Lecture 20

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 $\dot{W}$

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

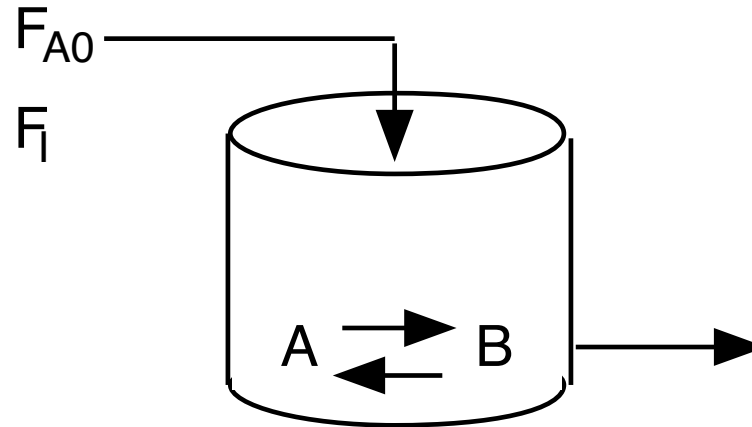$$\boxed{\sum F_{i0}H_{i0} - \sum F_i H_i + \dot{Q} - \dot{W}_S = \frac{dE_{sys}}{dt}}$$

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

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

F_{A0}

F_i

A ⇌ B

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.
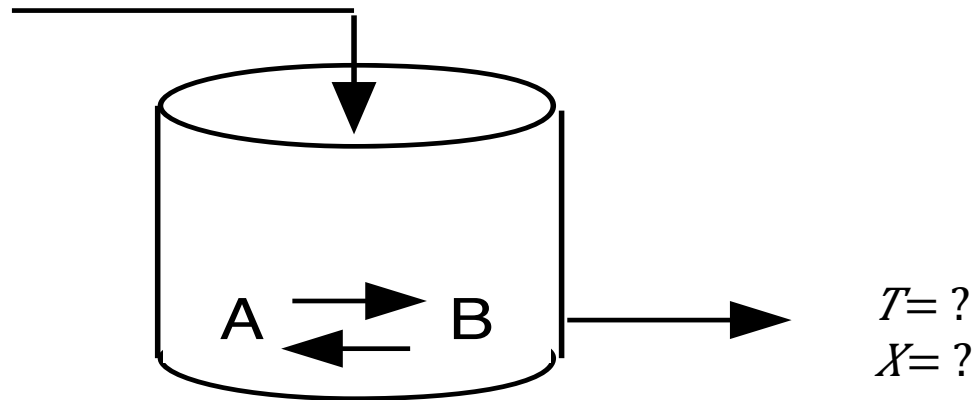
CSTR: Adiabatic Example

$F_{A0} = 5\,mol/min$ $\Delta H_{Rxn} = -20000\,cal/mol\,A$ (exothermic)

$T_0 = 300\,K$

$F_I = 10\,mol/min$

A ⇌ B

$T = ?$
$X = ?$

1) Mole Balances:

$$V = \frac{F_{A0}X}{-r_A\big|_{exit}}$$

CSTR: Adiabatic Example

2) Rate Laws:

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

$$k = k_1 e^{\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}$$

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

3) Stoichiometry:

