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.
CSTR With Heat Effects

- Multiple Steady States
- Ignition and Extinction Temperatures
CSTR with Heat Effects

Courtesy of Pfaudler, Inc.
Unsteady State Energy Balance

\[ \dot{Q} - \dot{W}_S + \sum_{i=1}^{n} F_{i0} H_{i0} - \sum_{i=1}^{n} F_i H_i = \frac{d\hat{E}_{sys}}{dt} \]

Using \( \hat{E}_{sys} = \sum N_i E_i = \sum N_i (H_i - PV_i) = \sum N_i H_i - PV \)

\[ \frac{dE_{sys}}{dt} = \frac{d \sum N_i H_i}{dt} = \sum N_i \frac{dH_i}{dt} = \sum H_i \frac{dN_i}{dt} \]

\[ \frac{dH_i}{dt} = C_{pi} \frac{dT}{dt} \]

\[ \frac{dN_i}{dt} = -v_i r_A V + F_{i0} - F_i \]
Unsteady State Energy Balance

We obtain after some manipulation:

\[
\frac{dT}{dt} = \dot{Q} - \dot{W}_S - \sum F_{i0} C_{Pi} (T - T_{i0}) + \left[- \Delta H_{Rx}(T) \right] (-r_A V) \]
\[
\sum N_i C_{Pi}
\]

Collecting terms with \( \dot{Q} = UA(T_a - T) \) and \( \dot{W}_S = 0 \) high coolant flow rates, and \( F_{i0} = F_{A0} \Theta_i \)
Unsteady State Energy Balance

\[
\frac{dT}{dt} = \frac{\left( \Delta H_{Rx} \right) r_A V - \left[ \frac{C_P}{\sum \Theta_i C_{P_i}} \left( T - T_0 \right) + \left( UA \left( T - T_a \right) \right) \right]}{\sum N_i C_{P_i}}
\]

\[
= \frac{F_{A0}}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} - \left[ \frac{G(T)}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} \right] - \left[ \frac{R(T)}{\sum N_i C_{P_i}} \right]
\]

\[
= \frac{F_{A0}}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} - \left[ \frac{G(T)}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} \right] - \left[ \frac{R(T)}{\sum N_i C_{P_i}} \right]
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= \frac{F_{A0}}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} - \left[ \frac{G(T)}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} \right] - \left[ \frac{R(T)}{\sum N_i C_{P_i}} \right]
\]

\[
= \frac{F_{A0}}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} - \left[ \frac{G(T)}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} \right] - \left[ \frac{R(T)}{\sum N_i C_{P_i}} \right]
\]

\[
= \frac{F_{A0}}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} - \left[ \frac{G(T)}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} \right] - \left[ \frac{R(T)}{\sum N_i C_{P_i}} \right]
\]

\[
= \frac{F_{A0}}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} - \left[ \frac{G(T)}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} \right] - \left[ \frac{R(T)}{\sum N_i C_{P_i}} \right]
\]

\[
= \frac{F_{A0}}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} - \left[ \frac{G(T)}{\sum N_i C_{P_i}} \Delta H_R \frac{r_A V}{F_{A0}} \right] - \left[ \frac{R(T)}{\sum N_i C_{P_i}} \right]
\]
Unsteady State Energy Balance

\[
\frac{dT}{dt} = \frac{F_{A0}}{\sum N_i C_{P_i}} \left[ G(T) - R(T) \right]
\]

\[
G(T) = (r_A V) \Delta H_{Rx}
\]

\[
R(T) = C_{P_0} \left[ (1 + \kappa)T - (T_0 + \kappa T_a) \right]
\]

\[
R(T) = C_{P_0} (1 + \kappa) \left( T - T_0 + \kappa T_a \right) = C_{P_0} (1 + \kappa) (T - T_C)
\]

\[
\kappa = \frac{UA}{F_{A0} C_{P0}} \quad T_C = \frac{T_0 + \kappa T_a}{1 + \kappa}
\]
Unsteady State Energy Balance

\[ \frac{dT}{dt} = G(T) - R(T) \]

