

# 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 3/19/2013

- Gas Phase Reactions
- Trends and Optimums

## Review Last Lecture

# User Friendly Equations relate T, X, or F<sub>i</sub>

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

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

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

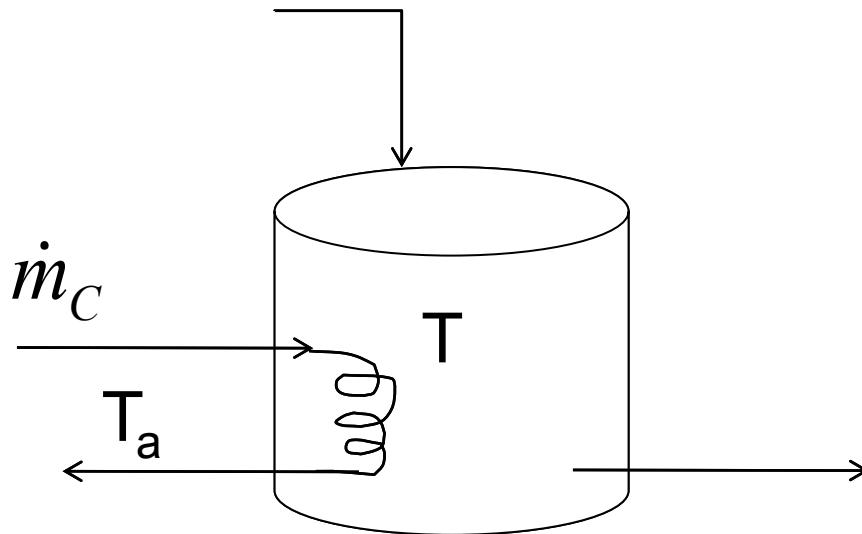
$$X = \frac{\tilde{C}_{P_A} (T - T_0)}{-\Delta H_{Rx}}$$

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

# User Friendly Equations relate T, X, or F<sub>i</sub>

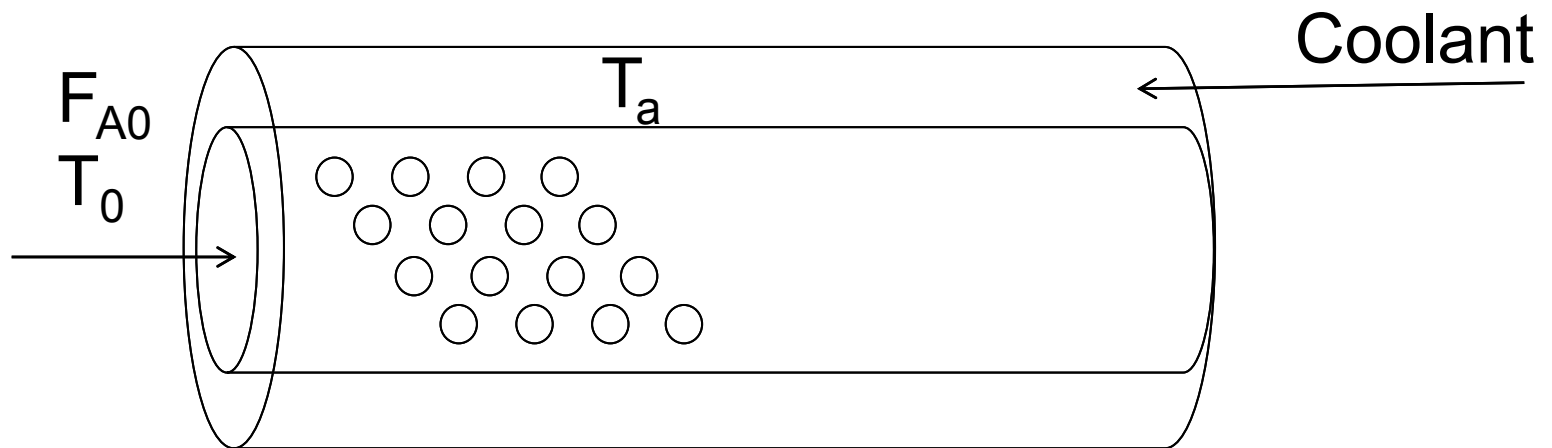
2. **CSTR** with **heat exchanger**,  $UA(T_a - T)$  and a large coolant flow rate:

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



# User Friendly Equations relate T, X, or F<sub>i</sub>

## 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<sub>i</sub>

3B. In terms of molar flow rates, F<sub>i</sub>

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

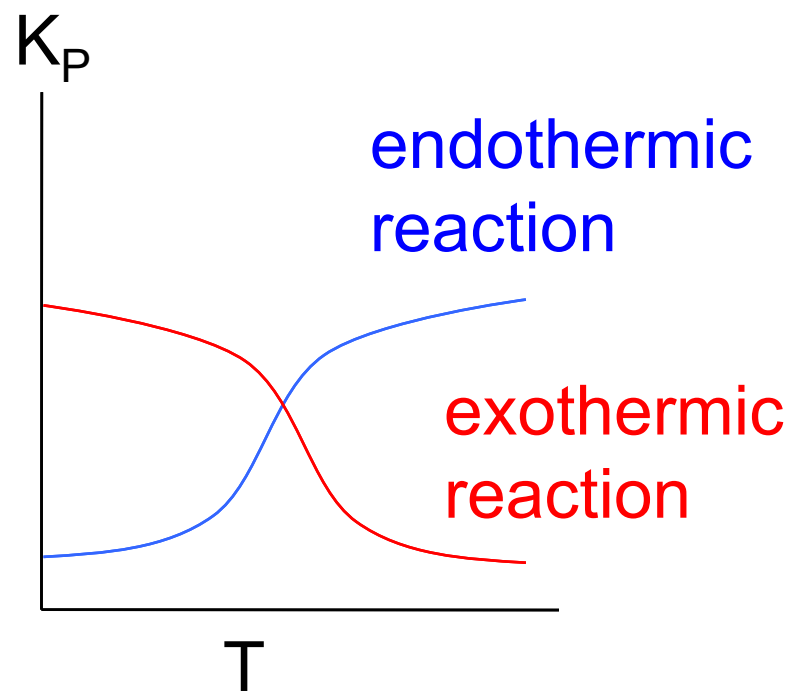
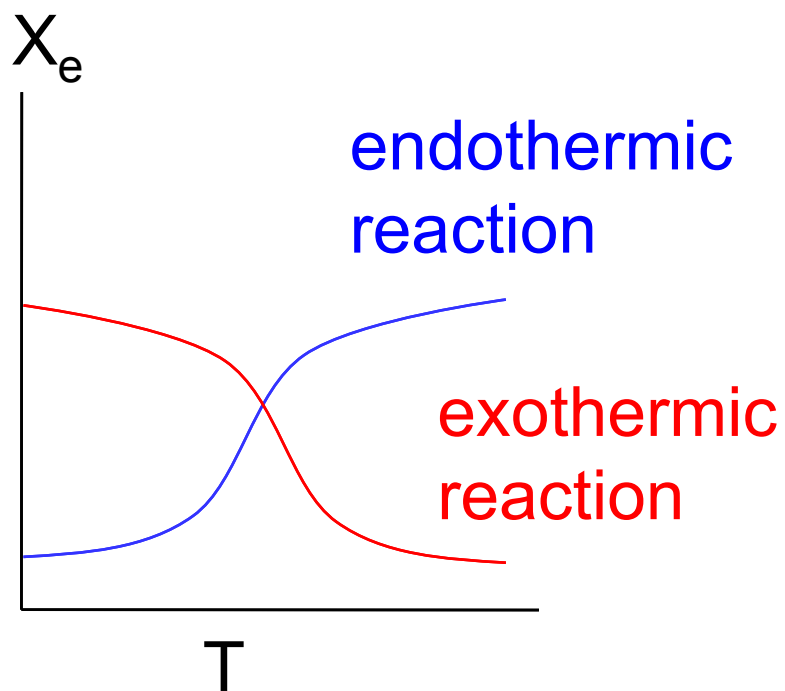
4. For multiple reactions

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

5. Coolant Balance

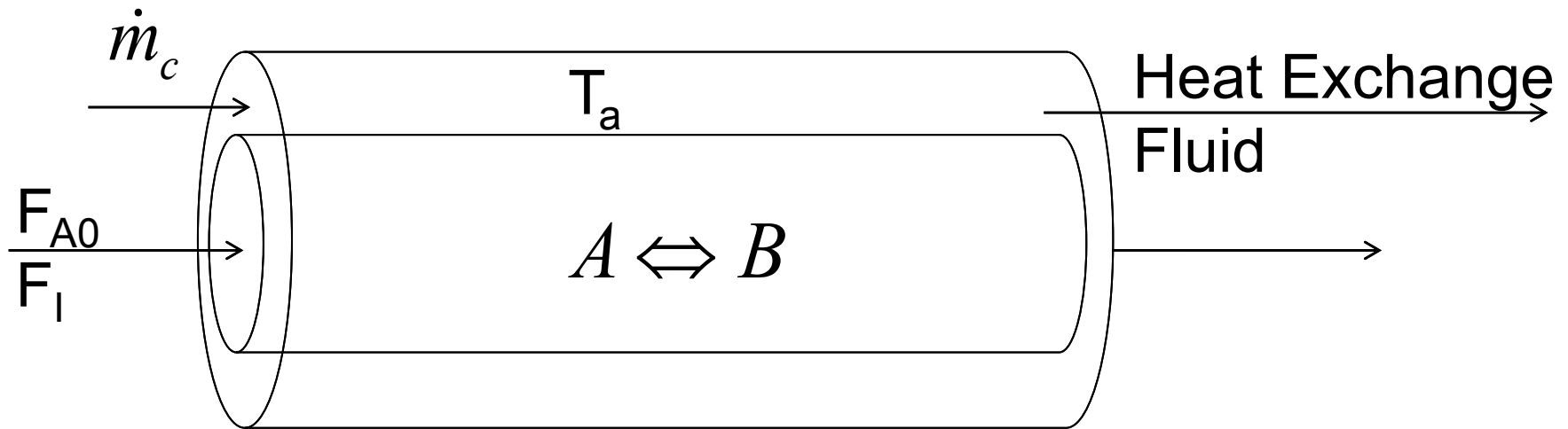
$$\frac{dT_A}{dV} = \frac{Ua(T - T_a)}{\dot{m}_c C_{P_c}}$$