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

$$C_B = C_{A0}X$$

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CSTR: Adiabatic Example

4) Energy Balance

Adiabatic, $\Delta C_p = 0$

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

$$T = 300 + \left[\frac{-(-20,000)}{164 + (2)(18)} \right] X = 300 + \frac{20,000}{164 + 36} X$$
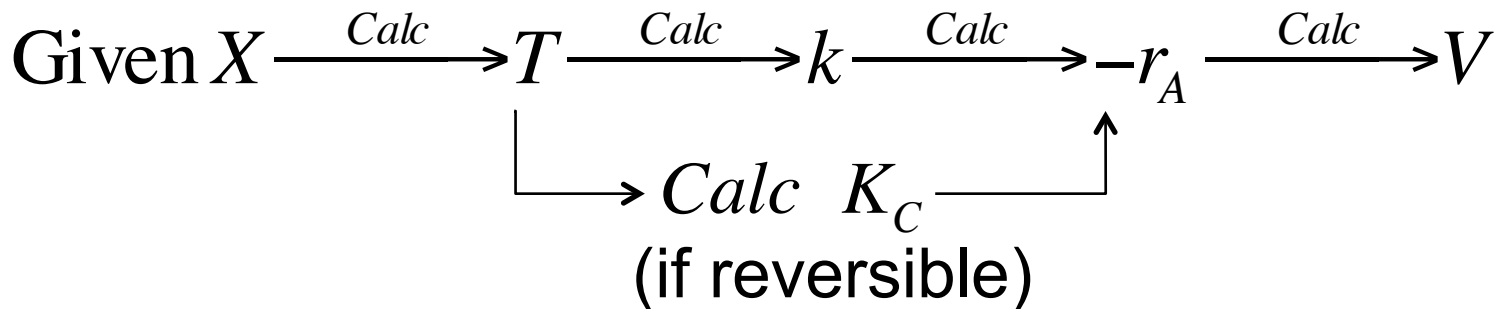
$$\boxed{T = 300 + 100\,X}$$

CSTR: Adiabatic Example

Irreversible for Parts (a) through (c)

$$-r_A = kC_{A0}(1-X)(\text{i.e., } K_C = \infty)$$

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

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

$$T \xrightarrow{} Calc \ K_C \xrightarrow{} -r_A$$

(if reversible)

CSTR: Adiabatic Example

Given X, Calculate T and V

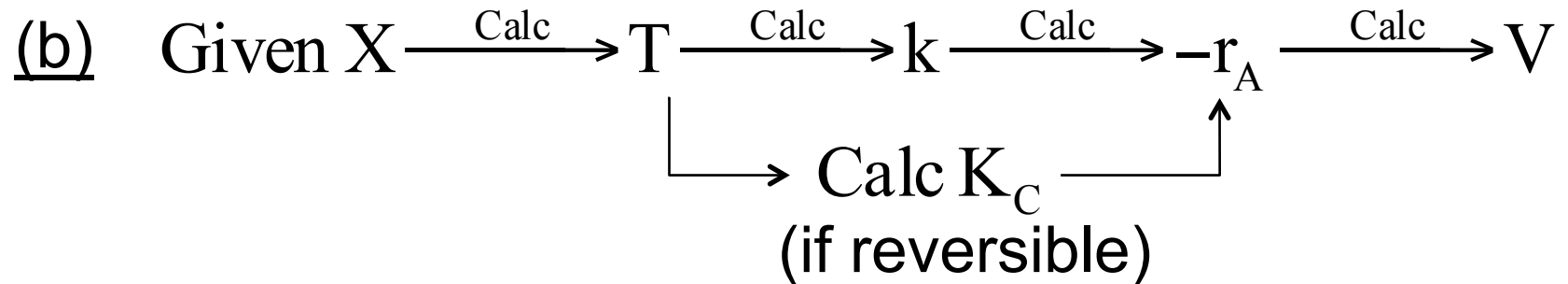$$V = \frac{F_{A0}X}{-r_A\big|_{exit}} = \frac{F_{A0}X}{kC_{A0}(1-X)}$$

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

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

$$V = \frac{F_{A0}X}{-r_A} = \frac{(5)(0.8)}{(3.81)(2)(1-0.8)} = 2.82\ dm^3$$

CSTR: Adiabatic Example

Given T, Calculate X and V

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

$\text{T} \longrightarrow \text{Calc K}_C \longrightarrow$ (to $-\text{r}_A$)

