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.
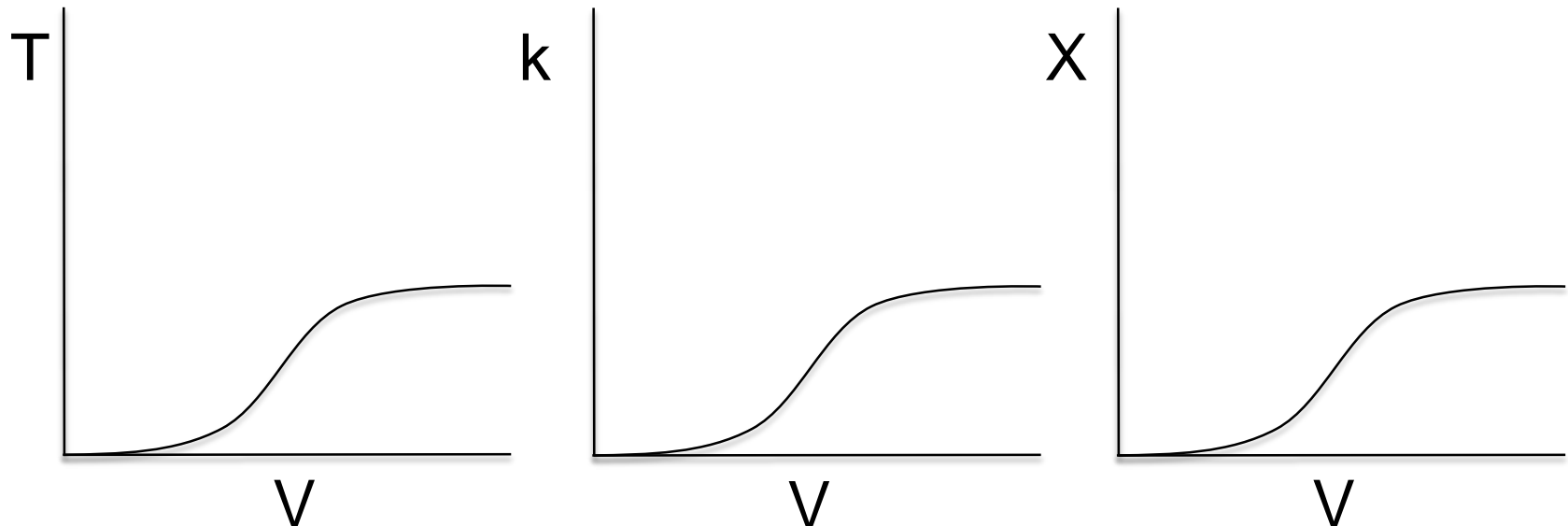
Web Lecture 19
Class Lecture 17 – Tuesday

- 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:

$$C_A = C_{A0}(1 - X)$$

Combine:

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

Energy Balance, Rationale and Overview

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

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
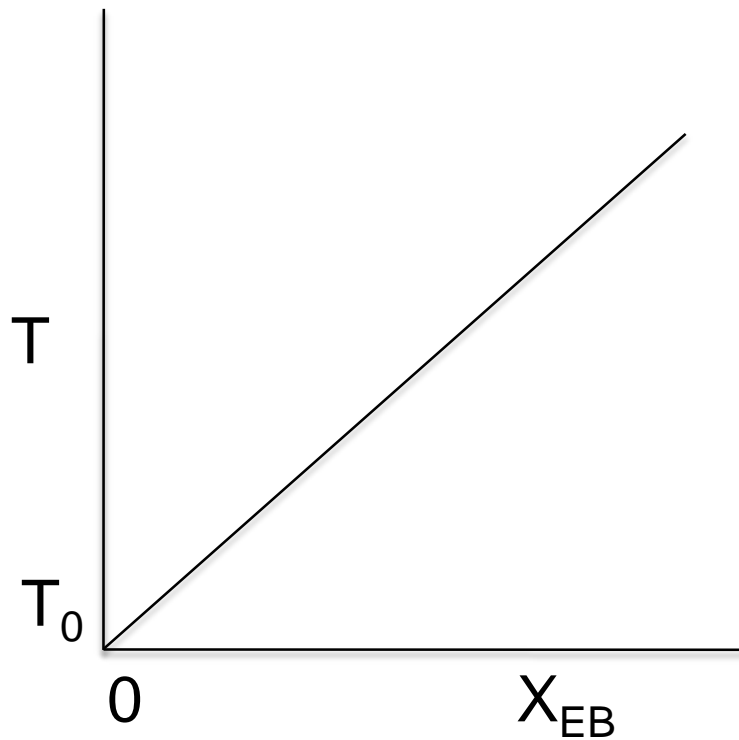
$$\dot{W}_S = 0 \qquad \Delta \hat{C}_P = 0$$