# Reversible Reactions



# Heat Exchange

**Example:** Elementary liquid phase reaction carried out in a **PFR**



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  $V = 40 \text{ dm}^3$ .
- 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  $300 \text{ K}$  for  $V = 40 \text{ dm}^3$ . 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  $V = 40 \text{ dm}^3$ . 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  $V = 20 \text{ dm}^3$ . 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: PBR  $A \leftrightarrow B$

## 5) Parameters

- For adiabatic:  $Ua = 0$
- Constant  $T_a$ :  $\frac{dT_a}{dW} = 0$
- Co-current: Equations as is
- Counter-current:  $\frac{dT}{dW} \cdot (-1)$  (or flip  $T - T_a$  to  $T_a - T$ )

# Reversible Reactions

**1) Mole Balances**  $\frac{dX}{dW} = -r_A' / F_{A0} \quad (1)$

$$W = \rho_b V$$

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

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

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

$$F_T = F_{T0}$$

$$\frac{dy}{dW} = \frac{\alpha}{y} \frac{F_T}{F_{T0}} \left( \frac{T}{T_0} \right) = -\frac{\alpha}{2y} \left( \frac{T}{T_0} \right)$$

$$W = \rho V$$

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

# 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:**  $v = v_0(1 + \varepsilon X) \frac{P_0}{P} \frac{T}{T_0}$   
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  $A \leftrightarrow B$

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

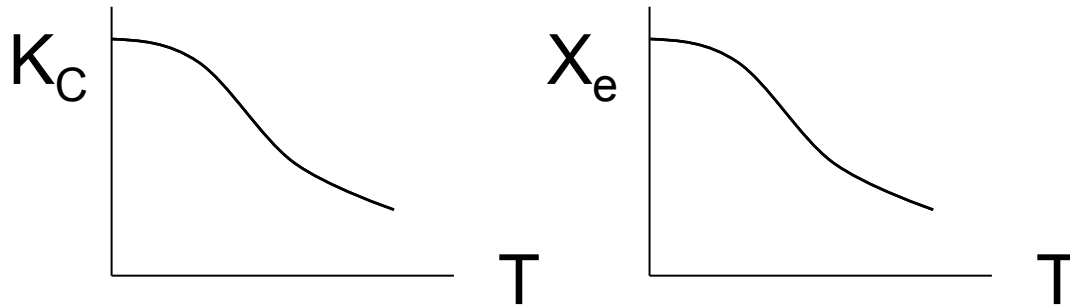
$$(8) \quad X_e = \frac{K_C}{1 + K_C}$$

# Reversible Reactions

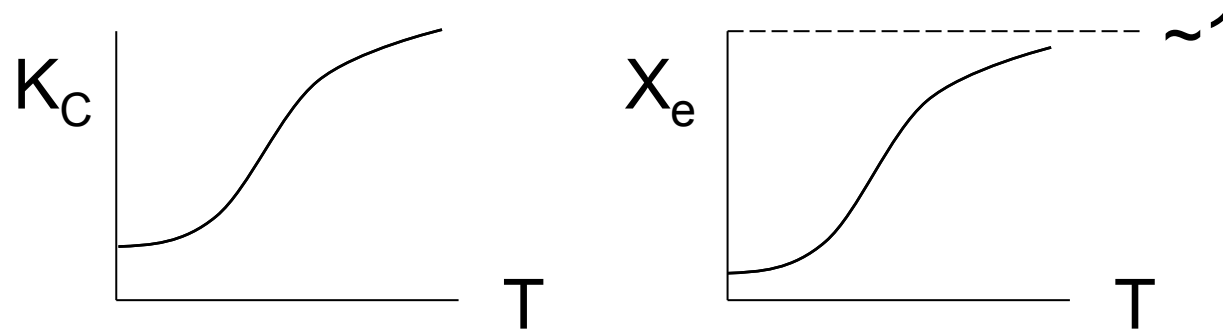
## Gas Phase Heat Effects

Example: PBR  $A \leftrightarrow B$

Exothermic Case:



Endothermic Case:



# Reversible Reactions

## Gas Phase Heat Effects

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

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

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

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

Additional Parameters (17A) & (17B)

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

# 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

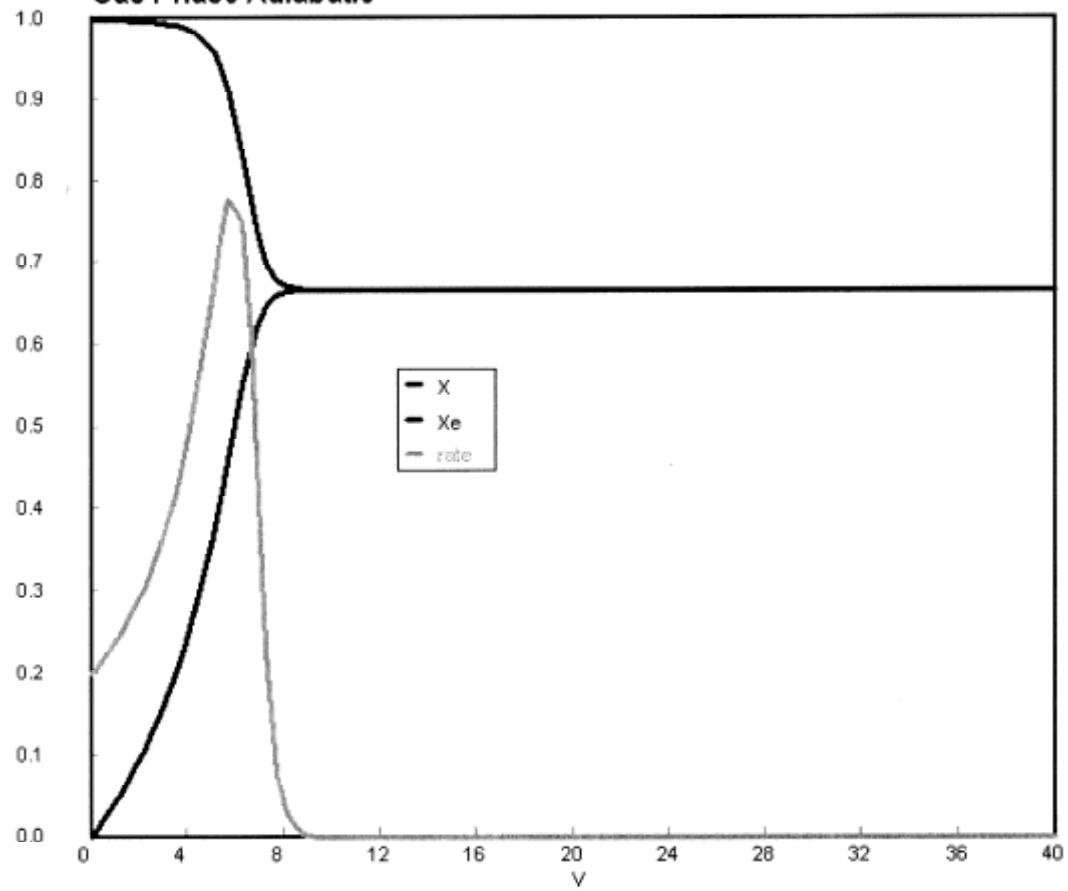
$$\frac{dT_a}{dV} = \frac{Ua(T - T_a)}{\dot{m}C_{P_{cool}}}, \quad V = 0 \quad T_a = T_{a0} \quad (17C)$$