(if reversible)

$$-r_A = kC_{A0}(1-X)\ (\text{Irreversible})$$

$$T = 360K$$

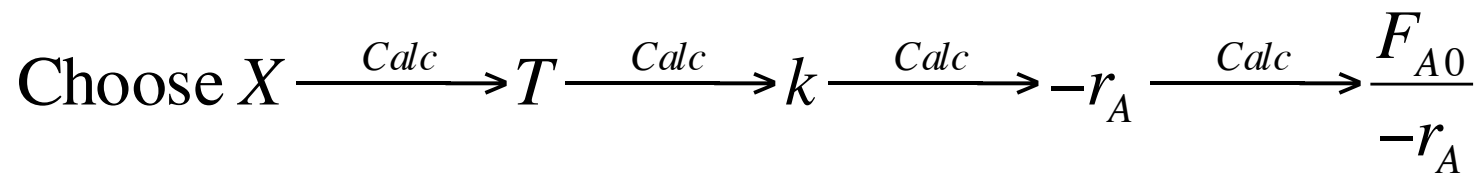$$X = \frac{T-300}{100} = 0.6$$

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

$$V = \frac{(5)(0.6)}{(1.83)(2)(0.4)} = 2.05\,dm^3$$

CSTR: Adiabatic Example

(c) Levenspiel Plot
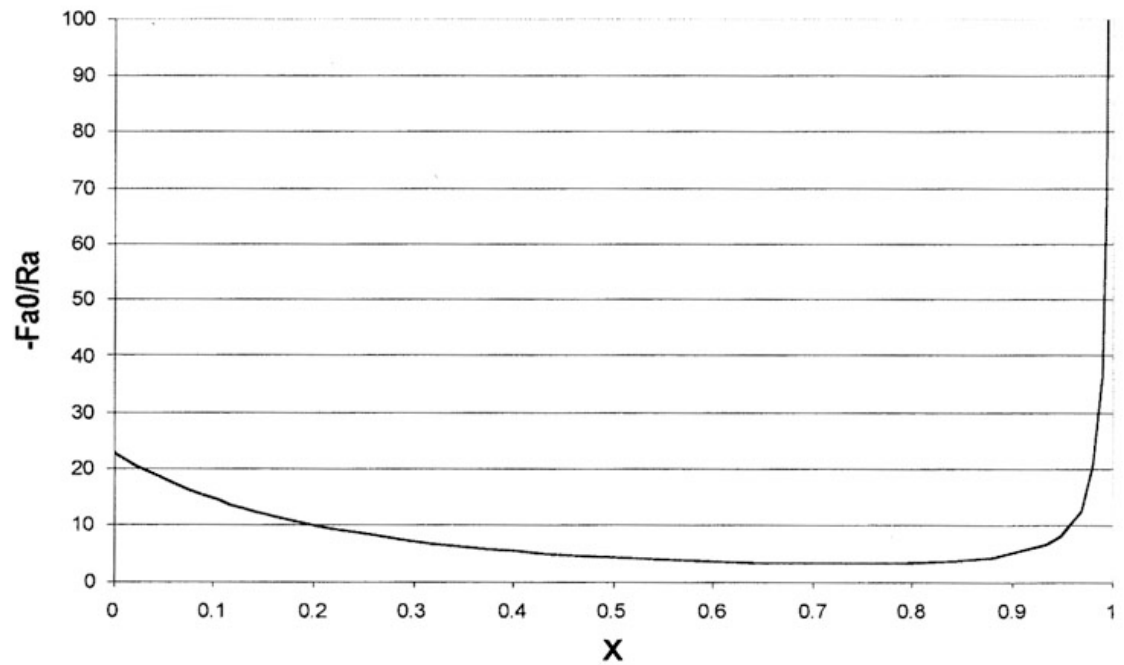
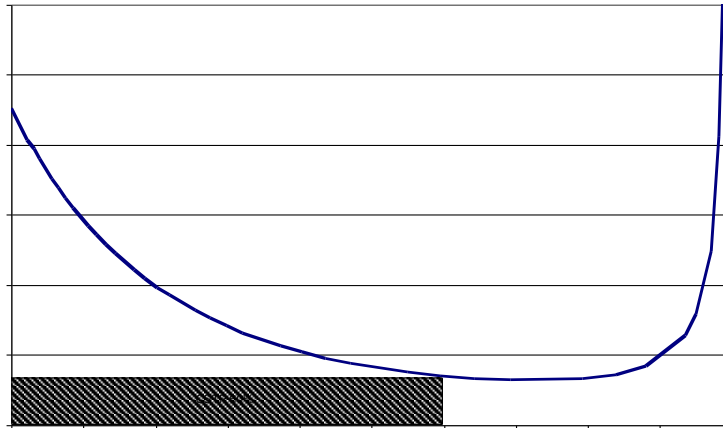$$\frac{F_{A0}}{-r_A} = \frac{F_{A0}}{kC_{A0}(1-X)}$$

