:

\[ G_{j_1} = r_{j_1} \Delta V_1 \]
\[ G_{j_2} = r_{j_2} \Delta V_2 \]
Building Block 1:

**General Mole Balances**

\[
G_j = \sum_{i=1}^{n} r_{ji} \Delta V_i
\]

Take limit

\[
G_j = \sum_{i=1}^{n} r_{ji} \Delta V_i = \int r_j dV
\]

\[
i=1 \lim_{\Delta V \to 0} \ n \to \infty
\]
Building Block 1:

**General Mole Balances**

General Mole Balance on System Volume $V$

\[ \text{In} - \text{Out} + \text{Generation} = \text{Accumulation} \]

\[ F_{A0} - F_A + \int r_A \, dV = \frac{dN_A}{dt} \]
Batch Reactor - Mole Balances

**Batch**

\[
\frac{dN_A}{dt} = r_A V
\]

\[
F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt}
\]

\[
F_{A0} = F_A = 0
\]

**Well-Mixed**

\[
\int r_A dV = r_A V
\]
Batch Reactor - Mole Balances

Integrating

\[ dt = \frac{dN_A}{r_A V} \]

when

\[ t = 0 \quad N_A = N_{A0} \]
\[ t = t \quad N_A = N_A \]

\[ t = \int_{N_{A0}}^{N_A} \frac{dN_A}{-r_A V} \]

Time necessary to reduce the number of moles of A from \( N_{A0} \) to \( N_A \).
Batch Reactor - Mole Balances

\[ t = \int_{N_{A0}}^{N_A} \frac{dN_A}{-r_A V} \]
CSTR - Mole Balances

\[ F_{A0} - F_A + \int r_A dV = \frac{dN_A}{dt} \]

Steady State

\[ \frac{dN_A}{dt} = 0 \]
CSTR - Mole Balances

Well Mixed

\[ \int r_A dV = r_A V \]

\[ F_{A0} - F_A + r_A V = 0 \]

\[ V = \frac{F_{A0} - F_A}{-r_A} \]

CSTR volume necessary to reduce the molar flow rate from \( F_{A0} \) to \( F_A \).
Plug Flow Reactor - Mole Balances

Polyethylene reactor; this 16-in inner-diameter reactor is designed to operate at 35,000 psi and 600°F; in operation, this reactor is in a vertical configuration. Courtesy of Autoclave Engineers, Division of Snap-tite, Inc.
Plug Flow Reactor - Mole Balances

\[ \Delta V \]

\[
\begin{bmatrix}
\text{In at } V \\
\text{Out at } V + \Delta V \\
\text{Generation in } \Delta V
\end{bmatrix}
- \begin{bmatrix}
\text{In at } V \\
\text{Out at } V + \Delta V \\
\text{Generation in } \Delta V
\end{bmatrix}
+ \begin{bmatrix}
\text{In at } V \\
\text{Out at } V + \Delta V \\
\text{Generation in } \Delta V
\end{bmatrix}
= 0
\]

\[
F_A\bigg|_V - F_A\bigg|_{V+\Delta V} + r_A \Delta V = 0
\]
Plug Flow Reactor - Mole Balances

Rearrange and take limit as $\Delta V \to 0$

$$\lim_{\Delta V \to 0} \frac{F_A|_{V+\Delta V} - F_A|_V}{\Delta V} = r_A$$

$$\frac{dF_A}{dV} = r_A$$

This is the volume necessary to reduce the entering molar flow rate (mol/s) from $F_{A0}$ to the exit molar flow rate of $F_A$. 
Plug Flow Reactor - Mole Balances

\[ F_{A0} - F_A + \int r_A \, dV = \frac{dN_A}{dt} \]

Steady State

\[ \frac{dN_A}{dt} = 0 \]

\[ F_{A0} - F_A + \int r_A \, dV = 0 \]
Alternative Derivation

Plug Flow Reactor - Mole Balances

Differientiate with respect to V

\[ 0 - \frac{dF_A}{dV} = -r_A \quad \Rightarrow \quad \frac{dF_A}{dV} = r_A \]

The integral form is:

\[ V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A} \]

This is the volume necessary to reduce the entering molar flow rate (mol/s) from \( F_{A0} \) to the exit molar flow rate of \( F_A \).
Packed Bed Reactor - Mole Balances

\[ F_A(W) - F_A(W + \Delta W) + r_A' \Delta W = \frac{dN_A}{dt} \]