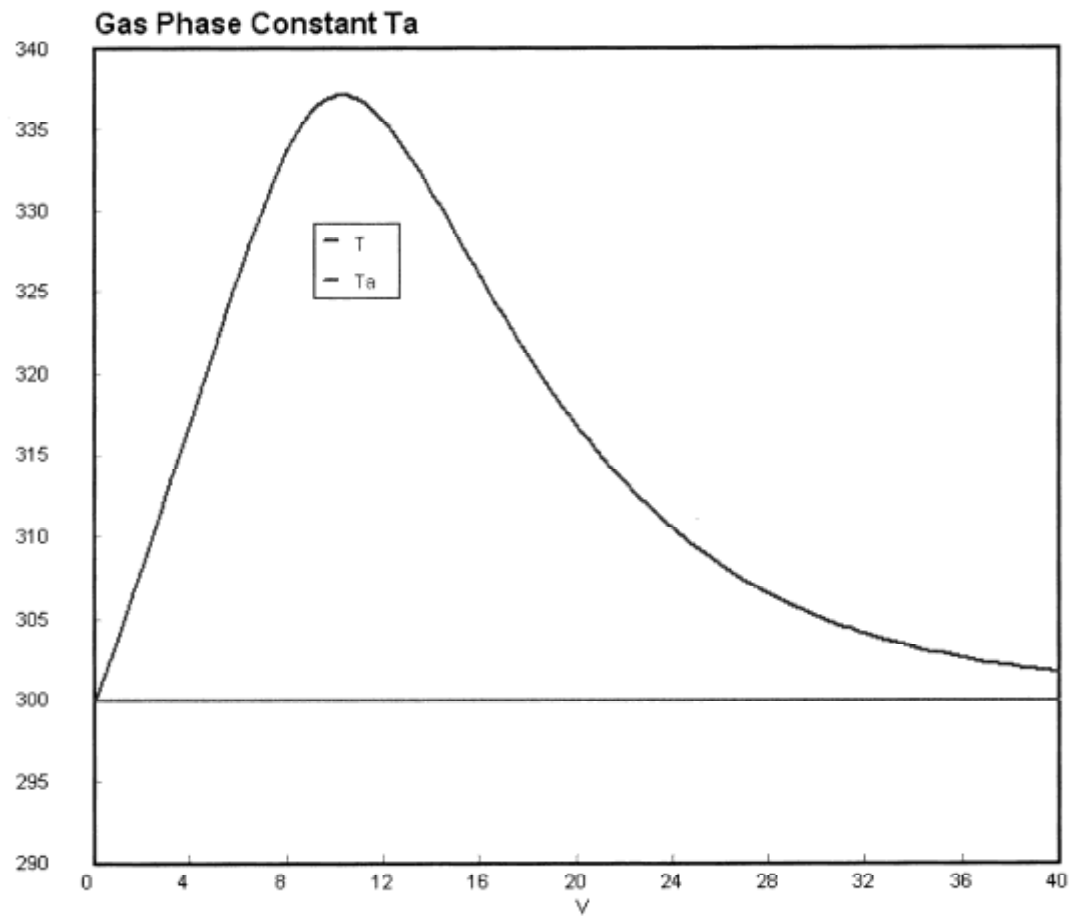
### Case 4. Variable $T_a$ Countercurrent

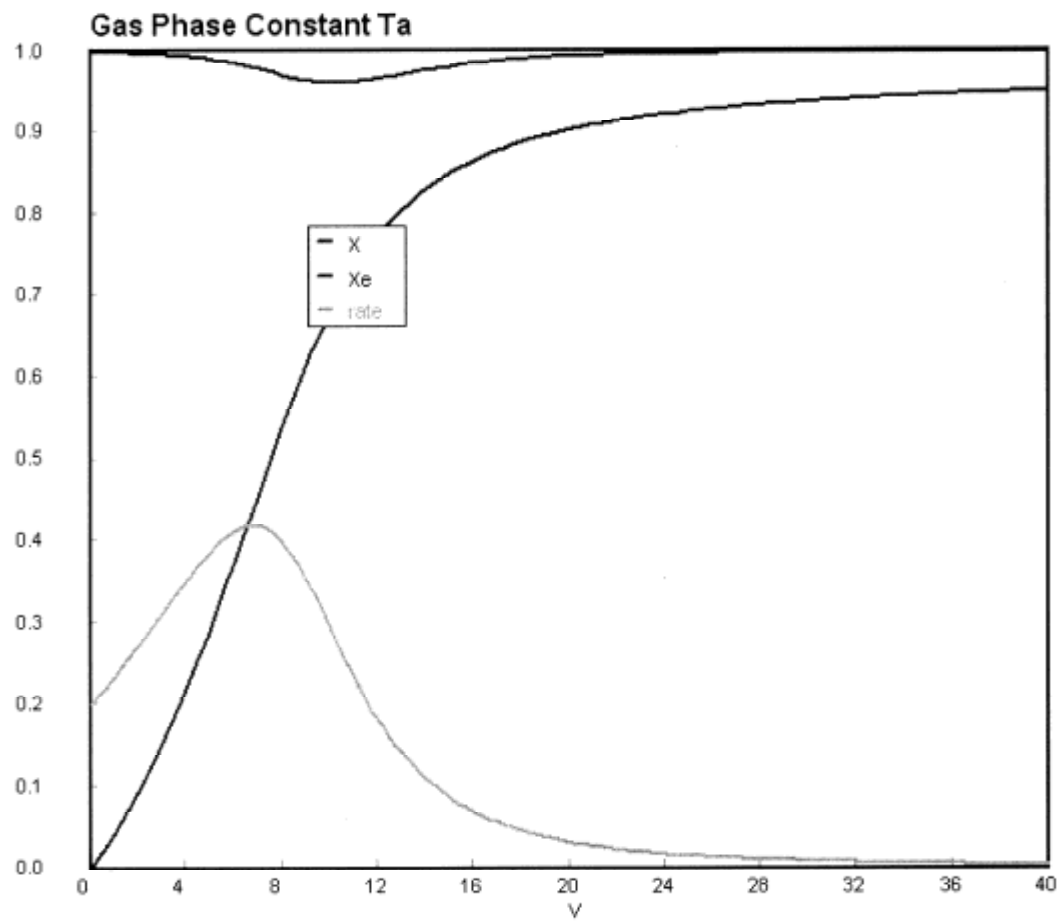
$$\frac{dT_a}{dV} = \frac{Ua(T_a - T)}{\dot{m}C_{P_{cool}}} \quad V = 0 \quad T_a = ?$$