$$T = 300 + 100X$$

$$\text{Choose } X \xrightarrow{Calc} T \xrightarrow{Calc} k \xrightarrow{Calc} -r_A \xrightarrow{Calc} \frac{F_{A0}}{-r_A}$$

CSTR: Adiabatic Example

(c) Levenspiel Plot

X	T(K)	$\dfrac{F_{A0}}{-r_A}(dm^3)$
0	300	25
0.1	310	14.4
0.2	320	9.95
0.4	340	5.15
0.6	360	3.42
0.8	380	3.87
0.9	390	4.16
0.95	395	8.0

CSTR: Adiabatic Example

CSTR   X = 0.6   T = 360 K

CSTR   X = 0.95   T = 395 K

CSTR 95%

CSTR: Adiabatic Example

PFR   X = 0.6

PFR   X = 0.95

CSTR: Adiabatic Example - Summary

CSTR	X = 0.6	T = 360	V = 2.05 dm^3
PFR	X = 0.6	T$_{exit}$ = 360	V = 5.28 dm^3
CSTR	X = 0.95	T = 395	V = 7.59 dm^3
PFR	X = 0.95	T$_{exit}$ = 395	V = 6.62 dm^3

Energy Balance in terms of Enthalpy

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

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

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

PFR Heat Effects

$$\frac{dF_i}{dV} = r_i = v_i\left(-r_A\right)$$

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

$$\frac{dH_i}{dV} = C_{Pi}\frac{dT}{dV}$$

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

$$\sum v_i H_i = \Delta H_{Rx}$$

PFR Heat Effects

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

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

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

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

Heat Exchange Example:
Case 1 - Adiabatic

Energy Balance:

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

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

User Friendly Equations

A. Constant Ta   e.g.,   Ta = 300K

B. Variable T_a Co-Current

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

C. Variable T_a Counter Current

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

Guess T_a at V = 0 to match T_{a0} = T_{a0} at exit, i.e., V = V

Heat Exchanger Energy Balance
Variable T_a Co-current

Coolant Balance:

In - Out + Heat Added = 0

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

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

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

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

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

Heat Exchanger Energy Balance
Variable T_a Counter-current

In - Out +   Heat Added = 0

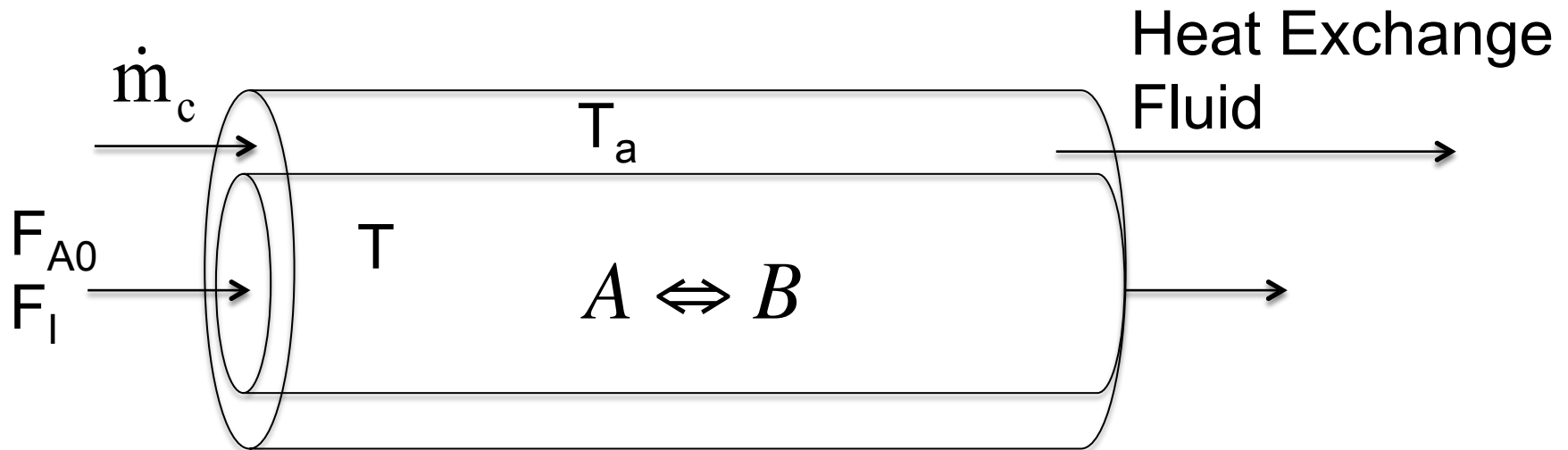$$\dot{m}_C H_C \big|_{V+\Delta V} - \dot{m}_C H_C \big|_V + Ua\Delta V \left(T - T_a \right) = 0$$

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

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

Heat Exchanger – Example
Case 1 – Constant T_a

Elementary liquid phase reaction carried out in a PFR

$\dot{m}_c$

T_a

Heat Exchange Fluid

F_{A0}
F_I

T

$A \Leftrightarrow B$

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:

$$(1) \quad \frac{dX}{dV} = -r_A / F_{A0}$$

2) Rate Laws:

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

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

$$(4) \quad K_C = K_{C2} \exp \left[\frac{\Delta H_{Rx}}{R} \left(\frac{1}{T_2} - \frac{1}{T} \right) \right]$$

Heat Exchanger – Example
Case 1 – Constant T_a

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

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

4) Heat Effects:

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

$$(\Delta C_P = 0)$$

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

$$\sum \theta_i C_{Pi} = C_{PA} + \theta_I C_{PI} \quad (9)$$

Heat Exchanger – Example
Case 1 – Constant T_a

Parameters: $\Delta H_R, \quad E, \quad R, \quad T_1, \quad T_2,$

$k_1, \quad k_{C2}, \quad Ua, \quad T_a, \quad F_{A0},$

$C_{A0}, \quad C_{PA}, \quad C_{PI}, \quad \theta_I,$

$rate = -r_A$

PFR Heat Effects

Heat generated   Heat removed

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

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

$$\frac{dT}{dV} = \frac{\left(\Delta H_R\right)\left(r_A\right) - Ua\left(T - T_a\right)}{F_{A0}\left[\sum \theta_i C_{Pi} + \Delta C_P X\right]}$$