$$X_{EB} = \frac{\sum \Theta_i C_{P_i}(T - T_0)}{-\Delta H^o_{Rx}}$$

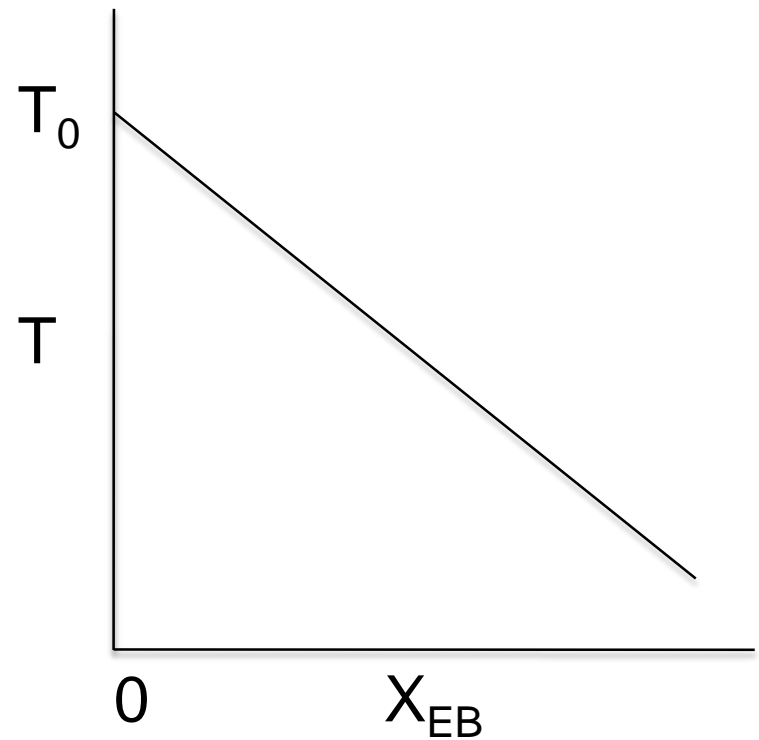$$X = \frac{\tilde{C}_{P_A}(T - T_0)}{-\Delta H_{Rx}}$$

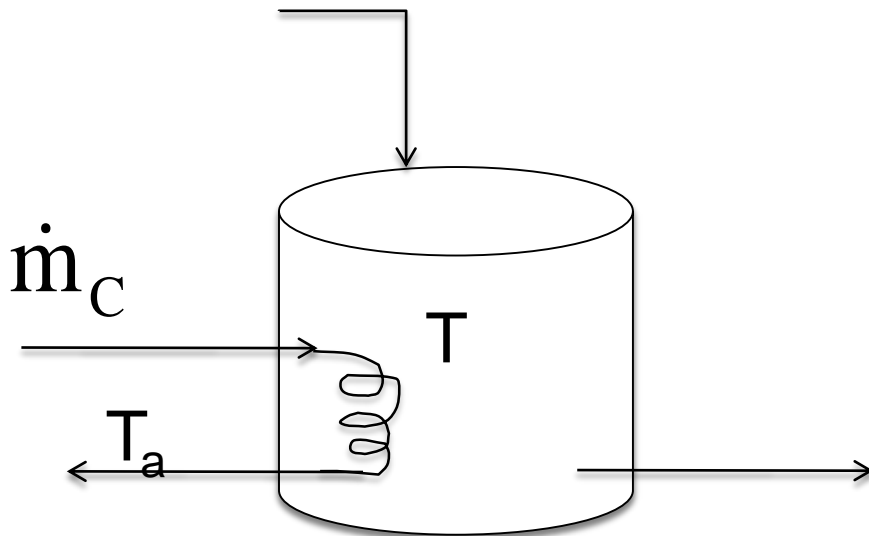$$T = T_0 + \frac{(-\Delta H^o_{Rx})X_{EB}}{\sum \Theta_i C_{P_i}}$$

Adiabatic

Exothermic

Endothermic

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
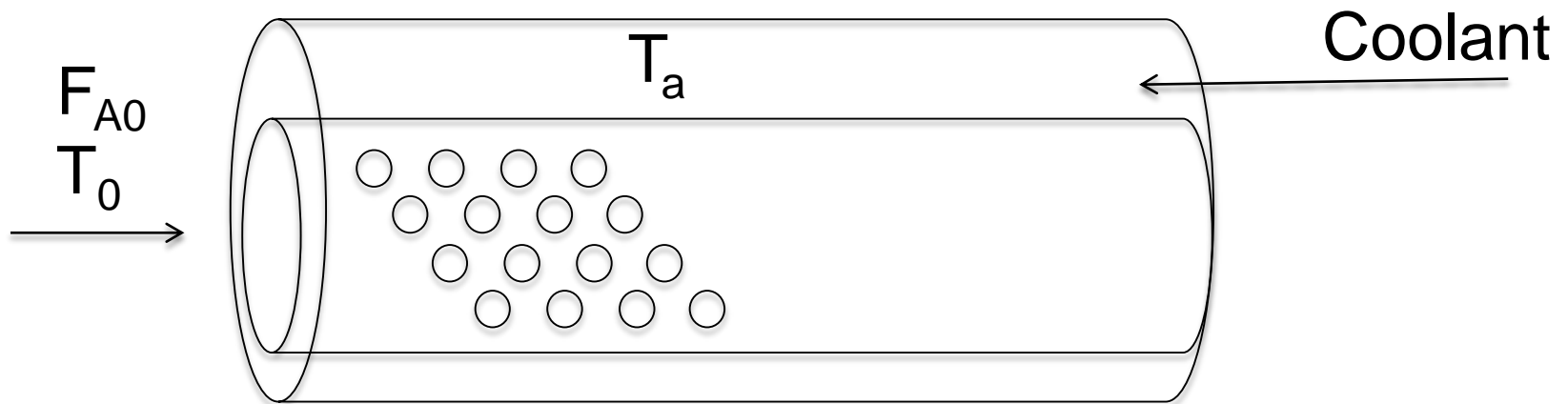
$$X_{EB} = \frac{\left(\dfrac{UA}{F_{A0}}(T - T_a)\right) + \sum \Theta_i C_{P_i}(T - T_0)}{-\Delta H^o_{Rx}}$$

