Lecture 21

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 21
Class Lecture 17 – Tuesday

- Gas Phase Reactions
- Trends and Optimums

User Friendly Equations relate T, X, or F_i

1. Adiabatic CSTR, PFR, Batch, PBR achieve this:

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

$$X_{EB} = \frac{\sum \Theta_i \hat{C}_{P_i}(T - T_0)}{-\Delta H_{Rx}}$$
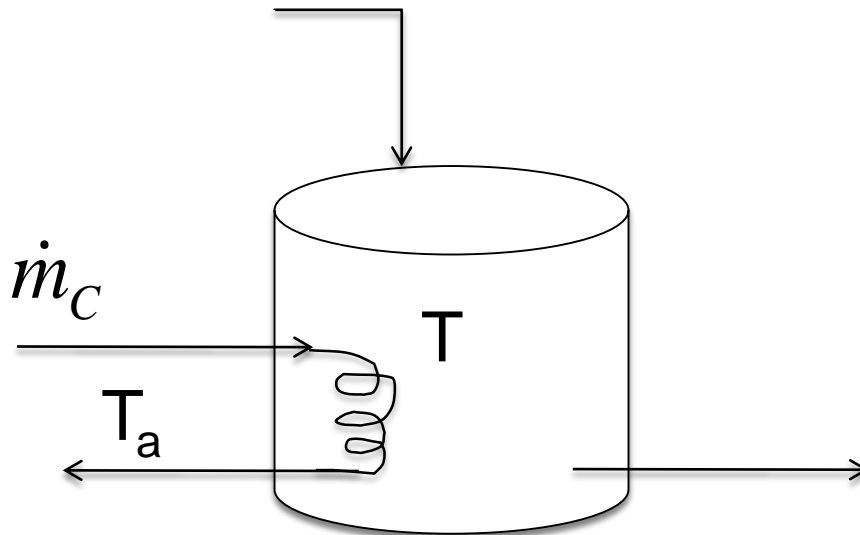
$$X = \frac{\tilde{C}_{P_A}(T - T_0)}{-\Delta H_{Rx}}$$

$$T = T_0 + \frac{(-\Delta H_{Rx})X}{\sum \Theta_i C_{P_i}}$$
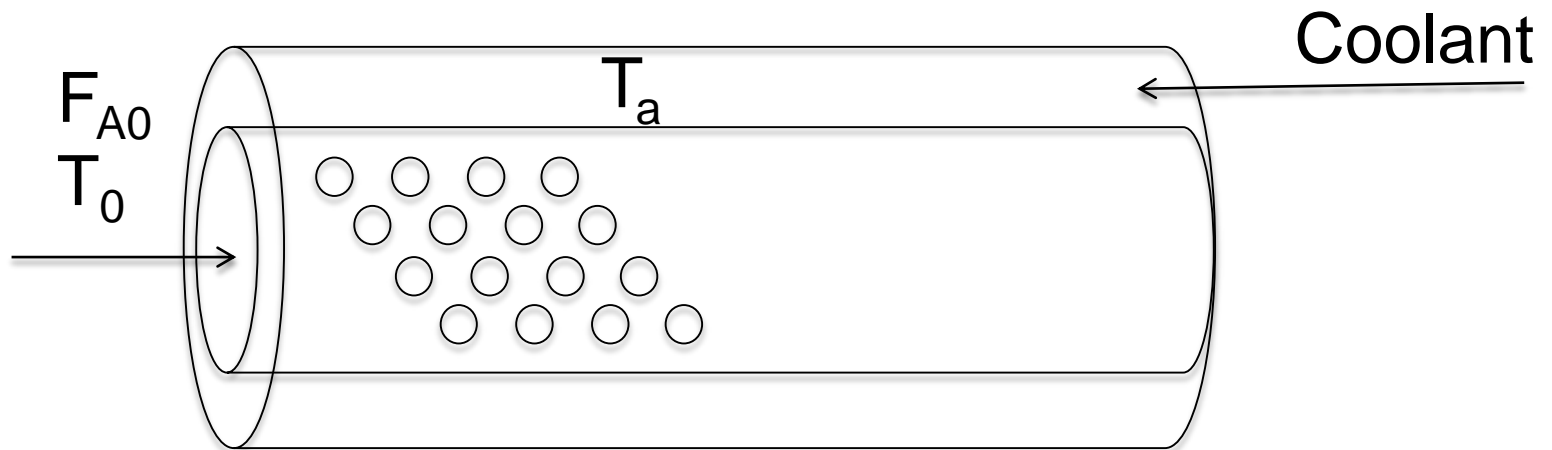
3

User Friendly Equations relate T, X, or F_i

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

$$X_{EB} = \frac{\left(\dfrac{UA}{F_{A0}} (T - T_a) \right) + \sum \Theta_i \tilde{C}_{P_i} (T - T_0)}{-\Delta H_{Rx}}$$

$\dot{m}_C$

T

T_a

User Friendly Equations relate T, X, or F_i

3. PFR/PBR with heat exchange:

3A. In terms of conversion, X

$$\frac{dT}{dW} = \frac{\frac{Ua}{\rho_B}(T_a - T) + r_A{}'\Delta H_{Rx}(T)}{F_{A0}\left(\sum \Theta_i \tilde{C}_{P_i} + \Delta C_p X\right)}$$

User Friendly Equations relate T, X, or F_i

3B. In terms of molar flow rates, F_i

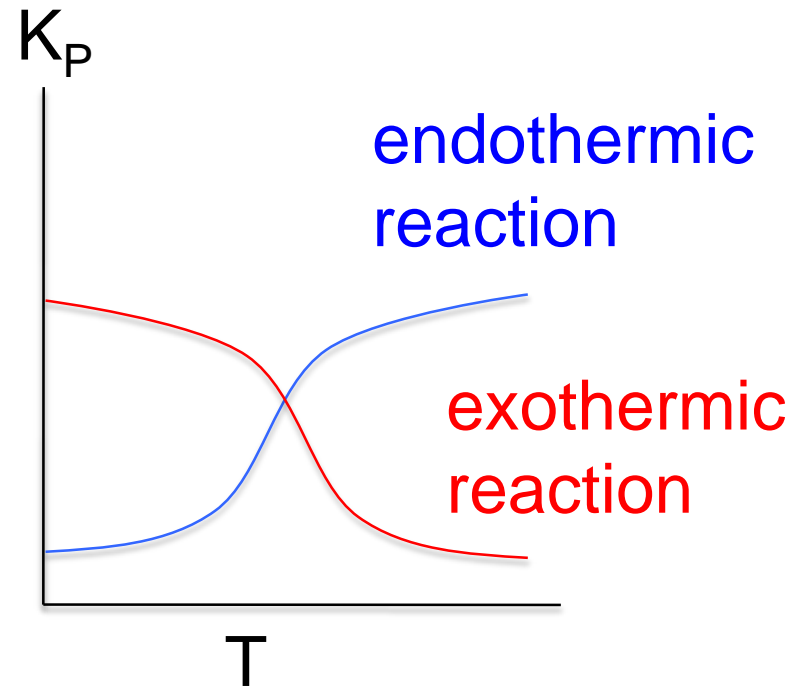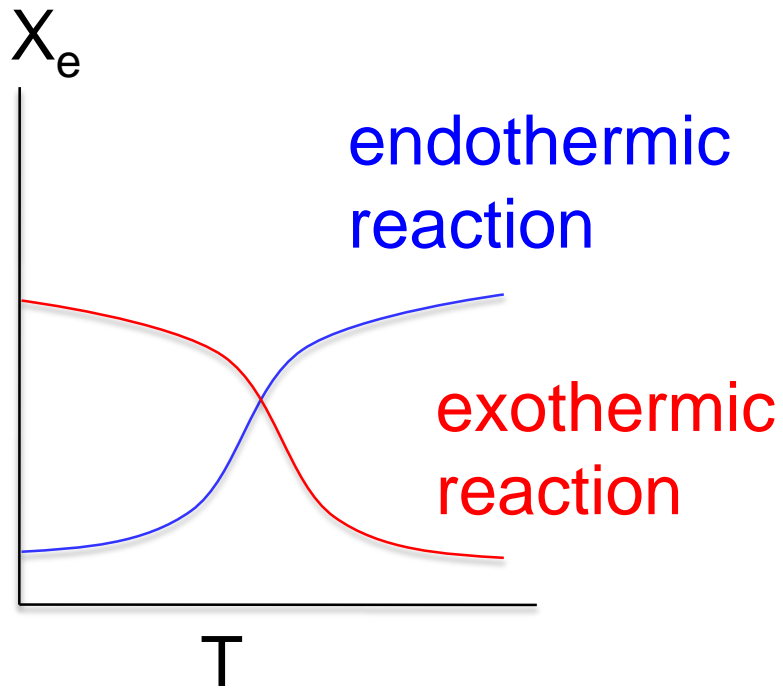$$\frac{dT}{dW} = \frac{\dfrac{Ua}{\rho_B}(T_a - T) + r_A{}'\Delta H_{Rx_{ij}}(T)}{\sum F_i C_{P_i}}$$