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

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

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 $d(X)/d(V) = -ra/Fao$

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 $E = 10000$

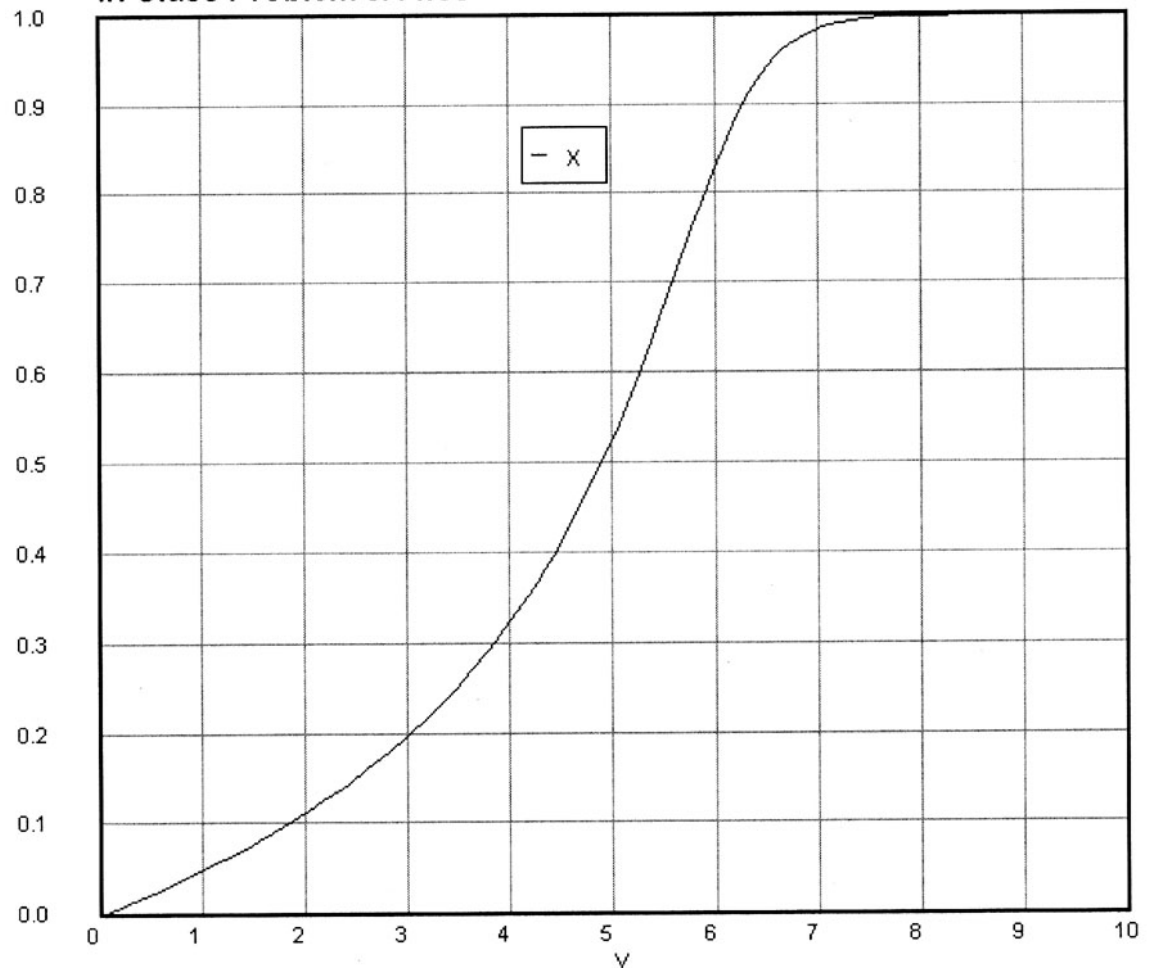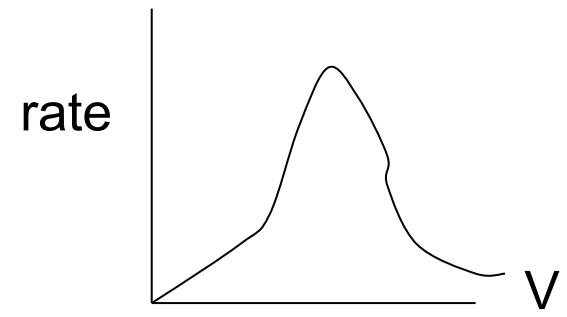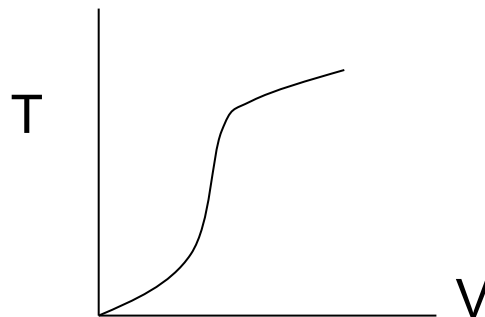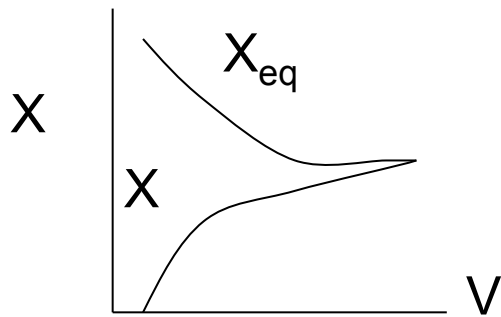12 $R = 1.987$