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

Gas Phase Adiabatic

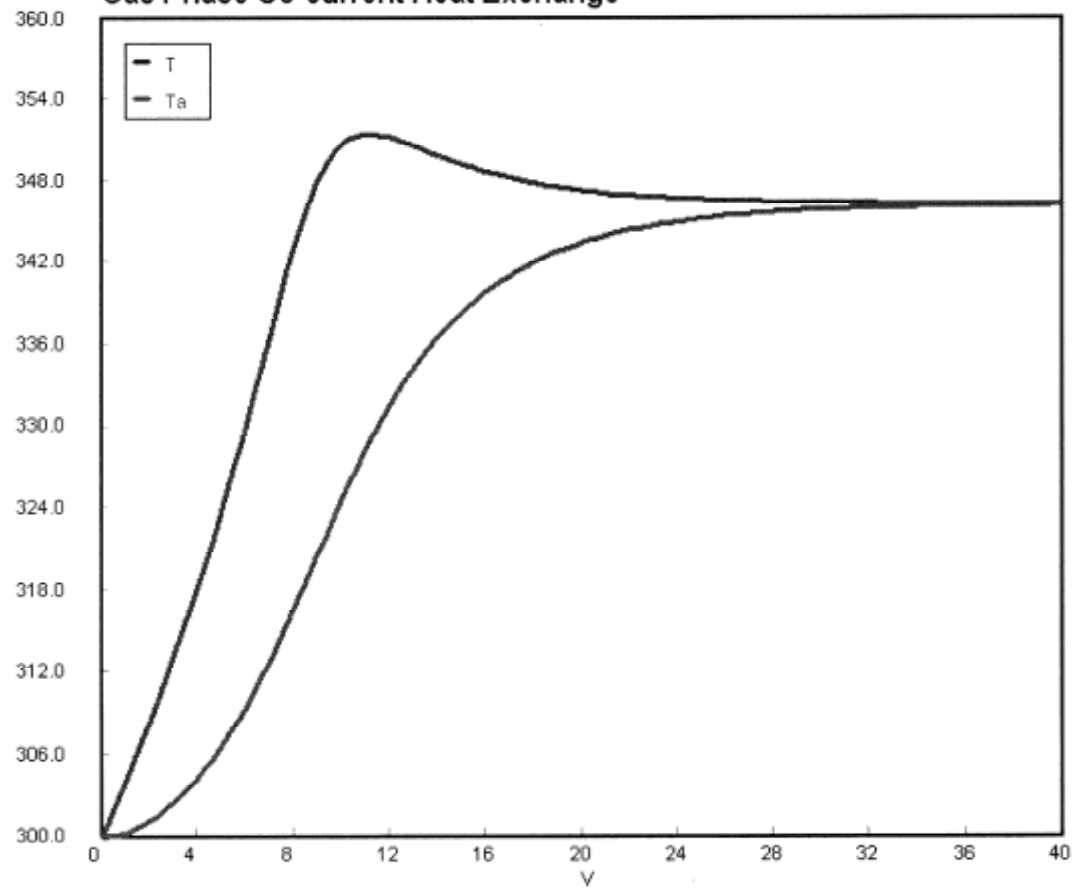




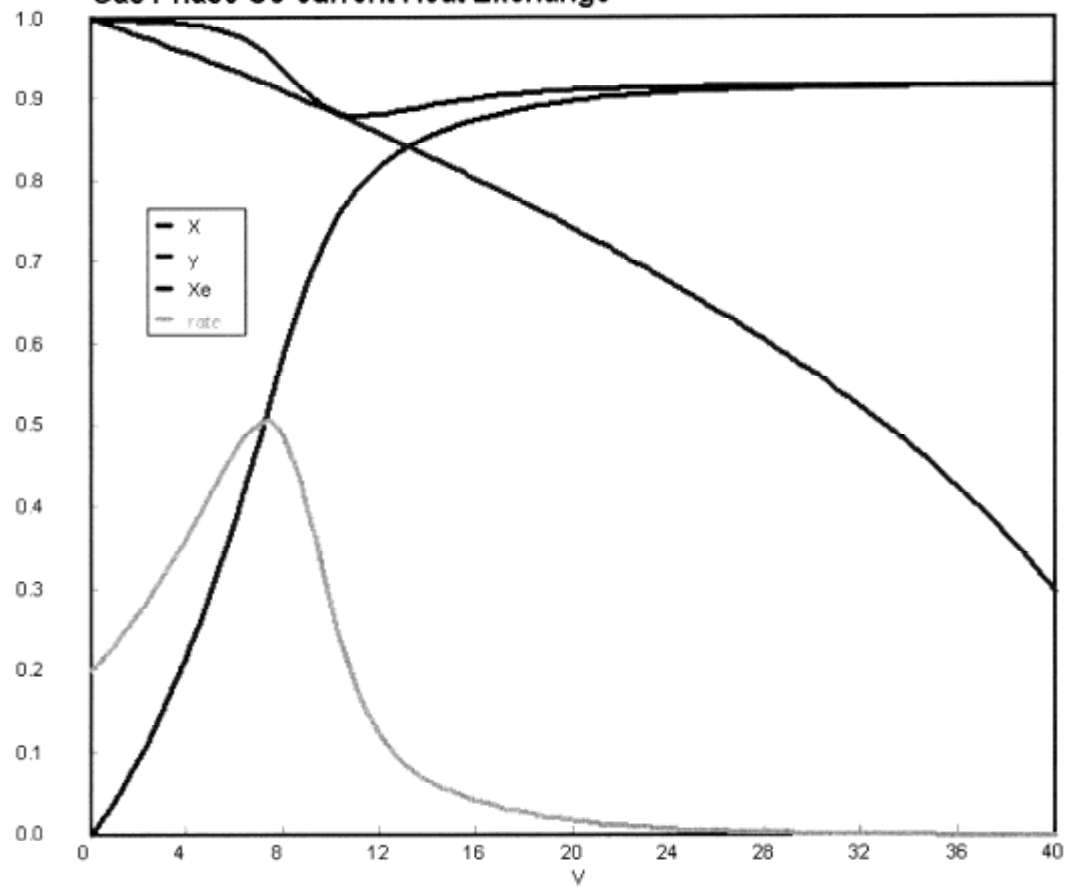




Gas Phase Co-current Heat Exchange



