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.
Last Lecture

Energy Balance Fundamentals

\[
\sum F_{i0} E_{i0} - \sum F_i E_i + \dot{Q} - \dot{W} = \frac{dE_{sys}}{dt}
\]

Substituting for \( \dot{W} \)

\[
\sum F_{i0} \left[ U_{i0} + P\tilde{V}_{i0} \right] - \sum F_i \left[ U_i + P\tilde{V}_i \right] + \dot{Q} - \dot{W}_S = \frac{dE_{sys}}{dt}
\]

\[
\sum F_{i0} H_{i0} - \sum F_i H_i + \dot{Q} - \dot{W}_S = \frac{dE_{sys}}{dt}
\]

\[
\dot{Q} - \dot{W}_S + \sum F_{i0} H_{i0} - \sum F_i H_i = 0
\]
Web Lecture 20
Class Lecture 16-Thursday 3/14/2013

- Reactors with Heat Exchange
- User friendly Energy Balance Derivations
  - Adiabatic
  - Heat Exchange Constant $T_a$
  - Heat Exchange Variable $T_a$ Co-current
  - Heat Exchange Variable $T_a$ Counter Current
Adiabatic Operation CSTR

Elementary liquid phase reaction carried out in a CSTR

The feed consists of both - Inerts I and Species A with the ratio of inerts I to the species A being 2 to 1.
Adiabatic Operation CSTR

• Assuming the reaction is irreversible for CSTR, \( A \rightarrow B, (K_C = 0) \) what reactor volume is necessary to achieve 80% conversion?

• If the exiting temperature to the reactor is 360K, what is the corresponding reactor volume?

• Make a Levenspiel Plot and then determine the PFR reactor volume for 60% conversion and 95% conversion. Compare with the CSTR volumes at these conversions.

• Now assume the reaction is reversible, make a plot of the equilibrium conversion as a function of temperature between 290K and 400K.
CSTR: Adiabatic Example

\[ F_{\downarrow} A_0 = 5 \text{ mol/min} \]
\[ \Delta H_{\downarrow} \text{Rxn} = -20000 \text{ cal/mol A} \quad \text{(exothermic)} \]
\[ T_{\downarrow 0} = 300 \text{ K} \]
\[ F_{\downarrow I} = 10 \text{ mol/min} \]

\[ T = \, ? \]
\[ X = \, ? \]

1) Mole Balances:
\[ V = \frac{F_{A_0} X}{-r_A |_{\text{exit}}} \]
CSTR: Adiabatic Example

2) Rate Laws:

\[- r_A = k \left[ C_A - \frac{C_B}{K_C} \right] \]

\[ k = k_1 e^{ \frac{E}{RT} \left( \frac{1}{T_1} - \frac{1}{T} \right)} \]

\[ K_C = K_{C1} \exp \left[ \frac{\Delta H_{Rx}}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right) \right] \]

3) Stoichiometry:

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

\[ C_B = C_{A0} X \]
CSTR: Adiabatic Example

4) Energy Balance

Adiabatic, $\Delta C_p = 0$

$$T = T_0 + \frac{(-\Delta H_{Rx})X}{\sum \Theta_i C_{p_i}} = T_0 + \frac{(-\Delta H_{Rx})X}{C_{p_A} + \Theta_I C_{p_i}}$$

$$T = 300 + \left[\frac{-(-20,000)}{164 + (2)(18)}\right]X = 300 + \frac{20,000}{164 + 36}X$$

$$T = 300 + 100X$$
\textbf{CSTR: Adiabatic Example}

Irreversible for Parts (a) through (c)

\[- r_A = k C_{A0} (1 - X) \text{ (i.e., } K_C = \infty) \]

(a) Given $X = 0.8$, find $T$ and $V$

Given $X \xrightarrow{\text{Calc}} T \xrightarrow{\text{Calc}} k \xrightarrow{\text{Calc}} -r_A \xrightarrow{\text{Calc}} V$

\[\xrightarrow{\text{Calc}} K_C \quad \text{(if reversible)}\]
CSTR: Adiabatic Example

Given $X$, calculate $T$ and $V$

$$ V = \frac{F_{A0}X}{-r_A \bigg|_{\text{exit}}} = \frac{F_{A0}X}{kC_{A0}(1 - X)} $$

$$ T = 300 + 100(0.8) = 380K $$

$$ k = 0.1 \exp \left( \frac{10,000}{1.989} \left[ \frac{1}{298} - \frac{1}{380} \right] \right) = 3.81 $$

$$ V = \frac{F_{A0}X}{-r_A} = \frac{(5)(0.8)}{(3.81)(2)(1 - 0.8)} = 2.82 \text{ dm}^3 $$
Given T, Calculate X and V