$\dot{m}_C$

T

T_a

User Friendly Equations Relate T and X or F_i

3. PFR/PBR with heat exchange

3A. PFR in terms of conversion

$$\frac{dT}{dV} = \frac{\overbrace{r_A \Delta H_{Rx}(T)}^{Q_g} - \overbrace{Ua(T - T_a)}^{Q_r}}{F_{A0}\left(\sum \Theta_i C_{Pi} + \Delta C_p X\right)} = \frac{Q_g - Q_r}{F_{A0}\left(\sum \Theta_i C_{Pi} + \Delta C_p X\right)}$$

User Friendly Equations Relate T and X or F_i

3B. PBR in terms of conversion

$$\frac{dT}{dW} = \frac{r_A'\Delta H_{Rx}(T) - \frac{Ua}{\rho_b}(T - T_a)}{F_{A0}\left(\sum \Theta_i C_{Pi} + \Delta C_p X\right)}$$

3C. PBR in terms of molar flow rates

$$\frac{dT}{dW} = \frac{r_A'\Delta H_{Rx}(T) - \frac{Ua}{\rho_b}(T - T_a)}{\sum F_i C_{P_i}}$$

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

$$\frac{dT}{dt} = \frac{\dot{Q} - \dot{W}_S - \sum_{i=1}^{n} F_{i0}\left(C_{P_i}\left(T - T_{i0}\right) + \left[-\Delta H_{Rx}\left(T\right)\right]\left(-r_A V\right)\right)}{\sum_{i=1}^{n} N_i C_{P_i}}$$
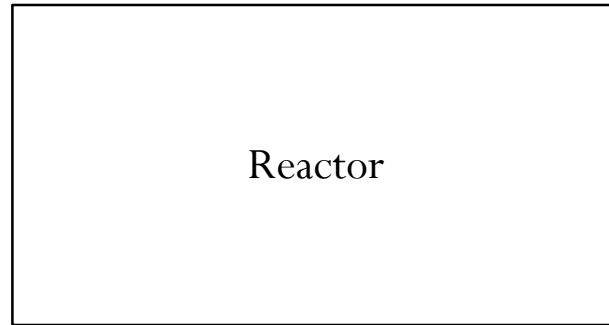
6. For multiple reactions in a PFR (q reactions and m species)

$$\frac{dT}{dV} = \frac{\sum_{i=1}^{q} r_{ij}\Delta H_{Rx_{ij}} - Ua\left(T - T_a\right)}{\sum_{j=1}^{m} F_i C_{Pj}}$$
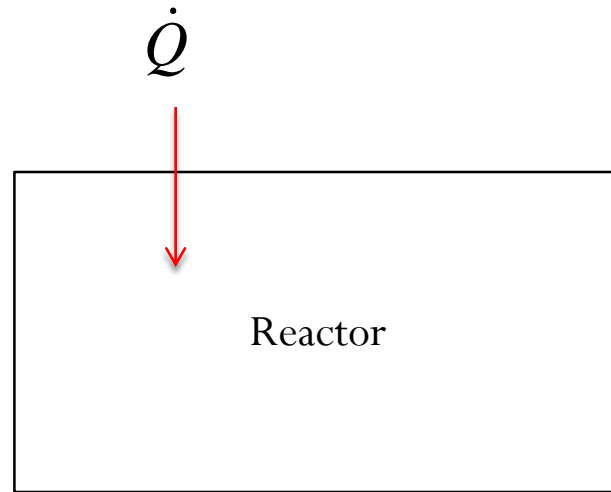
Let's look where these User Friendly Equations came from.