Steady State

\[ \lim_{\Delta W \to 0} \frac{F_A|_{W+\Delta W} - F_A|_W}{\Delta W} = r_A' \]
Packed Bed Reactor - Mole Balances

Rearrange:

\[
\frac{dF_A}{dW} = r'_A
\]

The integral form to find the catalyst weight is:

\[
W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A}
\]

PBR catalyst weight necessary to reduce the entering molar flow rate \( F_{A0} \) to molar flow rate \( F_A \).
## Reactor Mole Balances Summary

The GMBE applied to the four major reactor types (and the general reaction $A \rightarrow B$)

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Differential</th>
<th>Algebraic</th>
<th>Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>$\frac{dN_A}{dt} = r_A V$</td>
<td>$t = \int_{N_{A0}}^{N_A} \frac{dN_A}{r_A V}$</td>
<td></td>
</tr>
<tr>
<td>CSTR</td>
<td>$V = \frac{F_{A0} - F_A}{-r_A}$</td>
<td></td>
<td>$N_A$</td>
</tr>
<tr>
<td>PFR</td>
<td>$\frac{dF_A}{dV} = r_A$</td>
<td>$V = \int_{F_{A0}}^{F_A} \frac{dF_A}{dr_A}$</td>
<td>$F_A$</td>
</tr>
<tr>
<td>PBR</td>
<td>$\frac{dF_A}{dW} = r_A'$</td>
<td>$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A'}$</td>
<td>$F_A$</td>
</tr>
</tbody>
</table>

![Graphs](image)
Reactors with Heat Effects

- **EXAMPLE**: Production of Propylene Glycol in an Adiabatic CSTR
- Propylene glycol is produced by the hydrolysis of propylene oxide:

\[
CH_2\text{-}CH\text{-}CH_3 + H_2O \xrightarrow{H_2SO_4} CH_2\text{-}CH\text{-}CH_3\text{OH} + OH
\]
What are the exit conversion $X$ and exit temperature $T$?

**Solution**

Let the reaction be represented by

$$A + B \rightarrow C$$
1. Mole Balance and design equation:

\[ F_{A0} - F_A + r_A V = 0 \]

The design equation in terms of \( X \) is

\[ V = \frac{F_{A0} X}{-r_A} \]

2. Rate Law:

\[ -r_A = k C_A \]
3. Stoichiometry (liquid phase, \( v = v_0 \)):

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

4. Combining yields

\[
V = \frac{F_{A0} X}{kC_{A0} (1 - X)} = \frac{v_0 X}{k(1 - X)}
\]

Solving for \( X \) as a function of \( T \) and recalling that \( \tau = V/v_0 \) gives

\[
X_{MB} = \frac{\tau k}{1 + \tau k} = \frac{\tau A e^{-E/RT}}{1 + \tau A e^{-E/RT}}
\]

This equation relates temperature and conversion through the mole balance.
b. *Stoichiometry* \((C_A^0, \Theta_i, \tau)\): The total liquid volumetric flow rate entering the reactor is

\[
V = 300 \text{ gal} = 40.1 \text{ ft}^3
\]

\[
\tau = \frac{V}{v_0} = \frac{40.1 \text{ ft}^3}{326.3 \text{ ft}^3/\text{h}} = 0.123 \text{ h}
\]

\[
C_A^0 = \frac{F_{A^0}}{v_0} = \frac{43.0 \text{ lb mol/h}}{326.3 \text{ ft}^3/\text{h}} = 0.132 \text{ lb mol/ft}^3
\]

For methanol: \(\Theta_M = \frac{F_{M^0}}{F_{A^0}} = \frac{71.87 \text{ lb mol/h}}{43.0 \text{ lb mol/h}} = 1.67\)

For water: \(\Theta_B = \frac{F_{B^0}}{F_{A^0}} = \frac{802.8 \text{ lb mol/h}}{43.0 \text{ lb mol/h}} = 18.65\)
c. Evaluate mole balance terms: The conversion calculated from the mole balance, $X_{MB}$, is found from Equation (E8-8.5).

$$X_{MB} = \frac{(2.084 \times 10^{12}) \exp(-16,306/T)}{1 + (2.084 \times 10^{12}) \exp(-16,306/T)}, \quad T \text{ is in } ^\circ\text{R}$$
5. The energy balance for this adiabatic reaction in which there is negligible energy input provided by the stirrer is

\[ X_{EB} = \frac{\sum \Theta_i C_{P_i} (T - T_{i0})}{-[\Delta H_{R}^{\circ} (T_R) + \Delta C_{P} (T - T_R)]} \]
d. Evaluate energy balance terms

\[ \sum \Theta_i C_{P_i} = C_{P_A} + \Theta_B C_{P_B} + \Theta_M C_{P_M} \]

\[ = 35 + (18.65)(18) + (1.67)(19.5) \]