4. For multiple reactions

$$\frac{dT}{dV} = \frac{\dfrac{Ua}{\rho_B}(T_a - T) + \sum r_{ij}\Delta H_{Rx_{ij}}}{\sum F_i C_{P_i}}$$
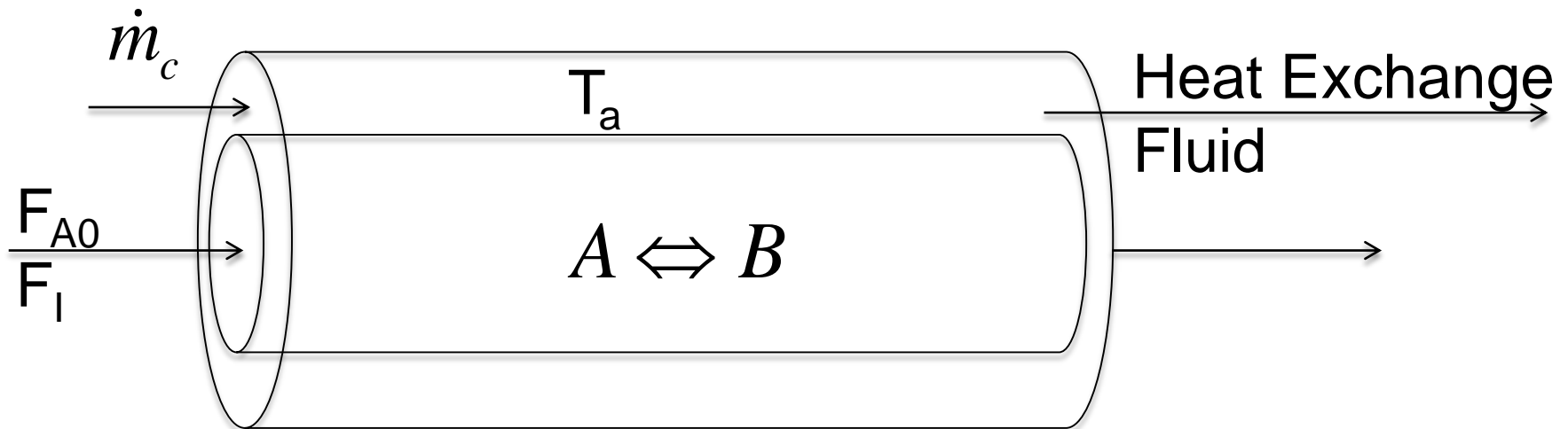
5. Coolant Balance

$$\frac{dT_A}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{P_c}}$$

Reversible Reactions

Heat Exchange

Example: Elementary liquid phase reaction carried out in a PFR

$\dot{m}_c$

T_a

Heat Exchange Fluid

$\dfrac{F_{A0}}{F_I}$

$$A \Leftrightarrow B$$

The feed consists of both inerts I and Species A with the ratio of inerts to the species A being 2 to 1.

Heat Exchange

a) **Adiabatic.** Plot X, X_e, T and the rate of disappearance as a function of V up to V = 40 dm^3.

b) **Constant T_a.** Plot X, X_e, T, T_a and rate of disappearance of A when there is a heat loss to the coolant and the coolant temperature is constant at 300 K for V = 40 dm^3. How do these curves differ from the adiabatic case.

Heat Exchange

c) **Variable T_a Co-Current**. Plot X, X_e, T, T_a and rate of disappearance of A when there is a heat loss to the coolant and the coolant temperature varies along the length of the reactor for V = 40 dm^3. The coolant enters at 300 K. How do these curves differ from those in the adiabatic case and part (a) and (b)?

d) **Variable T_a Countercurrent**. Plot X, X_e, T, T_a and rate of disappearance of A when there is a heat loss to the coolant and the coolant temperature varies along the length of the reactor for V = 20 dm^3. The coolant enters at 300 K. How do these curves differ from those in the adiabatic case and part (a) and (b)?

Heat Exchange

Example: <u>PBR</u> A ↔ B

5) Parameters

- For adiabatic: $\qquad Ua = 0$

- Constant T_a: $\qquad \dfrac{dT_a}{dW} = 0$

- Co-current: $\qquad\qquad$ Equations as is

- Counter-current: $\qquad \dfrac{dT}{dW} \cdot (-1) \quad (\text{or flip } T - T_a \text{ to } T_a - T)$

Reversible Reactions

1) Mole Balances

$$\frac{dX}{dW} = -r_A{'}\Big/F_{A0} \qquad (1)$$

$$W = \rho_b V$$

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

Reversible Reactions

2) Rate Laws

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

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

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

Reversible Reactions

3) Stoichiometry

$$(5) \quad C_A = C_{A0}(1-X)y(T_0/T)$$

$$(6) \quad C_B = C_{A0}Xy(T_0/T)$$

$$F_T = F_{T0}$$

$$\frac{dy}{dW} = \frac{\alpha}{y}\frac{F_T}{F_{T_0}}\left(\frac{T}{T_0}\right) = -\frac{\alpha}{2y}\left(\frac{T}{T_0}\right)$$

$$W = \rho V$$

$$\frac{dy}{dV} = -\frac{\alpha\rho_b}{2y}\left(\frac{T}{T_0}\right)$$

Reversible Reactions

Parameters
$$F_{A0}, k_1, E, R, T_1, K_{C2}, \quad (7)-(15)$$
$$\Delta H_{Rx}, T_2, C_{A0}, T_0, \alpha, \rho_b$$

Reversible Reactions
Gas Phase Heat Effects

Example: PBR   A $\leftrightarrow$ B

3) Stoichiometry: $v = v_0 (1 + \varepsilon X) \dfrac{P_0}{P} \dfrac{T}{T_0}$

Gas Phase

$$(5) \quad C_A = \frac{F_{A0}(1-X)}{v_0(1+\varepsilon X)} \frac{P}{P_0} \frac{T_0}{T} = \frac{C_{A0}(1-X)}{(1+\varepsilon X)} y \frac{T_0}{T}$$

$$(6) \quad C_B = \frac{C_{A0}X}{(1+\varepsilon X)} y \frac{T_0}{T}$$

$$(7) \quad \frac{dy}{dW} = \frac{-\alpha}{2y} \frac{F_T}{F_{T0}} \frac{T}{T_0} = \frac{-\alpha}{2y}(1+\varepsilon X)\frac{T}{T_0}$$

Reversible Reactions
Gas Phase Heat Effects

Example: PBR   A $\leftrightarrow$ B

$$K_C = \frac{C_{Be}}{C_{Ae}} = \frac{C_{A0} X_e y\, T_0/T}{C_{A0}(1 - X_e) y\, T_0/T}$$

$$(8) \quad X_e = \frac{K_C}{1 + K_C}$$

Reversible Reactions
Gas Phase Heat Effects

Example: PBR   A ↔ B

Exothermic Case:
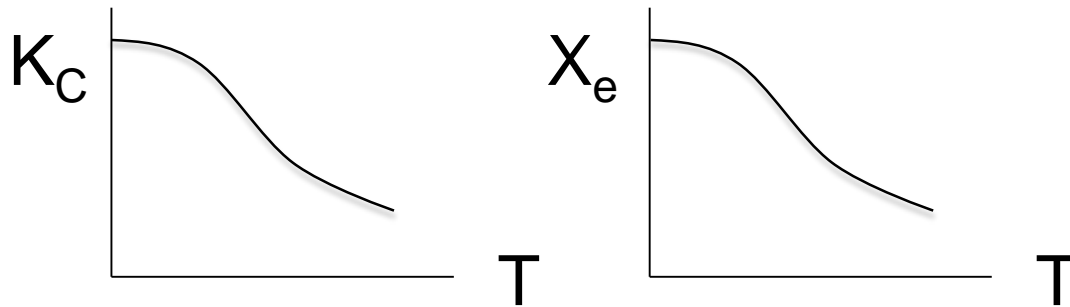
Endothermic Case:
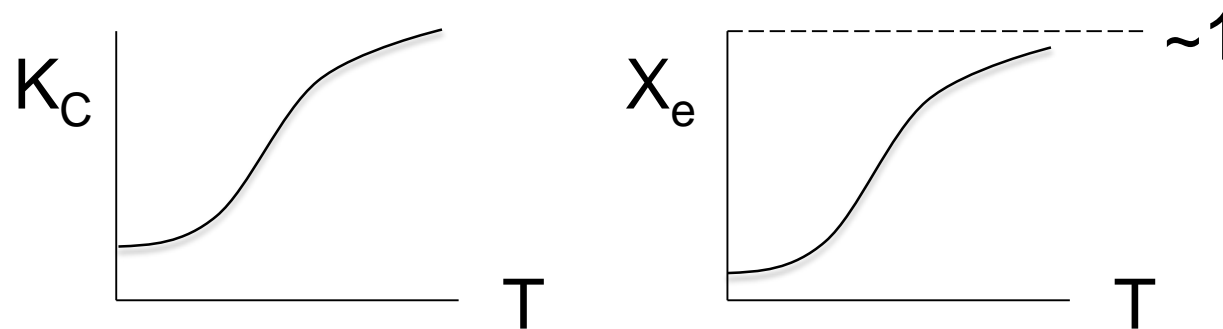
Reversible Reactions
Gas Phase Heat Effects

