Lecture 19

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.
• Energy Balance Fundamentals
  • Adiabatic reactors
Today’s Lecture

Energy Balance, Rationale and Overview

Let’s calculate the volume necessary to achieve a conversion, $X$, in a PFR for a first-order, exothermic and adiabatic reaction.

The temperature profile might look something like this:
Energy Balance, Rationale and Overview

Mole Balance:

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

Rate Law:

\[
r_A = -k_i \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] C_A
\]

Stoichiometry:

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

Combine:

\[
\frac{dX}{dV} = \frac{k_i \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right]}{F_{A0}} C_{A0} \left( 1 - X \right)
\]
Energy Balance, Rationale and Overview

\[ \frac{dX}{dV} = \frac{k_i \exp \left[ \frac{E}{R \left( \frac{1}{T_1} - \frac{1}{T} \right)} \right]}{F_{A0}} C_{A0} (1 - X) \]

We cannot solve this equation because we don’t have \( X \) either as a function of \( V \) or \( T \).

We need another equation. That equation is:  

The Energy Balance
User Friendly Equations Relate $T$ and $X$ or $F_i$

1. Adiabatic CSTR, PFR, Batch or PBR

\[ V_S \dot{\theta} - \dot{\hat{C}}_P = 0 \]

\[ X_{EB} = \frac{\sum \Theta_i C_{P_i} (T - T_0)}{-\Delta H^{\circ}_{Rx}} \]

\[ X = \frac{\tilde{C}_{P_A} (T - T_0)}{-\Delta H_{Rx}} \]

\[ T = T_0 + \frac{(-\Delta H^{\circ}_{Rx})X_{EB}}{\sum \Theta_i C_{P_i}} \]
Exothermic

Endothermic

Adiabatic
User Friendly Equations Relate $T$ and $X$ or $F_i$

2. **CSTR with heat exchange**: $UA(T_a - T)$ and a large coolant flow rate

\[
X_{EB} = \frac{\left( \frac{UA}{F_{A0}} (T - T_a) \right) + \sum \Theta_i C_{P_i} (T - T_0)}{-\Delta H^o_{Rx}}
\]
User Friendly Equations Relate T and X or $F_i$

3. **PFR/PBR** with heat exchange

3A. **PFR** in terms of conversion

$$\frac{dT}{dV} = \frac{r_A \Delta H_{Rx} (T) - Ua (T - T_a)}{F_{A0} \left( \sum \Theta_i C_{Pi} + \Delta C_p X \right)} = \frac{Q_g - Q_r}{F_{A0} \left( \sum \Theta_i C_{Pi} + \Delta C_p X \right)}$$
User Friendly Equations Relate $T$ and $X$ or $F_i$

3B. **PBR in terms of conversion**

$$\frac{dT}{dW} = \frac{r_A' \Delta H_{Rx}(T) - \frac{U_a}{\rho_b} (T - T_a)}{F_{A_0} \left( \sum \Theta_i C_{P_i} + \Delta C_p X \right)}$$

3C. **PBR in terms of molar flow rates**

$$\frac{dT}{dW} = \frac{r_A' \Delta H_{Rx}(T) - \frac{U_a}{\rho_b} (T - T_a)}{\sum F_i C_{P_i}}$$
User Friendly Equations Relate T and X or \( F_i \)

3D. **PFR** in terms of molar flow rates

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

4. **Batch**

\[
\frac{dT}{dt} = \frac{(r_A V)(\Delta H_{Rx}) - UA(T - T_a)}{\sum N_i C_{P_i}}
\]
User Friendly Equations Relate T and X or $F_i$

5. For **Semibatch** or unsteady **CSTR**

\[
\frac{dT}{dt} = \zeta \sum_{i=1}^{n} \Delta H_{Rx_i} (T - T_{i0}) + \left[ -\Delta H_{Rx} (T) \right] (-r_A V)
\]

\[
\sum_{i=1}^{n} N_i C_{P_i}
\]

6. For **multiple reactions in a PFR** (q reactions and m species)

\[
\frac{dT}{dV} = \sum_{i=1}^{q} r_{ij} \Delta H_{Rx_{ij}} - Ua(T - T_a)
\]

\[
\frac{dV}{dV} = \sum_{j=1}^{m} F_i C_{P_j}
\]

Let’s look where these User Friendly Equations came from.
Energy Balance

Reactor with no Spatial Variations
Energy Balance

Reactor with no Spatial Variations

\[ \dot{Q} \]