(b) Given $X \xrightarrow{\text{Calc}} T \xrightarrow{\text{Calc}} k \xrightarrow{\text{Calc}} -r_A \xrightarrow{\text{Calc}} V$

$-r_A = kC_{A_0} \left(1 - X \right)$ (Irreversible)

$T = 360K$

$X = \frac{T - 300}{100} = 0.6$

$k = 1.83 \text{ min}^{-1}$

$V = \frac{(5)(0.6)}{(1.83)(2)(0.4)} = 2.05 \text{ dm}^3$
CSTR: Adiabatic Example

(c) Levenspiel Plot

\[
\frac{F_{A0}}{-r_A} = \frac{F_{A0}}{k C_{A0}(1 - X)}
\]

\[
T = 300 + 100X
\]

Choose \(X\) \(\xrightarrow{Calc} T \xrightarrow{Calc} k \xrightarrow{Calc} -r_A \xrightarrow{Calc} \frac{F_{A0}}{-r_A}\)
CSTR: Adiabatic Example

(c) Levenspiel Plot

<table>
<thead>
<tr>
<th>X</th>
<th>T(K)</th>
<th>$\frac{F_{A0}}{-r_A}$ (dm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>300</td>
<td>25</td>
</tr>
<tr>
<td>0.1</td>
<td>310</td>
<td>14.4</td>
</tr>
<tr>
<td>0.2</td>
<td>320</td>
<td>9.95</td>
</tr>
<tr>
<td>0.4</td>
<td>340</td>
<td>5.15</td>
</tr>
<tr>
<td>0.6</td>
<td>360</td>
<td>3.42</td>
</tr>
<tr>
<td>0.8</td>
<td>380</td>
<td>3.87</td>
</tr>
<tr>
<td>0.9</td>
<td>390</td>
<td>4.16</td>
</tr>
<tr>
<td>0.95</td>
<td>395</td>
<td>8.0</td>
</tr>
</tbody>
</table>
CSTR: Adiabatic Example

CSTR \hspace{0.5cm} X = 0.6 \hspace{0.5cm} T = 360 \text{ K}

CSTR \hspace{0.5cm} X = 0.95 \hspace{0.5cm} T = 395 \text{ K}
CSTR: Adiabatic Example

- **PFR X = 0.6**
- **PFR X = 0.95**
### CSTR: Adiabatic Example - Summary

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>T</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CSTR</strong></td>
<td>0.6</td>
<td>360</td>
<td>2.05 dm³</td>
</tr>
<tr>
<td><strong>PFR</strong></td>
<td>0.6</td>
<td>T_{exit} = 360</td>
<td>5.28 dm³</td>
</tr>
<tr>
<td><strong>CSTR</strong></td>
<td>0.95</td>
<td>395</td>
<td>7.59 dm³</td>
</tr>
<tr>
<td><strong>PFR</strong></td>
<td>0.95</td>
<td>T_{exit} = 395</td>
<td>6.62 dm³</td>
</tr>
</tbody>
</table>
Energy Balance in terms of Enthalpy

\[ \sum F_i H_i \bigg|_V - \sum F_i H_i \bigg|_{V+\Delta V} + Ua(T_a - T)\Delta V = 0 \]

\[ -\frac{d}{dV} \sum F_i H_i + Ua(T_a - T) = 0 \]

\[ -\frac{d}{dV} \sum F_i H_i = - \left[ \sum F_i \frac{dH_i}{dV} + \sum H_i \frac{dF_i}{dV} \right] \]
PFR Heat Effects

\[
\frac{dF_i}{dV} = r_i = v_i(-r_A)
\]

\[
H_i = H_i^0 + C_{Pi}(T - T_R)
\]

\[
\frac{dH_i}{dV} = C_{Pi} \frac{dT}{dV}
\]

\[
-d \sum \frac{F_i H_i}{dV} = -\left[ \sum F_i C_{Pi} \frac{dT}{dV} + \sum H_i v_i(-r_A) \right]
\]

\[
\sum v_i H_i = \Delta H_{Rx}
\]
PFR Heat Effects

\[- \left[ \sum C_{Pi} F_i \frac{dT}{dV} + \Delta H_{Rx} (-r_A) \right] + Ua(T_a - T) = 0 \]

\[ \sum F_i C_{Pi} \frac{dT}{dV} = \Delta H_{Rx} r_A - Ua(T - T_a) \]

\[
\frac{dT}{dV} = \frac{\left( \Delta H_{Rx} \right) (-r_A) - Ua(T - T_a)}{\sum F_i C_{Pi}}
\]