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

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

Case 1: Adiabatic and $\Delta C_P = 0$

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

Additional Parameters (17A) & (17B)

$$T_0, \qquad \sum \Theta_i C_{P_i} = C_{P_A} + \Theta_I C_{P_I}$$

Reversible Reactions
Gas Phase Heat Effects

Case 2: Heat Exchange – Constant T_a

Heat effects:

$$\frac{dT}{dW} = \frac{(-r_A)(-\Delta H_{Rx}) - \frac{Ua}{\rho_b}(T - T_a)}{F_{A0}\sum \theta_i C_{Pi}} \quad (9)$$

Reversible Reactions
Gas Phase Heat Effects

Case 3. Variable T_a Co-Current

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

Case 4. 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., $V = V_f$

Gas Phase Adiabatic
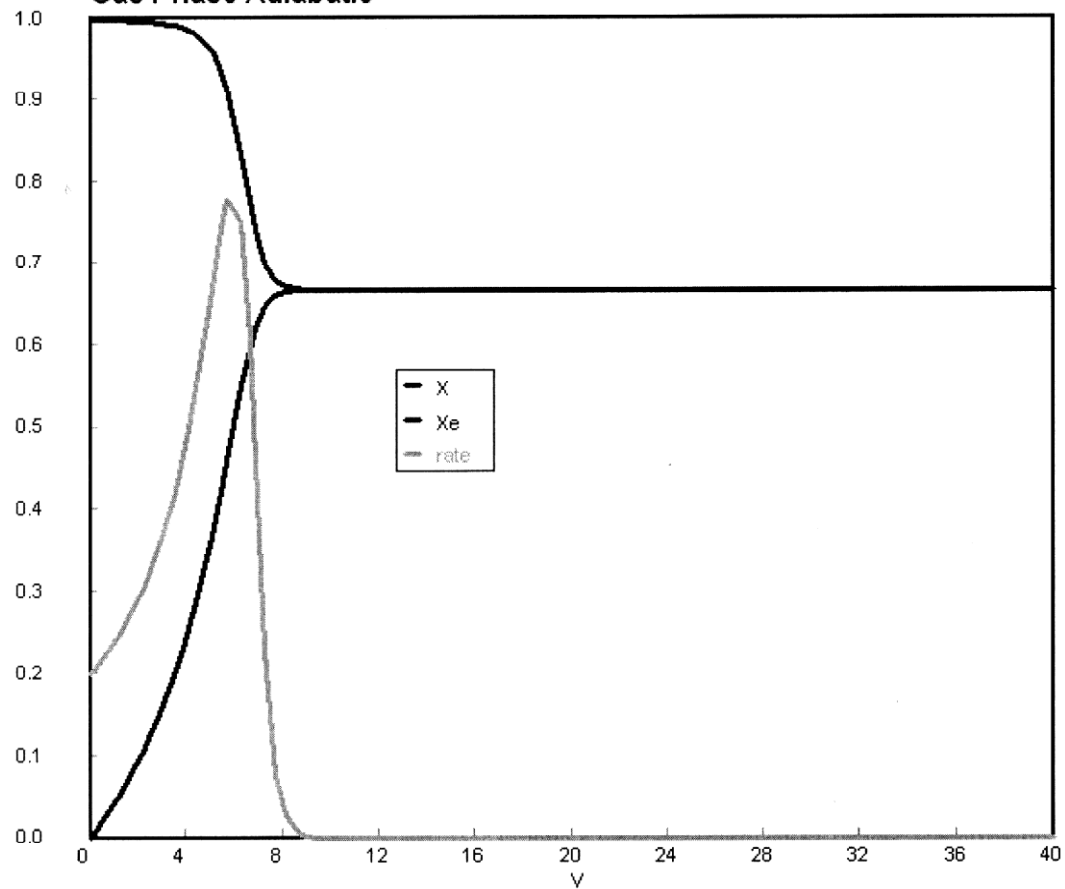
Gas Phase Constant Ta
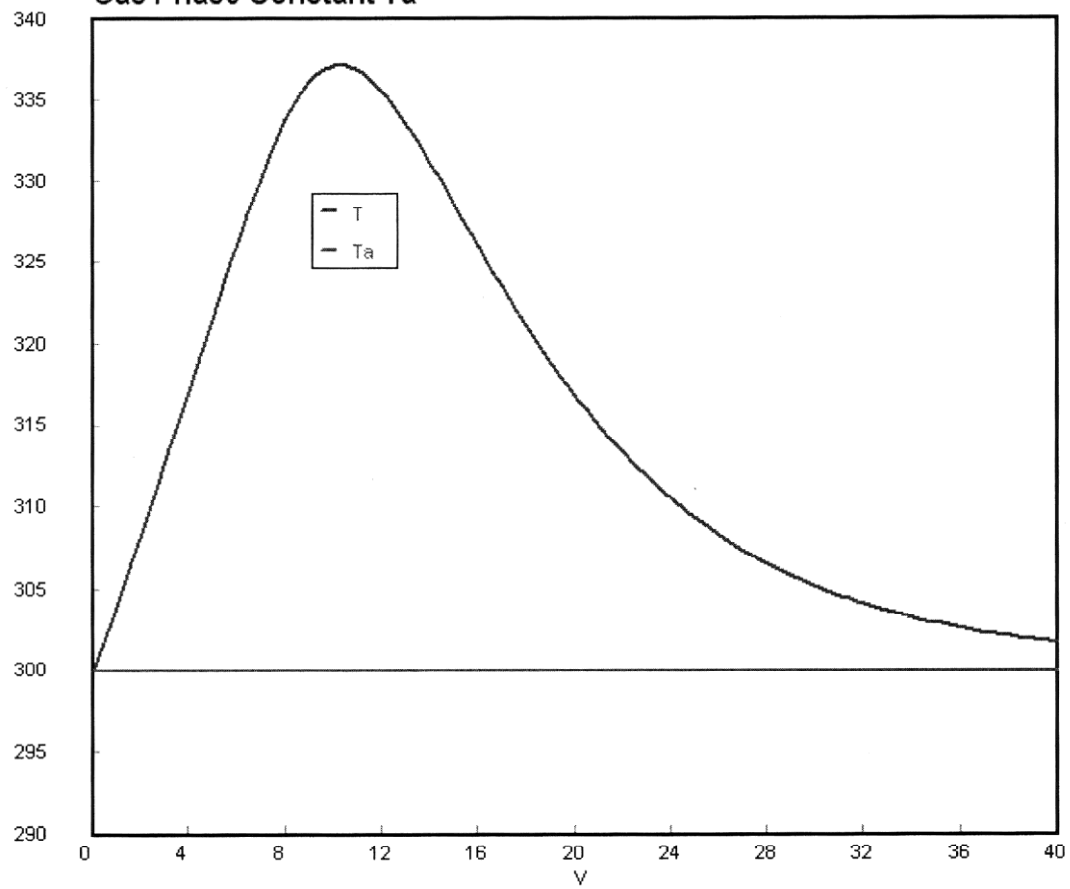
Gas Phase Constant Ta
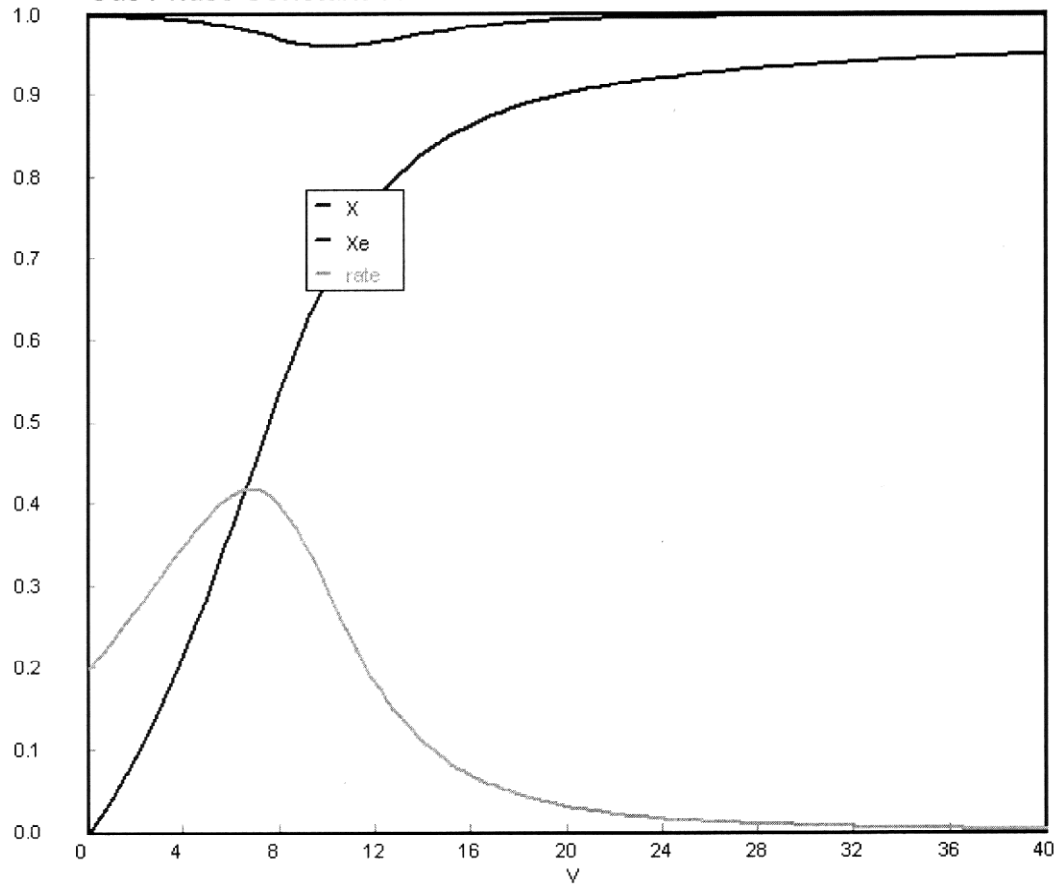
Gas Phase Co-current Heat Exchange
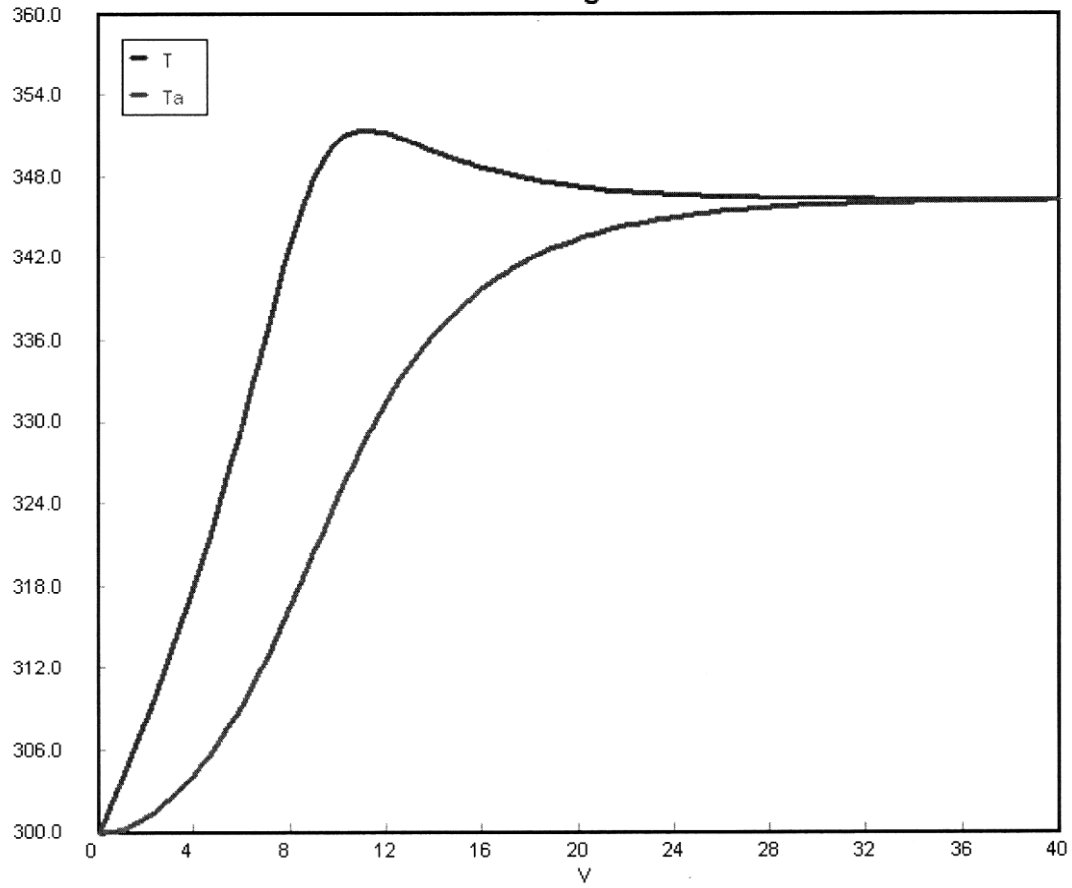
Gas Phase Co-current Heat Exchange