Energy Balance
Reactor with no Spatial Variations

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┌─────────────────────┐
│                     │
│                     │
│       Reactor       │
│                     │
│                     │
└─────────────────────┘
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Energy Balance
Reactor with no Spatial Variations

$$\dot{Q}$$

Reactor

$$\left[\text{Rate of flow of heat } \textbf{\textit{to}} \text{ the system } \textbf{\textit{from}} \text{ the surroundings} \right]$$

$$\dot{Q}$$
$$(\text{J/s})$$

Energy Balance
Reactor with no Spatial Variations
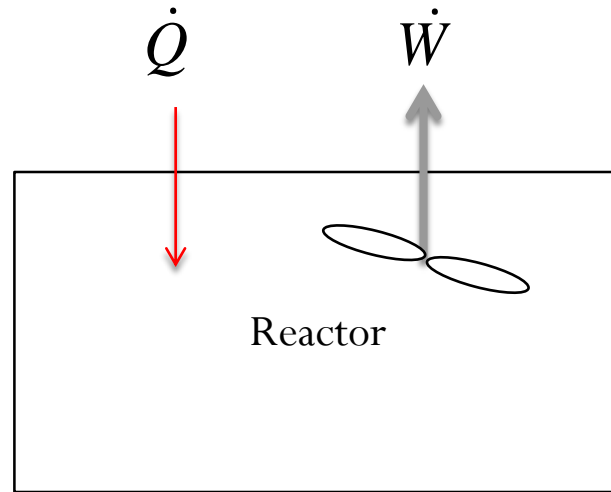
$$\dot{Q} \qquad \dot{W}$$

Reactor

$$\left[\text{Rate of flow of heat } \textbf{\textit{to}} \text{ the system } \textbf{\textit{from}} \text{ the surroundings} \right] - \left[\text{Rate of work } \textbf{\textit{done by}} \text{ the system } \textbf{\textit{on}} \text{ the surroundings} \right]$$

$$\dot{Q} \quad - \quad \dot{W}$$

$$\text{(J/s)} \qquad \text{(J/s)}$$

Energy Balance
Reactor with no Spatial Variations
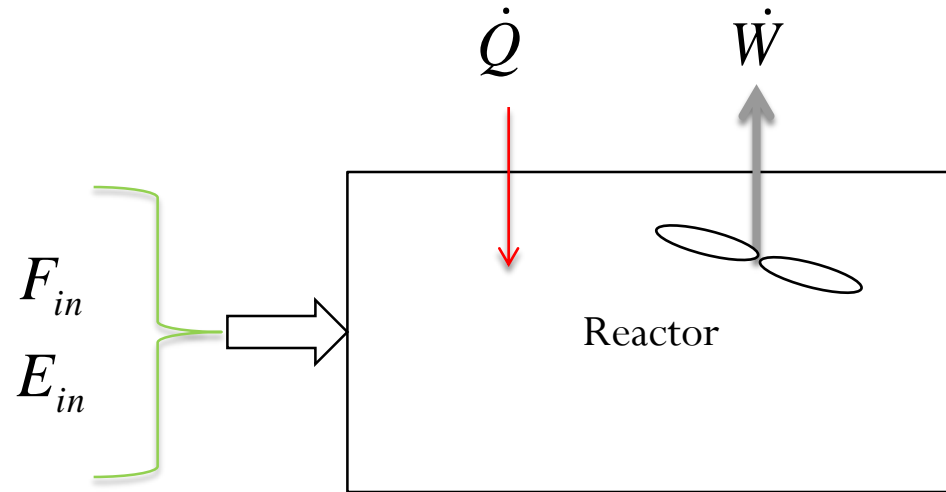
$$\dot{Q} \qquad \dot{W}$$

$$F_{in}$$
$$E_{in}$$

Reactor

$$\left[\begin{array}{c} \text{Rate of flow of} \\ \text{heat } \textbf{\textit{to}} \text{ the} \\ \text{system } \textbf{\textit{from}} \\ \text{the} \\ \text{surroundings} \end{array} \right] - \left[\begin{array}{c} \text{Rate of work} \\ \textbf{\textit{done by}} \text{ the} \\ \text{system } \textbf{\textit{on}} \text{ the} \\ \text{surroundings} \end{array} \right] + \left[\begin{array}{c} \text{Rate of energy} \\ \text{added to the} \\ \text{system by mass} \\ \text{flow } \textbf{\textit{into}} \text{ the} \\ \text{system} \end{array} \right]$$