13 $T1 = 298$

14 $Ca = Cao*(1-X)$

15 $k = k1*exp(E/R*(1/T1-1/T))$

In Class Problem 3/11/08

Example: Adiabatic

Find conversion, X_{eq} and T as a function of reactor volume

Heat Exchange

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

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

$$\frac{dT}{dV} = \frac{(-r_A)(-\Delta H_{Rx}) - Ua(T - T_a)}{F_{A0}\sum \Theta_i C_{P_i}} \qquad (16B)$$

Need to determine T_a

User Friendly Equations

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

Additional Parameters (18B – (20B):

$$T_a, \ \sum \Theta_i C_{P_i}, \ Ua$$

B. Variable T_a Co-Current

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

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

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

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

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

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

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

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

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

$$\dot{m}_C \frac{dH_C}{dV} + Ua\left(T - T_a\right) = 0 \qquad \boxed{\frac{dT_a}{dV} = \frac{Ua\left(T_a - T\right)}{\dot{m}_C C_{PC}}}$$

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

$$\int_0^W \frac{Ua}{\rho_B}\left(T_a - T\right)dW + \sum F_{i0}H_{i0} - \sum F_i H_i = 0$$

Differentiating with respect to W:

$$\frac{Ua}{\rho_B}\left(T_a - T\right) + 0 - \sum \frac{dF_i}{dW}H_i - \sum F_i \frac{dH_i}{dW} = 0$$

Derive the user-friendly Energy Balance for a PBR

Mole Balance on species i:

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

Enthalpy for species i:

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

Derive the user-friendly Energy Balance for a PBR

Differentiating with respect to W:

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

$$\frac{Ua}{\rho_B}\left(T_a - T\right) + r_A'\sum \upsilon_i H_i - \sum F_i C_{Pi}\frac{dT}{dW} = 0$$

Derive the user-friendly Energy Balance for a PBR

$$\frac{Ua}{\rho_B}\left(T_a - T\right) + r_A' \sum \upsilon_i H_i - \sum F_i C_{Pi} \frac{dT}{dW} = 0$$

$$\sum \upsilon_i H_i = \Delta H_R\left(T\right)$$

$$F_i = F_{A0}\left(\Theta_i + \upsilon_i X\right)$$

Final Form of the Differential Equations in Terms of Conversion:

A:

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}\left(T_a - T\right) + r_A'\Delta H_R\left(T\right)}{F_{A0}\left[\sum \Theta_i \widetilde{C}_{Pi} + \Delta \hat{C}_P X\right]} = f\left(X, T\right)$$

Derive the user-friendly Energy Balance for a PBR

Final form of terms of Molar Flow Rate:

$$\frac{dT}{dW} = \frac{\dfrac{Ua}{\rho_B}\left(T_a - T\right) + r_A{}'\Delta H}{F_i C_{Pi}}$$