Endothermic

PFR $A \underset{\longleftarrow}{\longrightarrow} B$

$$\frac{dX}{dV} = \frac{k\left(1 - \left(1 + \frac{1}{K_C}\right)X\right)}{\upsilon_0} \quad , \quad X_e = \frac{K_C}{1 + K_C}$$

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

(Graph with axes labeled X, X_{EB} showing curve X_e, with X_{EB} arrow)
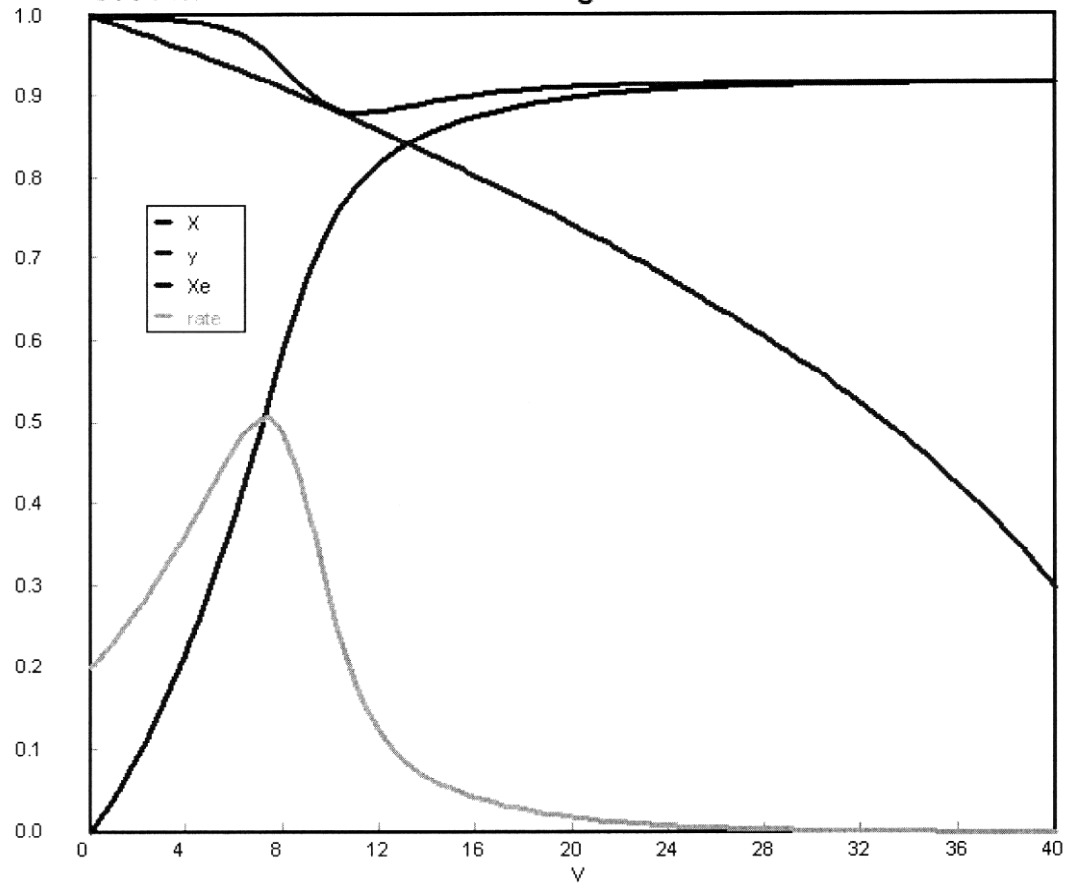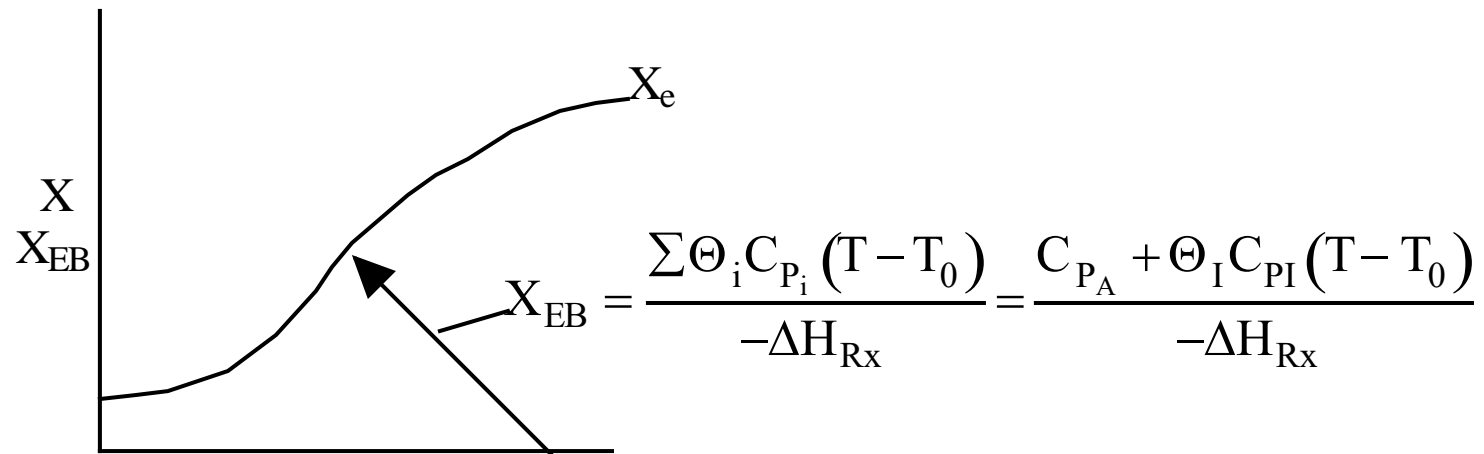
$$T = T_0 + \frac{(-\Delta H_{Rx})X}{C_{P_A} + \Theta_I C_{P_I}}$$