Need to determine $T_a$
Heat Exchange:

$$
\frac{dT}{dV} = \frac{-r_A(-\Delta H_{Rx}) - Ua(T - T_a)}{\sum F_i C_{p_i}}
$$

$$
\sum F_i C_{p_i} = F_{A0} \left[ \sum \Theta_i C_{p_i} + \Delta C_p X \right], \text{ if } \Delta C_p = 0 \text{ then}
$$

$$
\frac{dT}{dV} = \frac{-r_A(-\Delta H_{Rx}) - Ua(T - T_a)}{F_{A0} \sum \Theta_i C_{p_i}}
$$

Need to determine $T_a$
Energy Balance:  

Adiabatic (Ua=0) and $\Delta C_P=0$

$$T = T_0 + \left( -\Delta H_{Rx} \right) X \frac{\sum \Theta_i C_{P_i}}{\sum \Theta_i C_{P_i}} \quad (16A)$$

Heat Exchange Example:

Case 1 - Adiabatic
User Friendly Equations

A. Constant $T_a$ e.g., $T_a = 300K$

B. Variable $T_a$ Co-Current

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}C_{P_{cool}}}, V = 0 \quad T_a = T_{a_0} \quad (17C)$$

C. Variable $T_a$ Counter Current

$$\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}C_{P_{cool}}}, V = 0 \quad T_a = ? \quad \text{Guess}$$

Guess $T_a$ at $V = 0$ to match $T_{a_0} = T_{a_0}$ at exit, i.e., $V = V_f$.
Heat Exchanger Energy Balance

Variable $T_a$ Co-current

Coolant Balance:

$$\text{In - Out + Heat Added} = 0$$

$$\dot{m}_c H_C |_V - \dot{m}_c H_C |_{V+\Delta V} + Ua\Delta V (T - T_a) = 0$$

$$- \dot{m}_c \frac{dH_C}{dV} + Ua(T - T_a) = 0$$

$$H_C = H_C^0 + C_{PC} (T_a - T_r)$$

$$\frac{dH_C}{dV} = C_{PC} \frac{dT_a}{dV}$$

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{PC}}, \quad V = 0 \quad T_a = T_{a0}$$
Heat Exchanger Energy Balance
Variable $T_a$ Counter-current

\[ \text{In} - \text{Out} + \text{Heat Added} = 0 \]

\[ \dot{m}_C H_c \bigg|_{V+\Delta V} - \dot{m}_C H_c \bigg|_V + Ua \Delta V (T - T_a) = 0 \]

\[ \dot{m}_C \frac{dH_C}{dV} + Ua (T - T_a) = 0 \]

\[ \frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}_C C_{PC}} \]
Heat Exchanger – Example
Case 1 – Constant $T_a$

Elementary liquid phase reaction carried out in a PFR

The feed consists of both inerts I and species A with the ratio of inerts to the species A being 2 to 1.
Heat Exchanger – Example
Case 1 – Constant $T_a$

1) Mole Balance:

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

2) Rate Laws:

(2) \[ r_A = -k \left[ C_A - \frac{C_B}{K_C} \right] \]

(3) \[ k = k_1 \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] \]

(4) \[ K_C = K_{C2} \exp \left[ \frac{\Delta H_{Rx}}{R} \left( \frac{1}{T_2} - \frac{1}{T} \right) \right] \]
Heat Exchanger – Example
Case 1 – Constant $T_a$

3) Stoichiometry: $C_A = C_{A0}(1 - X)$ (5)

$$C_B = C_{A0}X$$ (6)

4) Heat Effects:

$$\frac{dT}{dV} = \frac{(\Delta H_R)(-r_A)}{F_{A0} \sum \theta_i C_{Pi}} - Ua(T - T_a)$$ (7)

($\Delta C_P = 0$)

$$X_{\text{eq}} = \frac{k_C}{1 + k_C}$$ (8)

$$\sum \theta_i C_{Pi} = C_{PA} + \theta_i C_{PI}$$ (9)
Heat Exchanger – Example
Case 1 – Constant $T_a$