Substituting all the known quantities into the energy balance gives us

\[ X_{EB} = \frac{(403.3 \text{ Btu/lb mol} \cdot \text{°F})(T - 535)\text{°F}}{-[36,400 - 7(T - 528)] \text{ Btu/lb mol}} \]

\[ X_{EB} = -\frac{\sum \Theta_i C_{P_i}(T - T_{i0})}{\Delta H^0_{Rx}(T_R) + \Delta C_P(T - T_R)} \]

\[ X_{EB} = \frac{403.3(T - 535)}{36,400 + 7(T - 528)} \]
7. Solving.

<table>
<thead>
<tr>
<th>$T$ (°R)</th>
<th>$X_{MB}$ [Eq. (E8-8.10)]</th>
<th>$X_{EB}$ [Eq. (E8-8.12)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>535</td>
<td>0.108</td>
<td>0.000</td>
</tr>
<tr>
<td>550</td>
<td>0.217</td>
<td>0.166</td>
</tr>
<tr>
<td>565</td>
<td>0.379</td>
<td>0.330</td>
</tr>
<tr>
<td>575</td>
<td>0.500</td>
<td>0.440</td>
</tr>
<tr>
<td>585</td>
<td>0.620</td>
<td>0.550</td>
</tr>
<tr>
<td>595</td>
<td>0.723</td>
<td>0.656</td>
</tr>
<tr>
<td>605</td>
<td>0.800</td>
<td>0.764</td>
</tr>
<tr>
<td>615</td>
<td>0.860</td>
<td>0.872</td>
</tr>
<tr>
<td>625</td>
<td>0.900</td>
<td>0.980</td>
</tr>
</tbody>
</table>
Analysis

We have applied our CRE algorithm to calculate the Conversion \((X=0.84)\) and Temperature \((T=614\, \degree R)\) in a 300 gallon CSTR operated adiabatically.

\[
\begin{align*}
T &= 535\, \degree R \\
A + B &\rightarrow C \\
X &= 0.84 \\
T &= 614\, \degree R
\end{align*}
\]
Keeping Up
Separations

Filtration  Distillation  Adsorption

These topics do not build upon one another.
Reaction Engineering

Mole Balance  Rate Laws  Stoichiometry

These topics build upon one another.
CRE Algorithm
Be careful not to cut corners on any of the CRE building blocks while learning this material!
Otherwise, your Algorithm becomes unstable.
End of Lecture 1
Supplemental Slides
Additional Applications of CRE

The reactor is 3.5 m in diameter and 38 m tall.
[Schematic and photo courtesy of Sasol/Sastech PT Limited.]
Supplemental Slides
Additional Applications of CRE

Corn Steep Liquor → Penicillium chrysogenum → Penicillin
Supplemental Slides
Additional Applications of CRE

Schematic diagrams of the Los Angeles basin.
Supplemental Slides
Additional Applications of CRE

Hippo Digestion (Ch. 2)
Supplemental Slides
Additional Applications of CRE

Modeling the Digestive System of a Hippopotamus
Matthew Robertson, Fredrik Persson, Brian Vicente, Professor H. Scott Fogler

"Even hippo's like Chemical Reaction Engineering."

*From a problem suggested by Professor Alice P. Gast
["Animal Guts as Ideal Reactors", Chemical Engineering Education, Winter 1998, pp 24-29]
Supplemental Slides
Additional Applications of CRE
Supplemental Slides
Additional Applications of CRE

Smog (Ch. 1)
Chemical Plant for Ethylene Glycol (Ch. 5)
Supplemental Slides
Additional Applications of CRE

Wetlands (Ch. 7 DVD-ROM)

Oil Recovery (Ch. 7)
Supplemental Slides
Additional Applications of CRE

Pharmacokinetics of Cobra Bites
Multiple Reactions in a Batch (Body) Reactor

Cobra Bites
(Ch. 8 DVD-ROM)
Supplemental Slides
Additional Applications of CRE

Effective Lubricant Design Scavenging Free Radicals

Lubricant Design (Ch. 9)
Supplemental Slides
Additional Applications of CRE

Nitroanaline Plant Explosion
Exothermic Reactions That Run Away

Plant Safety
(Ch. 11,12,13)