Adiabatic Equilibrium

Conversion on temperature

Exothermic ΔH is negative

Adiabatic Equilibrium temperature (T_{adia}) and conversion (Xe_{adia})

$$T = T_0 + \frac{(-\Delta H_{Rx})X}{C_{PA}}$$

$$X_e = \frac{K_C}{1 + K_C}$$

F_{A0}

T_0

F_{A1}

X_1

Q_1

T_0

F_{A2}

X_2

Q_2

T_0

F_{A3}

X_3

$$X_{EB} = \frac{\sum \theta_i C_{Pi}(T - T_0)}{-\Delta H_{Rx}}$$

X

X_e

X_3

X_2

X_1

T_0

T
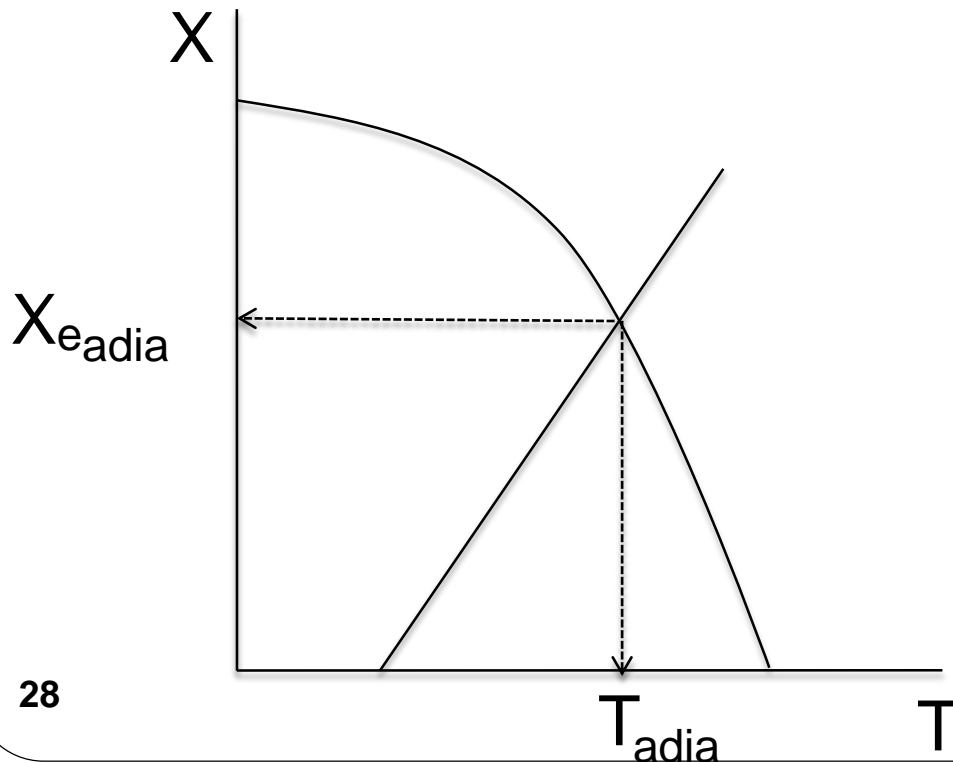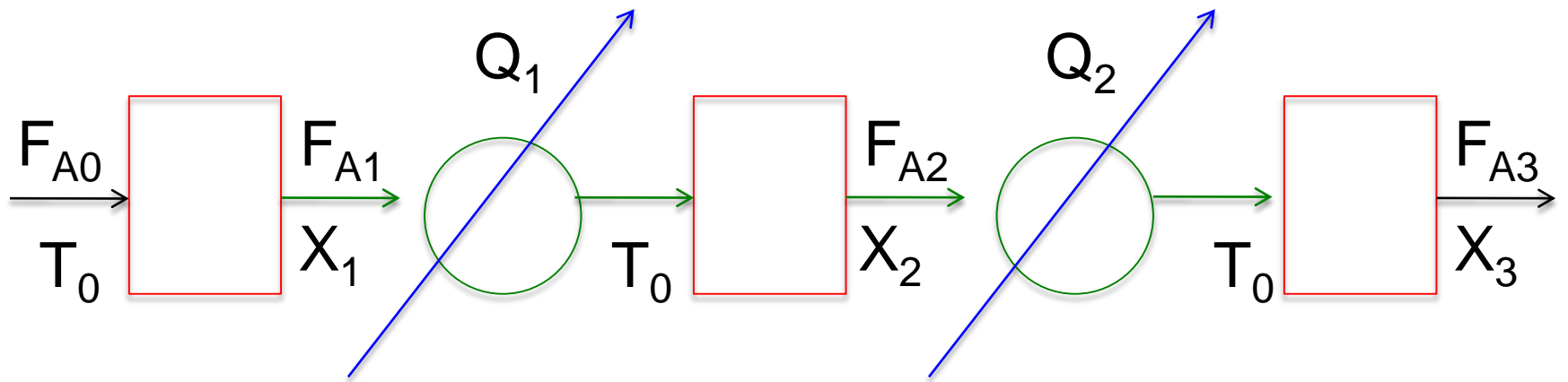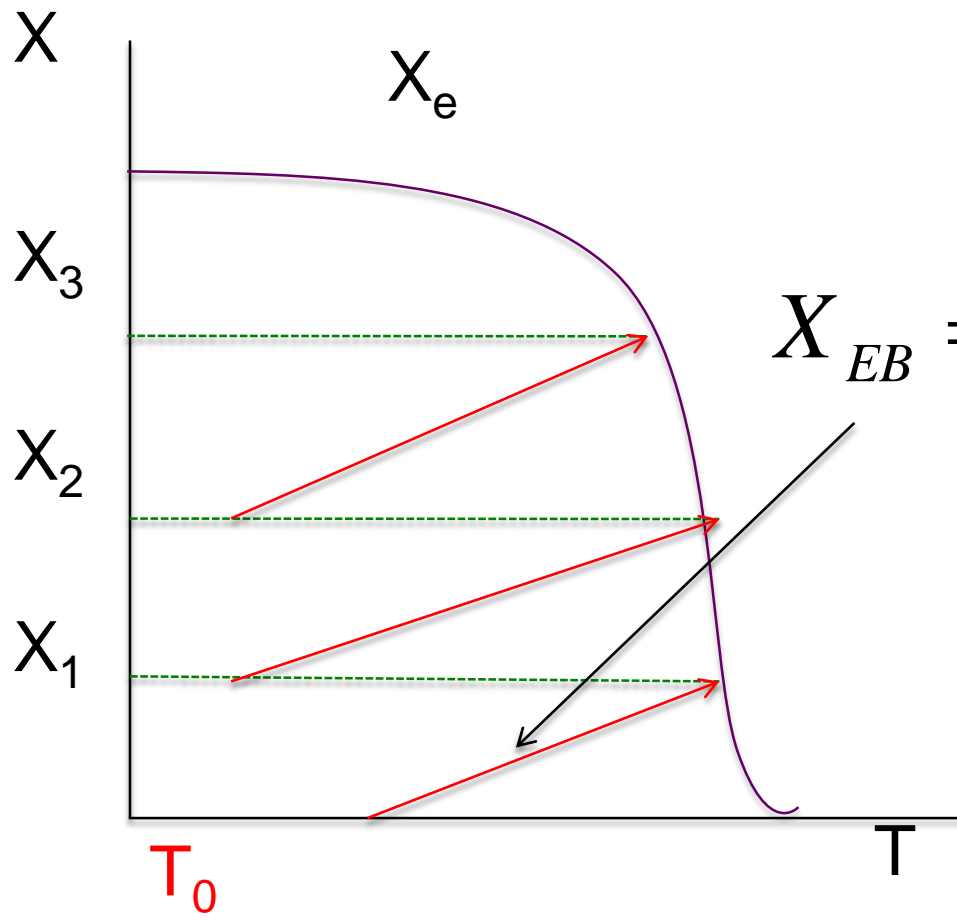
1st Order Reversible Adiabatic Endothermic Reaction
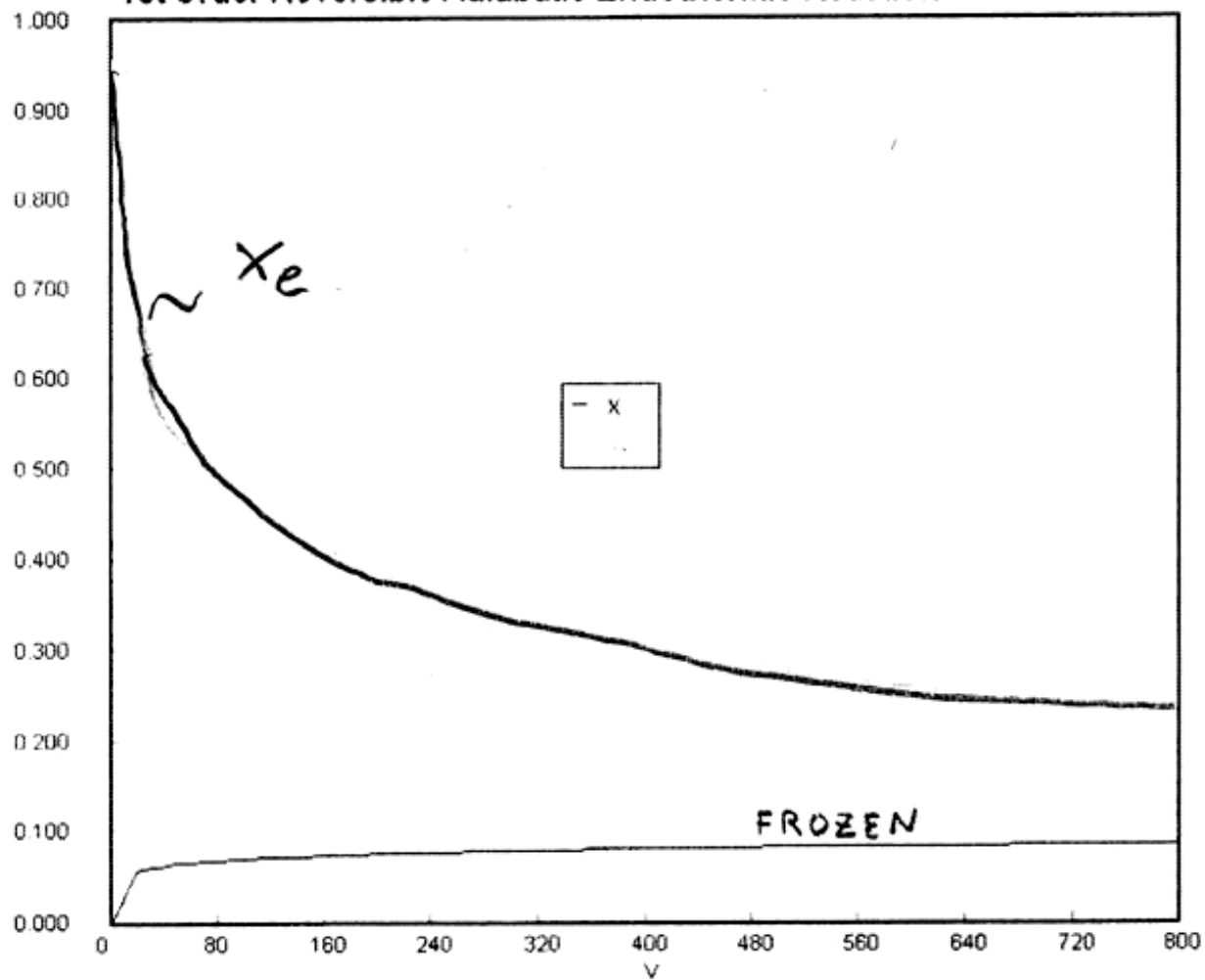
Gas Flow Heat Effects