Parameters: $\Delta H_R, E, R, T_1, T_2,$
$k_1, k_{C2}, Ua, T_a, F_{A0},$
$C_{A0}, C_{PA}, C_{PI}, \theta_I,$
$rate = -r_A$
PFR Heat Effects

Heat generated

Heat removed

\[ \frac{dT}{dV} = \frac{Q_g - Q_r}{\sum F_i C_{Pi}} \]

\[ \sum F_i C_{Pi} = \sum F_{A0} (\theta_i + \nu_i X) C_{Pi} = F_{A0} \left[ \sum \theta_i C_{Pi} + \Delta C_P X \right] \]

\[ \frac{dT}{dV} = \frac{ (\Delta H_R) (r_A) - Ua (T - T_a) }{ F_{A0} \left[ \sum \theta_i C_{Pi} + \Delta C_P X \right] } \]
Heat Exchanger – Example
Case 2 – Adiabatic

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

Energy Balance:
Adiabatic and \( \Delta C_P = 0 \)
\( Ua = 0 \)
\[
T = T_0 + \frac{(- \Delta H_{Rx})X}{\sum \Theta_i C_{P_i}}
\]
(16A)

Additional Parameters
(17A) & (17B)
\[
T_0, \sum \Theta_i C_{P_i} = C_{P_A} + \Theta_i C_{P_i}
\]
Adiabatic PFR

Differential equations
1 \( \frac{d(X)}{d(V)} = -\frac{ra}{Fao} \)

Explicit equations
1 \( k1 = 0.1 \)
2 \( Cao = 2 \)
3 \( DH = -20000 \)
4 \( To = 300 \)
5 \( CpI = 18 \)
6 \( Cpa = 164 \)
7 \( ThetaI = 2 \)
8 \( sumCp = Cpa + ThetaI * CpI \)
9 \( T = To + (-DH) * X / sumCp \)
10 \( Fao = 5 \)
11 \( E = 10000 \)
12 \( R = 1.987 \)
13 \( T1 = 298 \)
14 \( Ca = Cao * (1-X) \)
15 \( k = k1 * \exp(E/R*(1/T1-1/T)) \)
Example: Adiabatic

Find conversion, \( X_{eq} \) and \( T \) as a function of reactor volume.

![Graphs showing conversion, temperature, and rate as functions of reactor volume.](image)
Heat Exchange

\[
\frac{dT}{dV} = \left( -r_A \right) \left( -\Delta H_{Rx} \right) - Ua(T - T_a) \sum F_i C_{P_i}
\]

\[
\sum F_i C_{P_i} = F_{A0} \left[ \sum \Theta_i C_{P_i} + \Delta C_p X \right], \text{ if } \Delta C_p = 0 \text{ then }
\]

\[
\frac{dT}{dV} = \left( -r_A \right) \left( -\Delta H_{Rx} \right) - Ua(T - T_a) \frac{F_{A0} \sum \Theta_i C_{P_i}}{F_{A0} \sum \Theta_i C_{P_i}} \quad (16B)
\]

Need to determine \( T_a \)
User Friendly Equations

A. Constant Ta (17B) \( Ta = 300K \)

Additional Parameters (18B – (20B):

\[ Ta, \sum \Theta_i C_{p_i}, Ua \]

B. Variable \( T_a \) Co-Current

\[
\frac{dT_a}{dV} = \frac{Ua(T - Ta)}{\dot{m} C_{P_{cool}}} \quad V = 0 \quad T_a = T_{ao} \quad (17C)
\]

C. Variable \( T_a \) Countercurrent

\[
\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m} C_{P_{cool}}} \quad V = 0 \quad T_a = ?
\]

Guess \( T_a \) at \( V = 0 \) to match \( T_{a0} = T_{a0} \) at exit, i.e., \( V = V_f \)
Heat Exchange Energy Balance

Variable $T_a$ Counter-current

Coolant balance:

In - Out + Heat Added = 0

$$\dot{m}_c H_C|_{V} - \dot{m}_c H_C|_{V+\Delta V} + Ua\Delta V (T - T_a) = 0$$

$$- \dot{m}_c \frac{dH_C}{dV} + Ua(T - T_a) = 0$$

$$H_C = H_C^0 + C_{PC}(T_a - T_r)$$

$$\frac{dH_C}{dV} = C_{PC} \frac{dT_a}{dV}$$

$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{PC}}, \quad V = 0 \quad T_a = T_{a0}$$