$$\dot{Q} \qquad - \qquad \dot{W} \qquad + \qquad F_{in}E_{in}$$

$$\text{(J/s)} \qquad\qquad \text{(J/s)} \qquad\qquad \text{(J/s)}$$

Energy Balance
Reactor with no Spatial Variations

$$\dot{Q} \qquad \dot{W}$$

F_{in}
E_{in}

Reactor

F_{out}
E_{out}

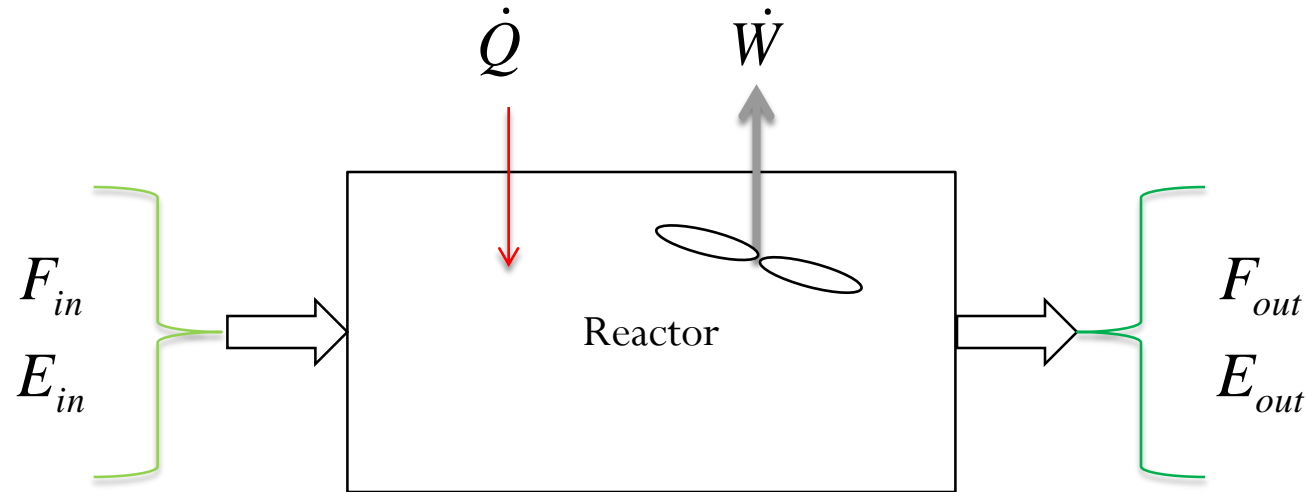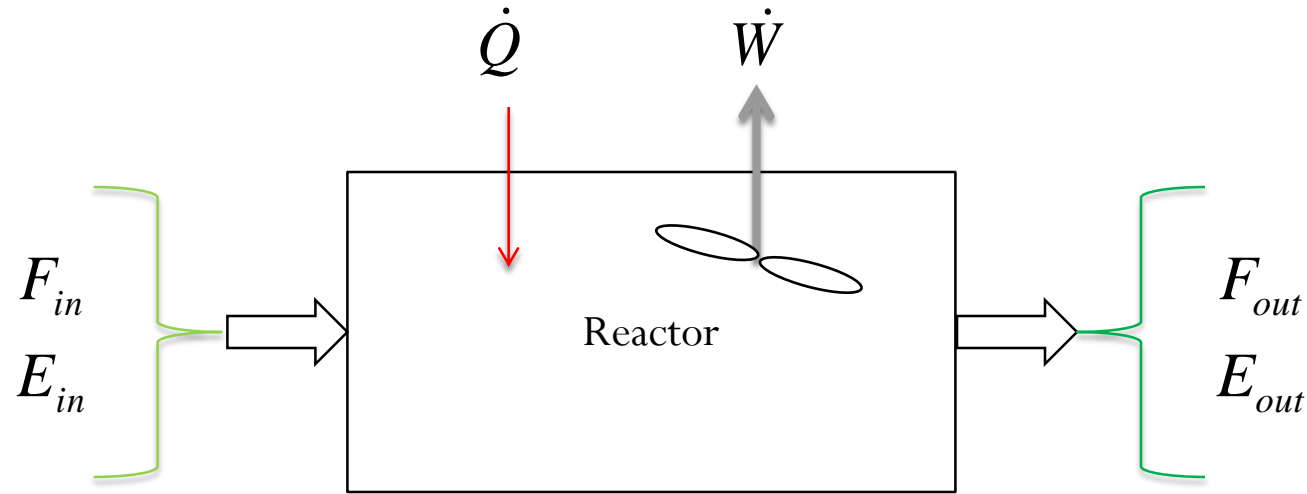| Rate of flow of heat *to* the system *from* the surroundings	-	Rate of work *done by* the system *on* the surroundings	+	Rate of energy added to the system by mass flow *into* the system	-	Rate of energy leaving system by mass flow *out* of the system

$$\dot{Q} \quad - \quad \dot{W} \quad + \quad F_{in}E_{in} \quad - \quad F_{out}E_{out}$$

$$\text{(J/s)} \qquad \text{(J/s)} \qquad \text{(J/s)} \qquad \text{(J/s)}$$

Energy Balance
Reactor with no Spatial Variations

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

(J/s)   (J/s)   (J/s)   (J/s)   (J/s)