B:

$$\frac{dX}{dW} = \frac{-r_A{}'}{F_{A0}} = g(X, T)$$

Reversible Reactions

$$A + B \Leftrightarrow C + D$$

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:

$$\frac{d \ln K_P}{dT} = \frac{\Delta H_R(T)}{RT^2} = \frac{\Delta H_R{}^o(T_R) + \Delta \hat{C}_P(T - T_R)}{RT^2}$$
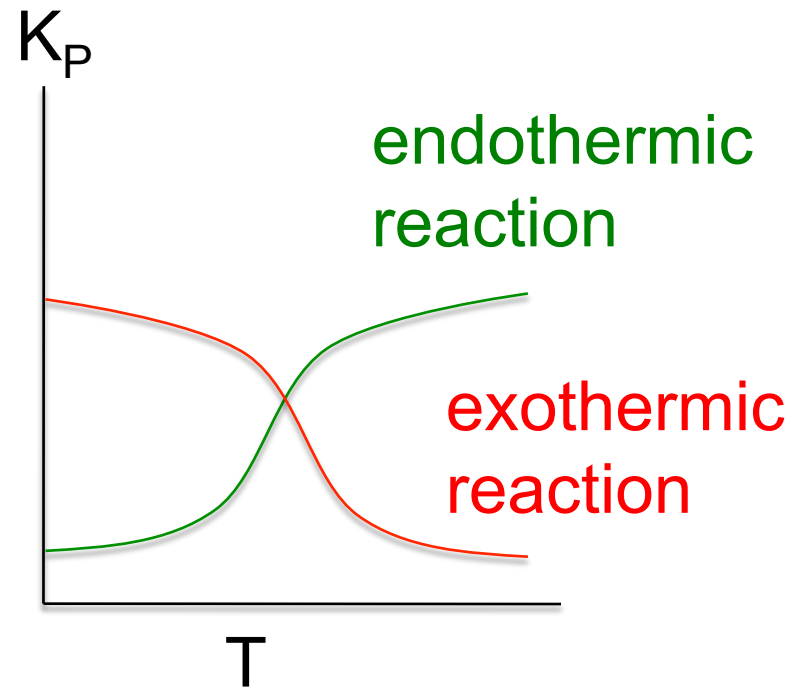
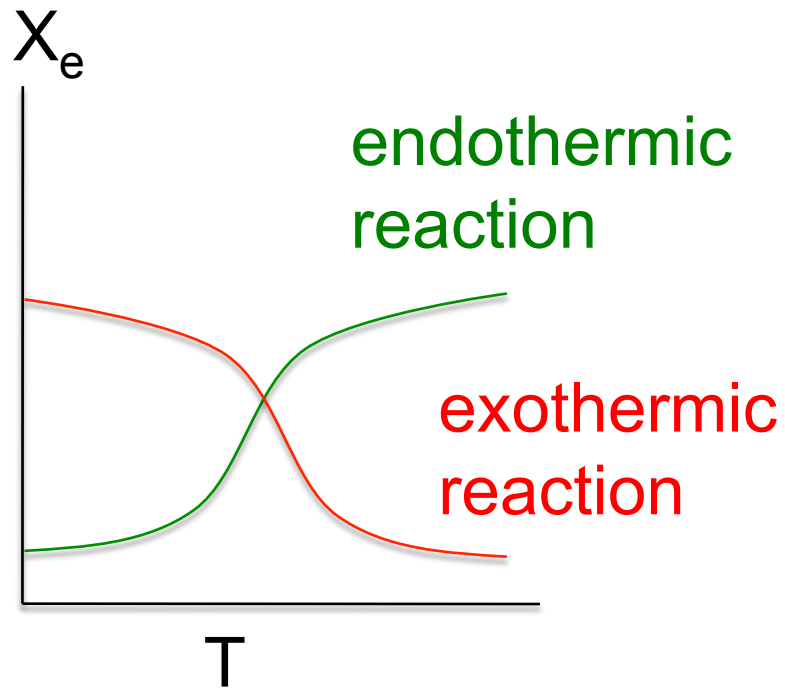# Reversible Reactions

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

End of Lecture 20