Trends:

Adiabatic

X   exothermic

Adiabatic
T and X_e

T_0

T

X   endothermic

T_0

T
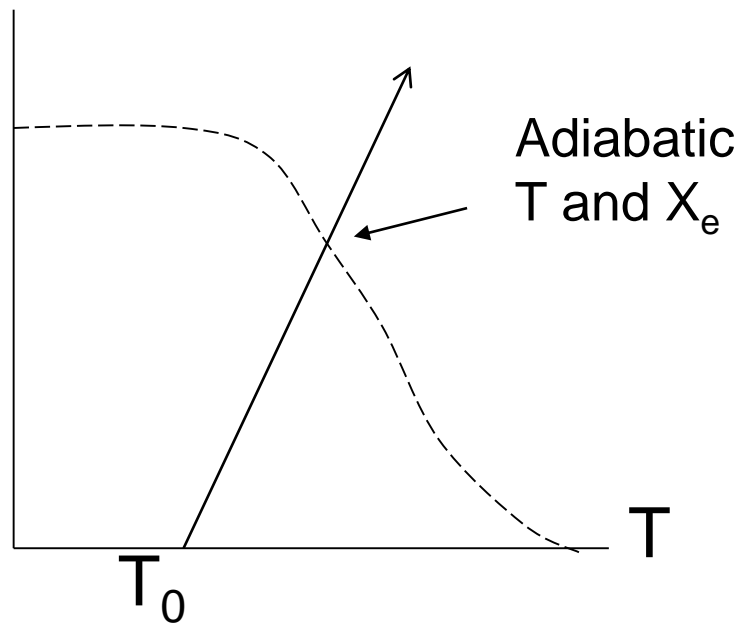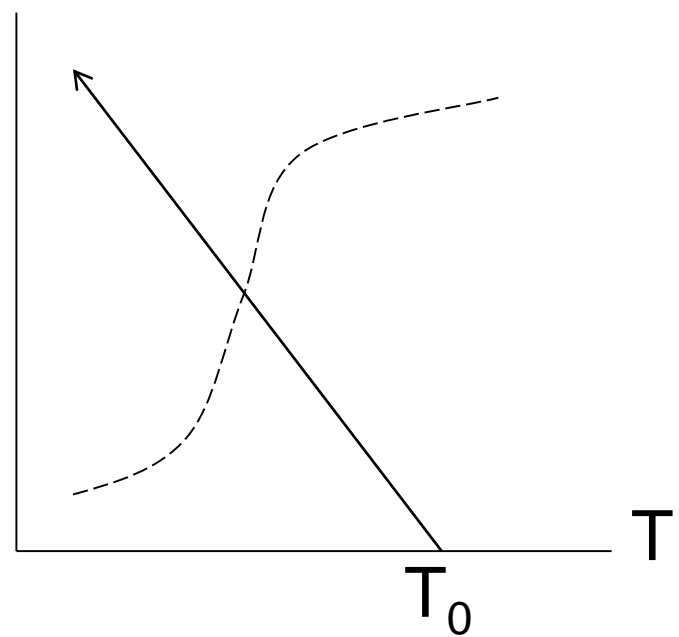
$$T = T_0 + \frac{-\Delta H_{Rx} X}{C_{PA} + \Theta_I C_{PI}}$$

Effects of Inerts in the Feed

PFR Adiabatic
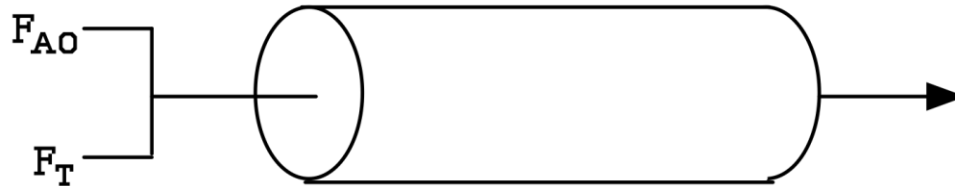
1. Irreversible A → B Liquid Phase, Keep F_{A0} Constant

    A. First order

$$\frac{dX}{dV} = \frac{-r_A}{F_{A0}} = \frac{kC_A}{F_{A0}} = k\frac{F_{A0}}{\upsilon}\frac{(1-X)}{F_{A0}} = \frac{k(1-X)}{\upsilon} = \frac{kC_{A0}(1-X)}{F_{A0}}$$

    Constant density liquid

    υ_0 = volumetric flow rate without inert

$$\upsilon = \upsilon_0\left(\frac{F_{A0}+F_I}{F_{A0}}\right) = \upsilon_0(1+\Theta_I)$$

$$\frac{dX}{dV} = \frac{k(1-X)}{\upsilon_0(1+\Theta_I)}$$

Endothermic
First Order Irreversible
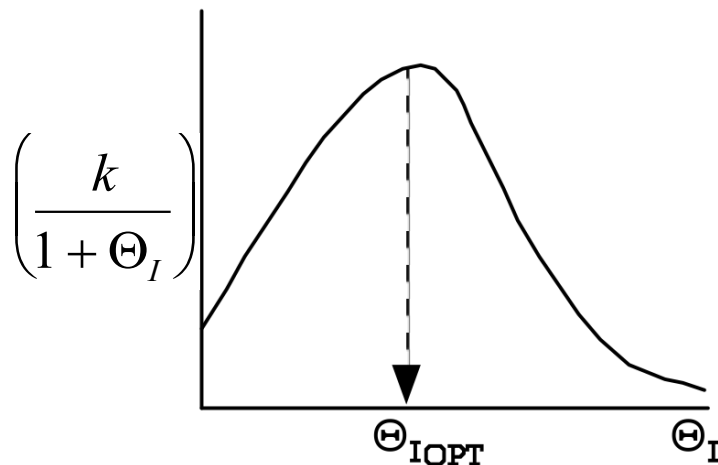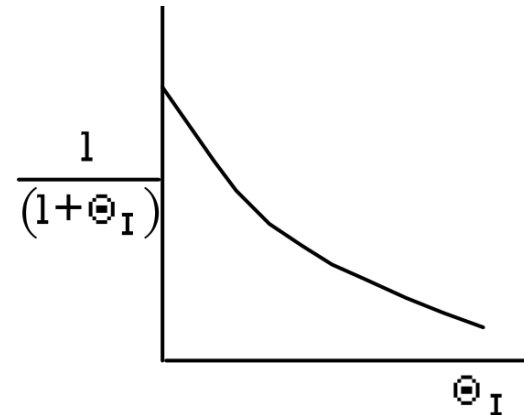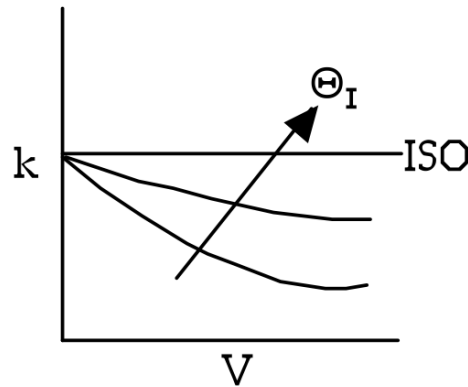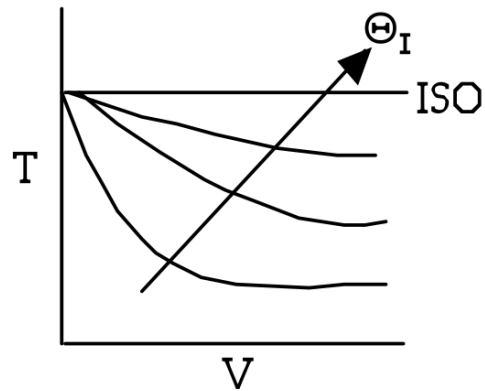
As inert flow increases the conversion will increase. However as inerts increase, reactant concentration decreases, slowing down the reaction. Therefore there is an optimal inert flow rate to maximize X.