Energy Balance
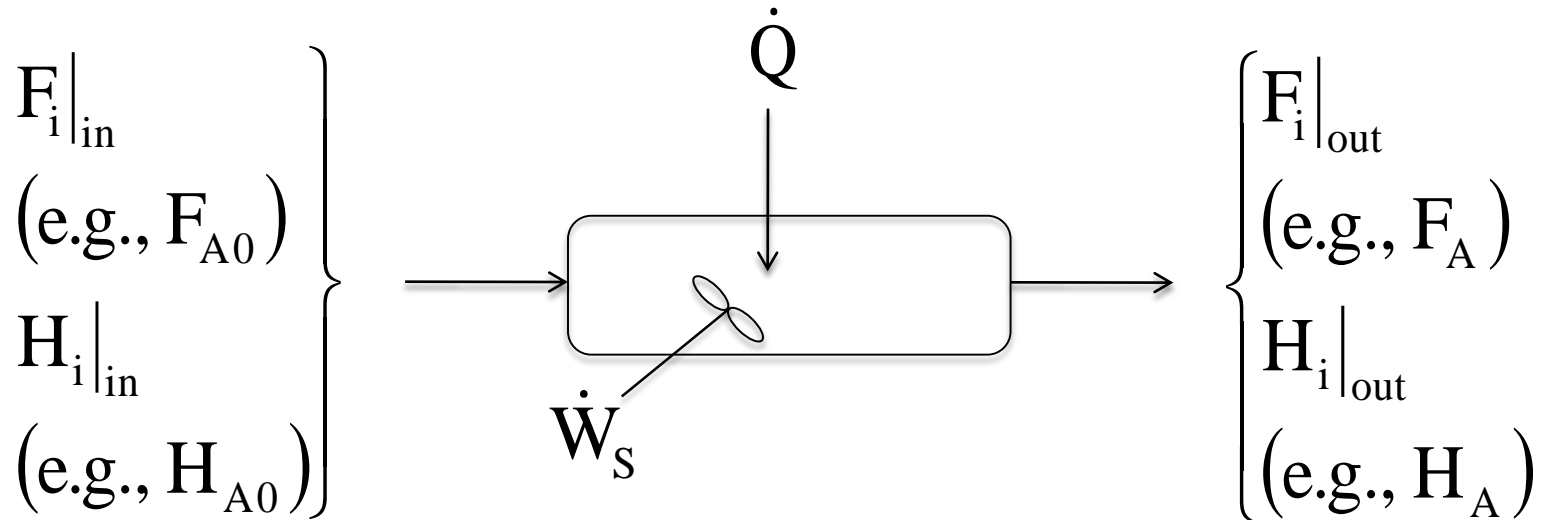
Energy Balance on an open system: schematic.

$$\dot{Q} - \dot{W}_S + \sum F_{i0}E_{i0}\Big|_{in} - \sum F_i E_i\Big|_{out} = \frac{dE_{system}}{dt} \quad (1)$$

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 ΔH_{Rx}

5. Define ΔC_P

6. Manipulate so that the overall energy balance is in terms of the User Friendly Equations.

Intro to Heat Effects

Assumptions:

$$E_i = U_i + \overset{=0}{\cancel{PE_i}} + \overset{=0}{\cancel{KE_i}}$$

Other energies small compared to internal

$$\dot{W} = \text{flow work} + \text{shaft work}$$

$$\text{flow work} = -\sum F_{i0} P_0 \tilde{V}_{i0} + \sum F_i P \tilde{V}_i \qquad \left(\tilde{V} = \frac{m^3}{mol} \right)$$

Recall:

$$H_i = U_i + P\tilde{V}_i$$

21

Intro to Heat Effects

Substituting for $\dot{W}$

$$\sum F_{i0}U_{i0} - \sum F_i U_i + \dot{Q} - \left[-\sum F_{i0}P_0 \tilde{V}_{i0} + \sum F_i P \tilde{V}_i + \dot{W}_S \right] = \frac{dE_{sys}}{dt}$$

$$\sum F_{i0} \overbrace{\left[U_{i0} + P_0 \tilde{V}_{i0} \right]}^{H_{i0}} - \sum F_i \overbrace{\left[U_i + P \tilde{V}_i \right]}^{H_i} + \dot{Q} - \dot{W}_S = \frac{dE_{sys}}{dt}$$

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

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 :

$$\dot{Q} - \dot{W}_S + \sum F_{i0} H_{i0} - \sum F_i H_i = \frac{dE_{system}}{dt}$$

For Steady State Operation:

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

Intro to Heat Effects

$$\sum F_{i0} H_{i0} = F_{A0} \sum \Theta_i H_{i0}$$

$$\sum F_i H_i = F_{A0} \sum \left(\Theta_i + \upsilon_i X \right) H_i = F_{A0} \sum \Theta_i H_i + F_{A0} X \overbrace{\sum \upsilon_i H_i}^{\Delta H_{Rx}}$$

$$\dot{Q} - \dot{W}_S + F_{A0} \left(\sum \Theta_i \left(H_{i0} - H_i \right) + F_{A0} X \Delta H_{Rx} \right) = 0$$

Intro to Heat Effects

For No Phase Changes

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

↳ Enthalpy of formation at temperature T_R

Constant Heat Capacities

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

$$H_{i0} - H_i = C_{Pi}(T - T_0)$$

$$\sum \upsilon_i H_i = \sum \upsilon_i H_i^0 + \sum \upsilon_i C_{Pi}(T - T_R)$$