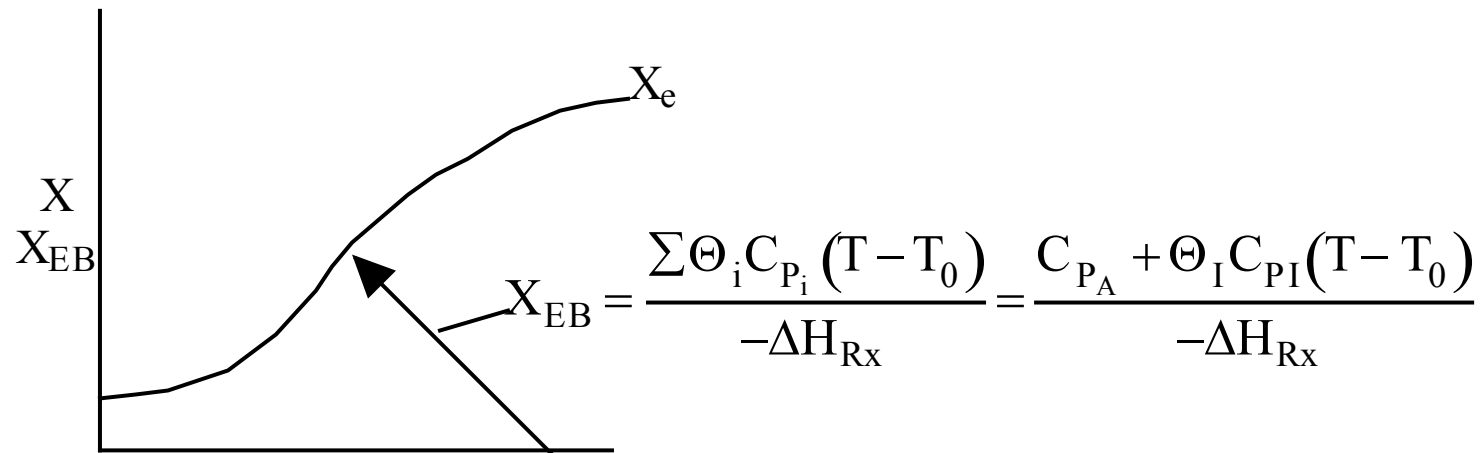
Gas Phase Co-current Heat Exchange



# Endothermic



$$\frac{dX}{dV} = \frac{k \left( 1 - \left( 1 + \frac{1}{K_C} \right) X \right)}{v_0}, \quad X_e = \frac{K_C}{1 + K_C}$$