If \( G(T) > R(T) \) Temperature Increases

If \( R(T) > G(T) \) Temperature Decreases
Steady State Energy Balance for CSTRs

At Steady State

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

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

\[
G(T) - R(T) = 0
\]

\[
(\Delta H_{Rx})F_{A0}X - F_{A0} \sum \Theta_i C_{pi} (T - T_0) - UA(T - T_a) = 0
\]

Solving for \(X\).
Steady State Energy Balance for CSTRs

Solving for X:

\[
X = \frac{\sum \Theta_i C_{Pi} (T - T_0) + \frac{UA}{F_{A0}} (T - T_a)}{- \Delta H^\circ_{Rx}} = X_{EB}
\]

Solving for T:

\[
T = \frac{F_{A0} X(- \Delta H_{Rx}) + UAT_a + F_{A0} \sum \Theta_i C_{Pi} T_0}{UA + \frac{F_{A0} \sum \Theta_i C_{Pi}}{}}
\]
Steady State Energy Balance for CSTRs

\[ X(-\Delta H_{Rx}) = C_{P_0} \left[ T - T_0 + \frac{UA}{F_{A0}C_{P_0}} (T - T_a) \right] \]

Let \( \kappa = \frac{UA}{F_{A0}C_{P_0}} \)

\[ X(-\Delta H_{Rx}) = C_{P_0} \left( T + \kappa T - T_0 - \kappa T_a \right) = C_{P_0} (1 + \kappa) \left( T - \frac{T_0 + \kappa T_a}{1 + \kappa} \right) \]

\[ = C_{P_0} (1 + \kappa) (T - T_C) \]

\[ T_C = \frac{T_0 + \kappa T_a}{1 + \kappa} \]
Steady State Energy Balance for CSTRs

\[ G(T) - X \Delta H^o_{Rx} = R(T) \]

\[ X = \frac{C_{P0}(1+\kappa)(T-T_C)}{\Delta H^o_{Rx}} \]

\[ T = T_C + \frac{(-\Delta H^o_{Rx})(X)}{C_{P0}(1+\kappa)} \]
Steady State Energy Balance for CSTRs

Variation of heat removal line with inlet temperature.
Steady State Energy Balance for CSTRs

Variation of heat removal line with $\kappa$ ($\kappa=UA/C_{P_0}F_{A_0}$)
\[ V = \frac{F_{A0}X}{-r_A(X, T)} \]

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

2) Rate Laws:  
\[ -r_A = kC_A \]
3) Stoichiometry: 
\[ C_A = C_{A0}(1 - X) \]

4) Combine: 
\[ V = \frac{F_{A0}X}{kC_{A0}(1 - X)} = \frac{C_{A0} \nu_0 X}{kC_{A0}(1 - X)} \]
\[ \tau k = \frac{X}{1 - X} \]
\[ X = \frac{\tau k}{1 + \tau k} = \frac{\tau Ae^{-E/RT}}{1 + Ae^{-E/RT}} \]
\[ G(T) = X(-\Delta H_{Rx}) = \frac{\tau Ae^{-E/RT}}{1 + Ae^{-E/RT}}(-\Delta H_{Rx}) \]
Multiple Steady States (MSS)

Variation of heat generation curve with space-time.
Finding Multiple Steady States (MSS)

Finding Multiple Steady States with $T_0$ varied
Multiple Steady States (MSS)

Finding Multiple Steady States with $T_0$ varied
Multiple Steady States (MSS)

Temperature ignition-extinction curve
Multiple Steady States (MSS)

Stability of multiple state temperatures
MSS - Generating G(T) and R(T)

\[
\frac{dT}{dt} = 1
\]

\[
G(T) = X \cdot (\Delta H_{Rx})
\]

\[
R = C_{P_0} \cdot (1 + \kappa) \cdot (T - T_C)
\]

Need to solve for $X$ after combining mole balance, rate law, and stoichiometry.
MSS - Generating $G(T)$ and $R(T)$

For a first order irreversible reaction

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

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

Parameters

\[ \text{Tau}, \left( -\Delta H_{Rx} \right), k_1, E, R, T_1, T_C, \kappa, \text{C}_{P_0} \]

Then plot $G$ and $R$ as a function of $T$. 
End of Web Lecture 23
Class Lecture 19