↳ Heat of reaction at temperature T

Intro to Heat Effects

$$\sum \upsilon_i H_i = \sum \upsilon_i H_i^0 + \sum \upsilon_i C_{Pi}\left(T - T_R\right)$$

$$\Delta H_R(T) = \Delta H_R^o(T_R) + \Delta \hat{C}_P\left(T - T_R\right)$$

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

<u>Substituting</u> back into the Energy Balance

$$\dot{Q} - \dot{W}_S - F_{A0}X\left[\Delta H_R^o(T_R) + \Delta \hat{C}_P\left(T - T_R\right)\right] - F_{A0}\sum \Theta_i \tilde{C}_{Pi}\left(T - T_{i0}\right) = 0$$

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

26

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

$$\dot{Q} - \dot{W}_S + F_{A0}\left(\sum \Theta_i \left(H_{i0} - H_i\right) + F_{A0} X \Delta H_{Rx}\right) = 0$$

Substituting back into the Energy Balance

$$\dot{Q} - \dot{W}_S - F_{A0} X \left[\Delta H_R^o\left(T_R\right) + \Delta \hat{C}_P\left(T - T_R\right)\right] - F_{A0} \sum \Theta_i \tilde{C}_{Pi}\left(T - T_{i0}\right) = 0$$

Adiabatic Energy Balance

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

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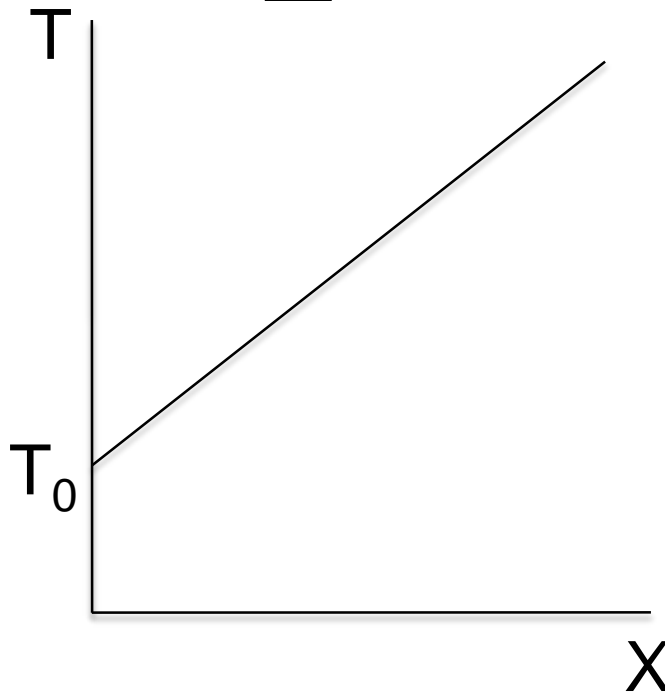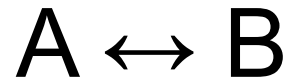
Exothermic

Example: Adiabatic PFR
A ↔ B
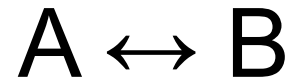
1) Mole Balance:

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

2) Rate Laws:

$$r_A = -k\left[C_A - \frac{C_B}{k_C}\right] \qquad k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$\Delta C_P = 0 \qquad k_C = k_{C2} \exp\left[\frac{\Delta H_X^0}{k}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]$$

Example: Adiabatic PFR

A ↔ B

3) Stoichiometry:

$$C_A = C_{A0}(1 - X)$$

$$C_B = C_{A0}X$$

4) Energy Balance

$$T = T_0 + \frac{-\Delta H_X^0 X}{\sum \theta_i C_{Pi}}$$

First need to calculate the maximum conversion which is at the *adiabatic equilibrium conversion.*