Gas Phase Heat Effects

Adiabatic:

As T_0 decreases the conversion X will increase, however the reaction will progress slower to equilibrium conversion and may not make it in the volume of reactor that you have.
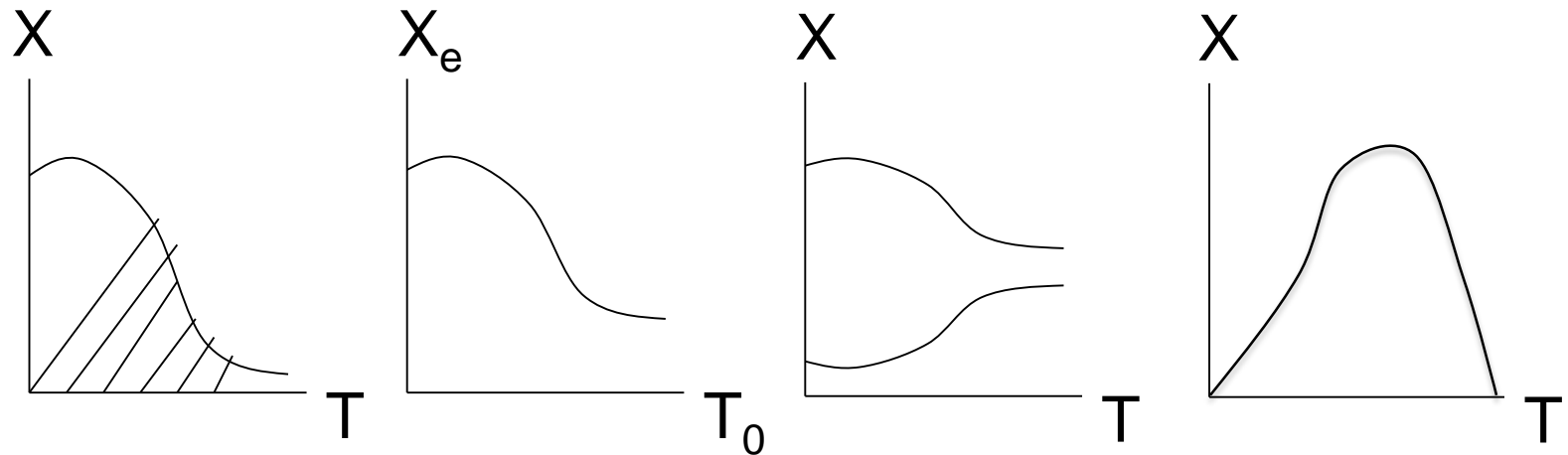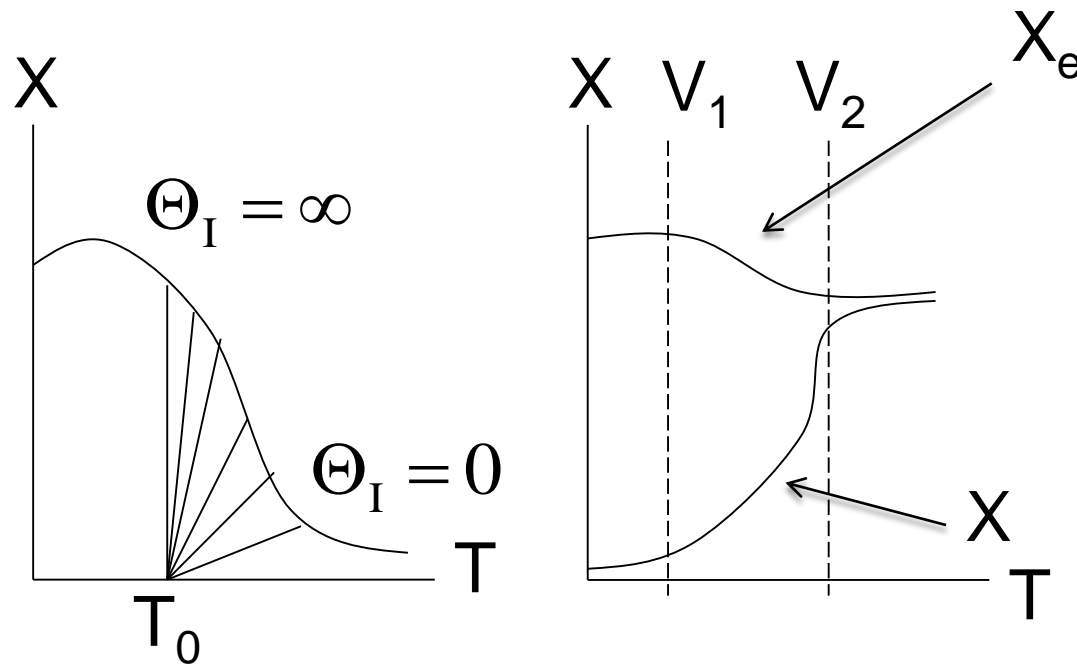

Therefore, for <u>exothermic</u> reactions there is an optimum inlet temperature, where X reaches X_{eq} right at the end of V. However, for <u>endothermic</u> reactions there is no temperature maximum and the X will continue to increase as T increases.
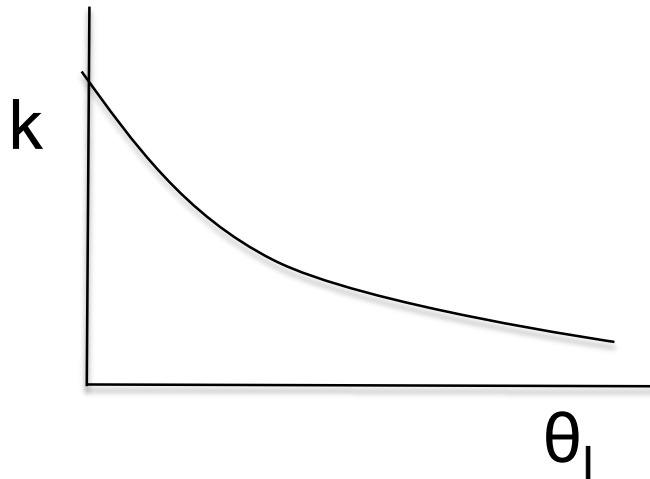
Gas Phase Heat Effects