Rate of flow of heat to the system from the surroundings

\[ \dot{Q} \quad (\text{J/s}) \]
Energy Balance

Reactor with no Spatial Variations

\[ \dot{Q} - \dot{W} \]

Rate of flow of heat to the system from the surroundings

Rate of work done by the system on the surroundings

\[ \dot{Q} \quad \text{(J/s)} \quad - \quad \dot{W} \quad \text{(J/s)} \]
Energy Balance

Reactor with no Spatial Variations

\[
\dot{Q} - \dot{W} + F_{in} E_{in} = 0
\]

Rate of flow of heat to the system from the surroundings

Rate of work done by the system on the surroundings

Rate of energy added to the system by mass flow into the system
Energy Balance

Reactor with no Spatial Variations

Rate of flow of heat to the system from the surroundings

Rate of work done by the system on the surroundings

Rate of energy added to the system by mass flow into the system

Rate of energy leaving system by mass flow out of the system

\[ \dot{Q} - \dot{W} + F_{in}E_{in} - F_{out}E_{out} \]

(J/s) (J/s) (J/s) (J/s)
Energy Balance

Reactor with no Spatial Variations

\[
\frac{d\hat{E}_{sys}}{dt} = \dot{Q} - \dot{W} + F_{in}E_{in} - F_{out}E_{out}
\]

- Rate of accumulation of energy within the system
  \[\frac{d\hat{E}_{sys}}{dt}\] (J/s)
- Rate of flow of heat to the system from the surroundings
  \(\dot{Q}\) (J/s)
- Rate of work done by the system on the surroundings
  \(\dot{W}\) (J/s)
- Rate of energy added to the system by mass flow into the system
  \(F_{in}E_{in}\) (J/s)
- Rate of energy leaving system by mass flow out of the system
  \(F_{out}E_{out}\) (J/s)
Energy Balance

\[ F_{i|\text{in}} \quad (\text{e.g., } F_{A0}) \quad H_{i|\text{in}} \quad (\text{e.g., } H_{A0}) \]

\[ \dot{Q} \quad \dot{W}_S \]

\[ F_{i|\text{out}} \quad (\text{e.g., } F_A) \quad H_{i|\text{out}} \quad (\text{e.g., } H_A) \]

**Energy Balance on an open system: schematic.**

\[ \dot{Q} - \dot{W}_S + \sum F_i E_{i0|\text{in}} - \sum F_i E_{i|\text{out}} = \frac{dE_{\text{system}}}{dt} \quad (1) \]
OK folks, here is what we are going to do to put the above equation into a usable form.

1. Replace $U_i$ by $U_i = H_i - PV_i$
2. Express $H_i$ in terms of heat capacities
3. Express $F_i$ in terms of either conversion or rates of reaction
4. Define $\Delta H_{Rx}$
5. Define $\Delta C_P$
6. Manipulate so that the overall energy balance is in terms of the User Friendly Equations.
Intro to Heat Effects

Assumptions:

\[ E_i = U_i + P\tilde{E}_i + K\tilde{E}_i = 0 \]

Other energies small compared to internal energy.

\[ \dot{W} = \text{flow work} + \text{shaft work} \]

\[
\text{flow work} = - \sum F_i P_0 \tilde{V}_i + \sum F_i P \tilde{V}_i
\]

\[
\tilde{V} = \frac{m^3}{\text{mol}}
\]

Recall:

\[ H_i = U_i + P\tilde{V}_i \]
Intro to Heat Effects

Substituting for $\dot{V}$

$$
\sum F_{i0} U_{i0} - \sum F_i U_i + \dot{Q} - \int_{0}^{t} P_0 \tilde{V}_{w} \, \text{d}t
$$

Steady State:

$$
\dot{Q} - \dot{W}_S + \sum F_{i0} H_{i0} - \sum F_i H_i = 0
$$
Intro to Heat Effects

General Energy Balance:

\[
\dot{Q} - \dot{W}_S + \sum F_{i0}H_{i0} - \sum F_iH_i = \frac{dE_{\text{system}}}{dt}
\]

For Steady State Operation:

\[
\dot{Q} - \dot{W}_S + \sum F_{i0}H_{i0} - \sum F_iH_i = 0
\]
Intro to Heat Effects

\[ \sum F_{i0} H_{i0} = F_{A0} \sum \Theta_i H_{i0} \]

\[ \sum F_i H_i = F_{A0} \sum (\Theta_i + \nu_i X)H_i = F_{A0} \sum \Theta_i H_i + F_{A0} X \sum \nu_i H_i \]

\[ \sum \Theta_i (H_{i0} - H_i) + F_{A0} X \Delta H_{Rx} = 0 \]
Intro to Heat Effects