Example: Adiabatic PFR

Differential equations
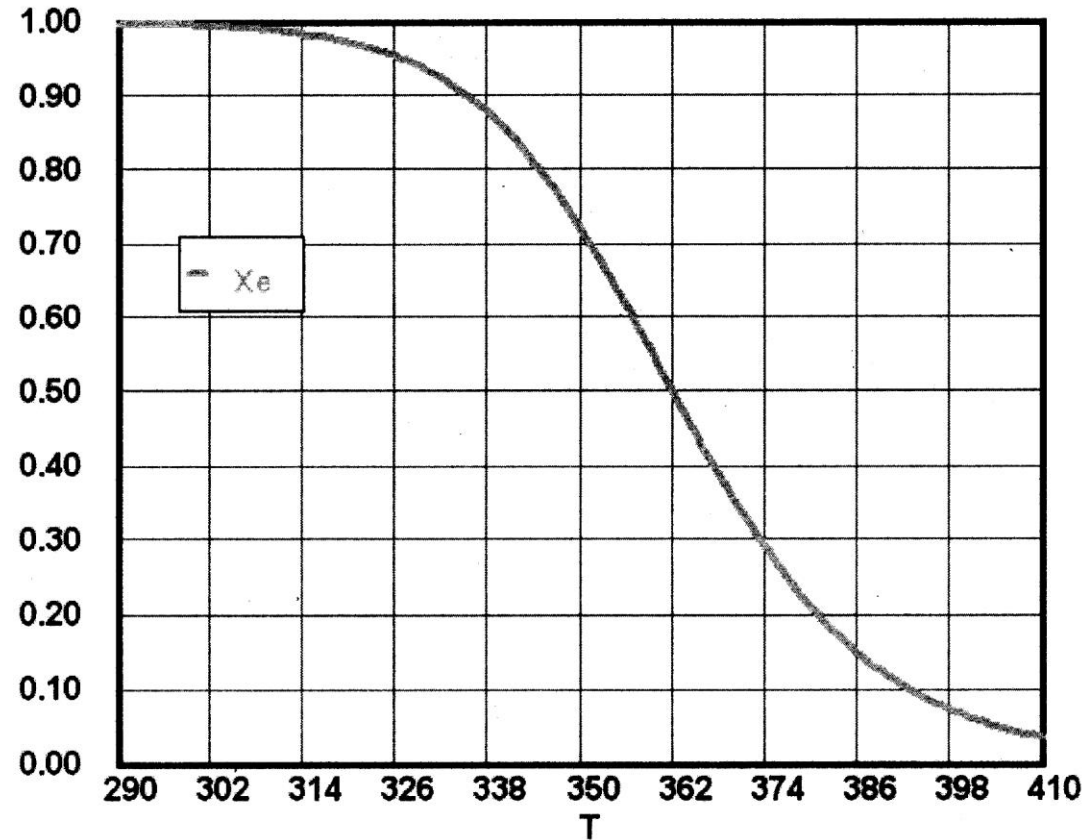
1 d(T)/d(t) = 1

Explicit equations

1 Kc1 = 1000

2 T1 = 290

3 R = 1.987

4 DeltaH = -20000

5 Kc = Kc1*exp((DeltaH/R)*(1/T1-1/T))

6 Xe = Kc/(1+Kc)

Example: Adiabatic PFR

A ↔ B

$$T = T_0 + \frac{-\Delta H_X^0 X}{\sum \theta_i C_{Pi}}$$

Adiabatic equilibrium conversion and temperature
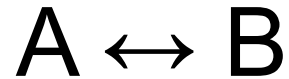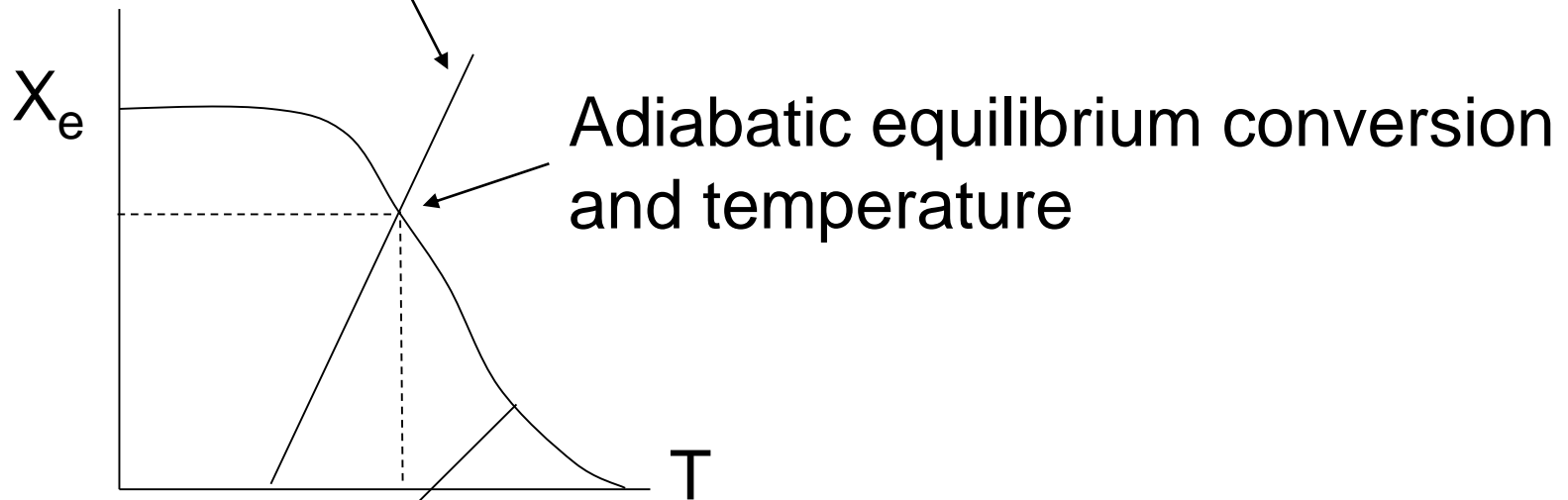
$$X_{eq} = \frac{K_C}{1 + K_C}$$

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:

$F_{A0}/-r_A$

X

End of Web Lecture 19
Class Lecture 17