Effect of adding inerts
Adiabatic:
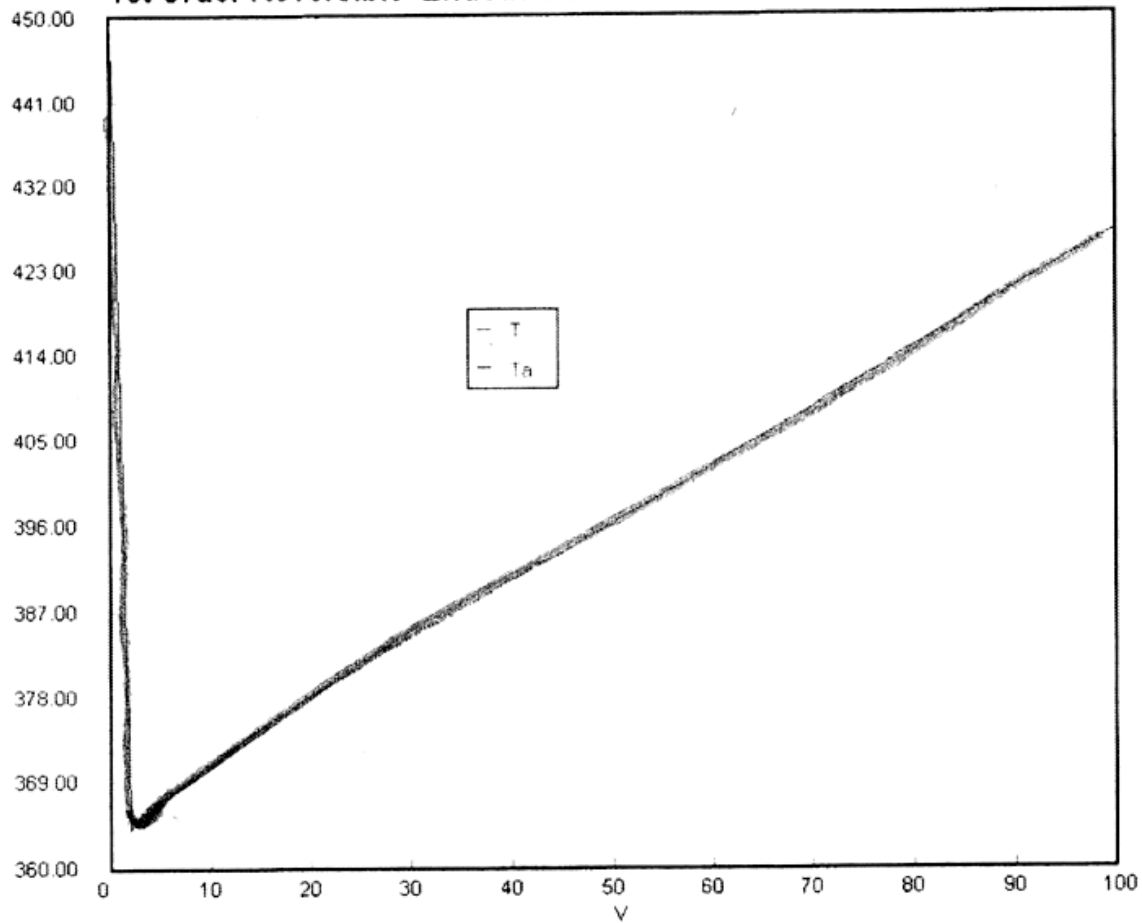

$$X = \frac{(T - T_0)\left[C_{pA} + \theta_I C_{pI}\right]}{-\Delta H_{Rx}}$$
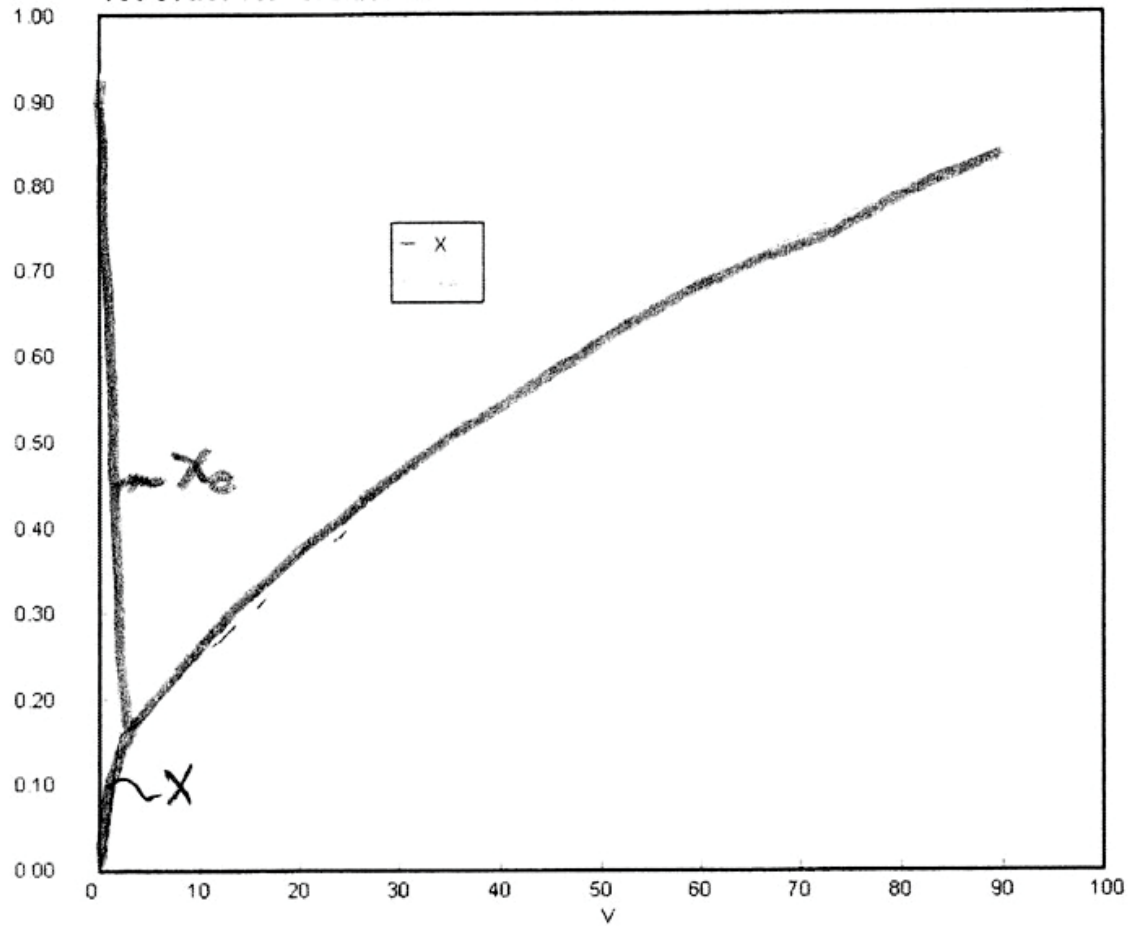
Exothermic Adiabatic

As θ_I increase, T decrease and

$$\frac{dX}{dV} = \frac{k}{\upsilon_0 (H\theta_I)}$$

1st Order Reversible Endothermic Reaction HE with Constant Ta
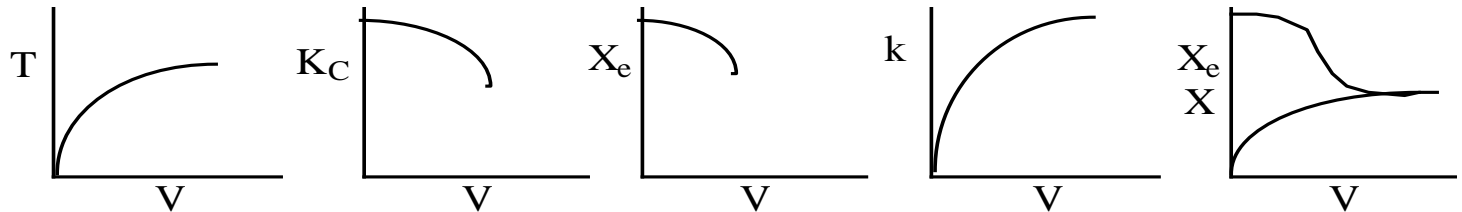
1st Order Reversible Endothermic Reaction HE with Constant Ta

Adiabatic

Exothermic

Endothermic

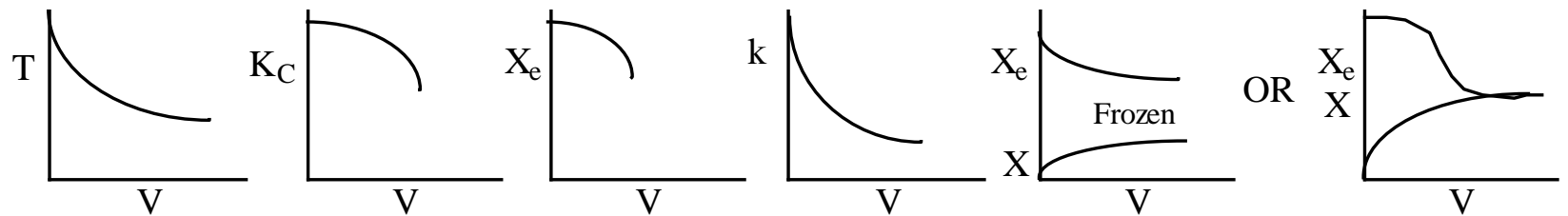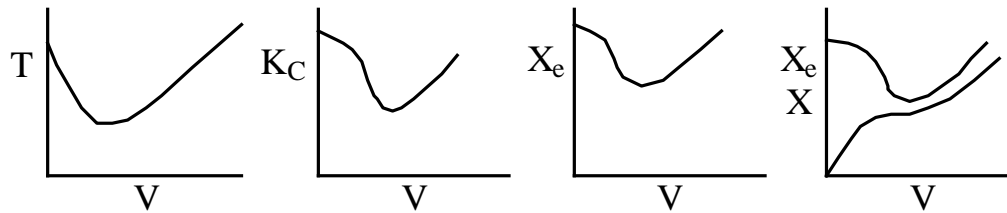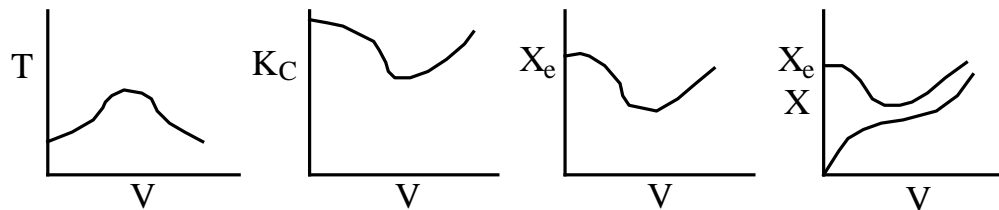# Heat Exchange

Exothermic

Endothermic

End of Web Lecture 21
End of Class Lecture 17