For No Phase Changes

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

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

\[ H_{i0} - H_i = C_{Pi}(T - T_0) \]

\[ \sum \nu_iH_i = \sum \nu_iH_i^0 + \sum \nu_iC_{Pi}(T - T_R) \]

Enthalpy of formation at temperature \( T_R \)

Constant Heat Capacities

Heat of reaction at temperature \( T \)
Intro to Heat Effects

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

\[ \Delta H_R(T) = \Delta H_R^o(T_R) + \Delta \hat{C}_P(T - T_R) \]

\[ \sum \nu_i \hat{C}_{Pi} = \Delta \hat{C}_P = \frac{d}{a} \hat{C}_{PD} + \frac{c}{a} \hat{C}_{PC} - \frac{b}{a} \hat{C}_{PB} - \hat{C}_{PA} \]

Substituting back into the Energy Balance

\[ \dot{Q} - A_0 \sum \nu_i \left( K - K \right) - P - A_0 \sum \nu_i \left( K - K \right) \]

Adiabatic (Q=0) and no Work \( (\dot{W}_S = 0) \)
**Intro to Heat Effects**

\[ \Delta H_{Rx} = \frac{d}{a} H_D + \frac{c}{a} H_C - \frac{b}{a} H_B - H_A \]

\[ \Delta C_P = \frac{d}{a} C_{PD} + \frac{c}{a} C_{PC} - \frac{b}{a} C_{PB} - C_{PA} \]
Intro to Heat Effects

\[ \dot{\mathcal{Q}} = -A_0 \left( \sum \Theta_i \left( H_{i0} - H_i \right) + F_{A_0} X \Delta H_{Rx} \right) = 0 \]

Substituting back into the Energy Balance
Adiabatic Energy Balance

Adiabatic (Q=0) and no Work \((\dot{W}_S = 0)\)

\[
T = T_0 - \frac{X \left[ \Delta H_R^o(T_R) + \Delta \hat{C}_P(T - T_R) \right]}{\sum \Theta_i \tilde{C}_{P_i} + X\Delta \hat{C}_P} = T_0 - \frac{X \left[ \Delta H_R(T) \right]}{\sum \Theta_i \tilde{C}_{P_i} + X\Delta \hat{C}_P}
\]

Exothermic
Example: Adiabatic PFR
A ↔ B

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

2) Rate Laws: \[ r_A = -k \left[ C_A - \frac{C_B}{k_C} \right] \]
\[ k = k_1 \exp \left[ \frac{E}{R \left( \frac{1}{T_1} - \frac{1}{T} \right)} \right] \]
\[ \Delta C_P = 0 \]
\[ k_C = k_{C2} \exp \left[ \frac{\Delta H_x^0}{k} \left( \frac{1}{T_2} - \frac{1}{T} \right) \right] \]
Example: Adiabatic PFR
A ↔ B

3) Stoichiometry:

\[ C_A = C_{A_0}(1 - X) \]
\[ C_B = C_{A_0}X \]

4) Energy Balance

\[ T = T_0 + \frac{-\Delta H_X^0 X}{\sum \theta_i C_{P_i}} \]

First need to calculate the maximum conversion which is at the adiabatic equilibrium conversion.
Example: Adiabatic PFR

**Differential equations**
1. \( \frac{d(T)}{d(t)} = 1 \)

**Explicit equations**
1. \( Kc1 = 1000 \)
2. \( T1 = 290 \)
3. \( R = 1.987 \)
4. \( \Delta H = -20000 \)
5. \( Kc = Kc1 \times \exp((\Delta H/R) \times (1/T1 - 1/T)) \)
6. \( Xe = Kc/(1+Kc) \)
Example: Adiabatic PFR

A ⟷ B

\[ T = T_0 + \frac{-\Delta H_X^0 X}{\sum \theta_i C_{P_i}} \]

Adiabatic equilibrium conversion and temperature

\[ X_{eq} = \frac{K_C}{1 + K_C} \]
Example: Adiabatic PFR

We can now form a table. Set $X$, then calculate $T$, $-V_A$, and $F_{A0}/-r_A$, increment $X$, then plot $F_{A0}/-r_A$ vs. $X$:
End of Web Lecture 19
Class Lecture 17