All equations can be used from before except $T_a$ parameter, use differential $T_a$ instead, adding $m_c$ and $C_{PC}$.
Heat Exchange Energy Balance

Variable $T_a$ Co-current

In - Out + Heat Added = 0

$$\dot{m}_C H_C \bigg|_{V+\Delta V} - \dot{m}_C H_C \bigg|_{V} + Ua\Delta V(T - T_a) = 0$$

$$\dot{m}_C \frac{dH_C}{dV} + Ua(T - T_a) = 0$$

$$\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}_C C_{PC}}$$

All equations can be used from before except $dT_a/dV$ which must be changed to a negative. To arrive at the correct integration we must guess the $T_a$ value at $V=0$, integrate and see if $T_{a0}$ matches; if not, re-guess the value for $T_a$ at $V=0$
Derive the user-friendly Energy Balance for a PBR

\[
\int_{0}^{W} \frac{U_{a}}{\rho_{B}} (T_{a} - T) dW + \sum F_{i0} H_{i0} - \sum F_{i} H_{i} = 0
\]

Differentiating with respect to \( W \):

\[
\frac{U_{a}}{\rho_{B}} (T_{a} - T) + 0 - \sum \frac{dF_{i}}{dW} H_{i} - \sum F_{i} \frac{dH_{i}}{dW} = 0
\]
Derive the user-friendly Energy Balance for a PBR

**Mole Balance** on species $i$:

$$\frac{dF_i}{dW} = r_i' = \nu_i \left( -r_A' \right)$$

Enthalpy for species $i$:

$$H_i = H_i^o(T_R) + \int_{T_R}^{T} C_{Pi} \, dT$$
Derive the user-friendly Energy Balance for a PBR

Differentiating with respect to $W$:

$$\frac{dH_i}{dW} = 0 + C_{pi} \frac{dT}{dW}$$

$$\frac{U_a}{\rho_B} (T_a - T) + r_A \sum \nu_i H_i - \sum F_i C_{pi} \frac{dT}{dW} = 0$$
Derive the user-friendly Energy Balance for a PBR

\[ \frac{Ua}{\rho_B} (T_a - T) + r_A' \sum v_i H_i - \sum F_i C_{pi} \frac{dT}{dW} = 0 \]

\[ \sum v_i H_i = \Delta H_R(T) \]

\[ F_i = F_A 0 \left( \Theta_i + v_i X \right) \]

Final Form of the Differential Equations in Terms of Conversion:

A:

\[ \frac{dT}{dW} = \frac{Ua}{\rho_B} (T_a - T) + r_A' \Delta H_R(T) \]

\[ \frac{dW}{dW} = \frac{f(X, T)}{F_A 0 \left[ \sum \Theta_i \tilde{C}_{pi} + \Delta \hat{C}_p X \right]} \]
Derive the user-friendly **Energy Balance** for a PBR

Final form of terms of Molar Flow Rate:

\[
\frac{dT}{dW} = \frac{U_a}{\rho_B} \left(T_a - T\right) + r_A' \Delta H
\]

\[
\frac{dX}{dW} = -\frac{r_A'}{F_{A0}} = g(X, T)
\]
Reversible Reactions

\[ A + B \rightleftharpoons C + D \]

The rate law for this reaction will follow an elementary rate law.

\[-r_A = k \left( C_A C_B - \frac{C_C C_D}{K_C} \right)\]

Where \( K_e \) is the concentration equilibrium constant. We know from Le Chaltlier’s law that if the reaction is exothermic, \( K_e \) will decrease as the temperature is increased and the reaction will be shifted back to the left. If the reaction is endothermic and the temperature is increased, \( K_e \) will increase and the reaction will shift to the right.
Reversible Reactions

\[ K_C = \frac{K_P}{(RT)^\delta} \]

Van’t Hoff Equation:

\[ \frac{d \ln K_P}{dT} = \frac{\Delta H_R(T)}{RT^2} = \frac{\Delta H_R^0(T_R)}{RT^2} + \frac{\Delta C_P(T - T_R)}{RT^2} \]
Reversible Reactions

For the special case of $\Delta C_P = 0$

Integrating the Van’t Hoff Equation gives:

$$K_P(T_2) = K_P(T_1) \exp \left[ \frac{\Delta H^o_R(T_R)}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right]$$
Reversible Reactions

\[ \text{K}_P \]

\[ X_e \]

endothermic reaction

exothermic reaction

endothermic reaction

exothermic reaction
End of Lecture 20