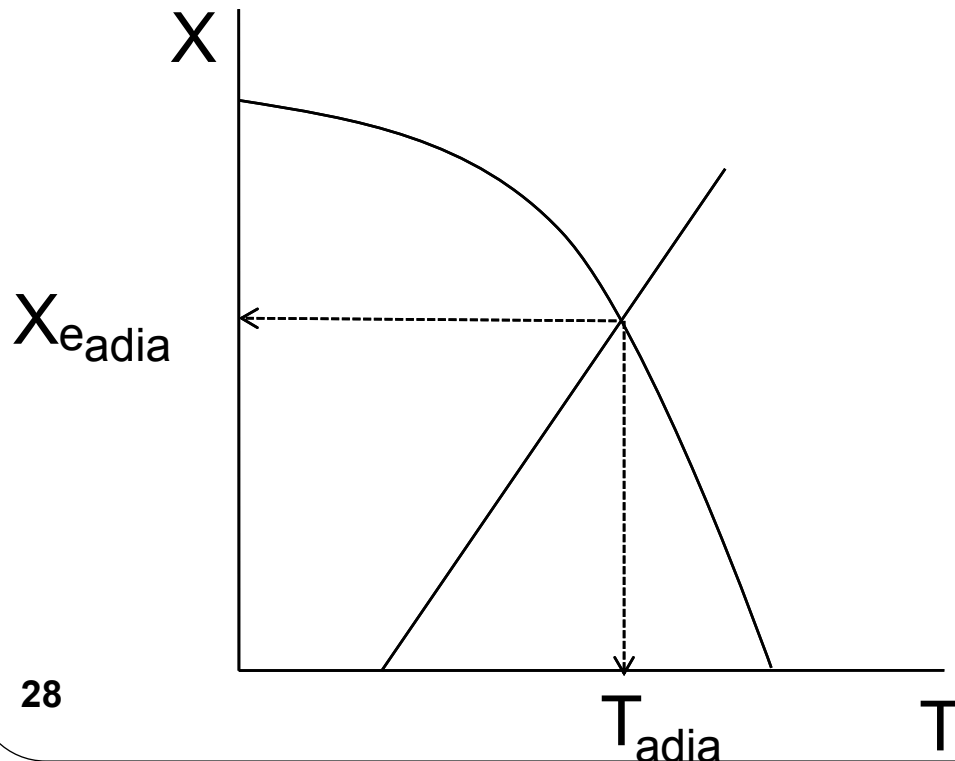
$$T = T_0 + \frac{(-\Delta H_{Rx})X}{C_{P_A} + \Theta_I C_{P_I}}$$

# Adiabatic Equilibrium

Conversion on temperature

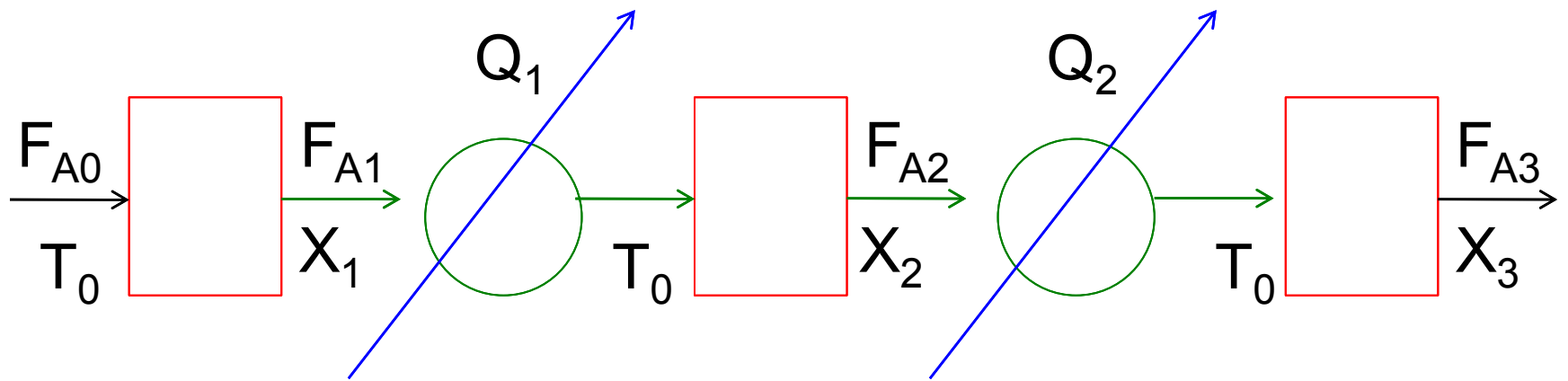
Exothermic  $\Delta H$  is negative

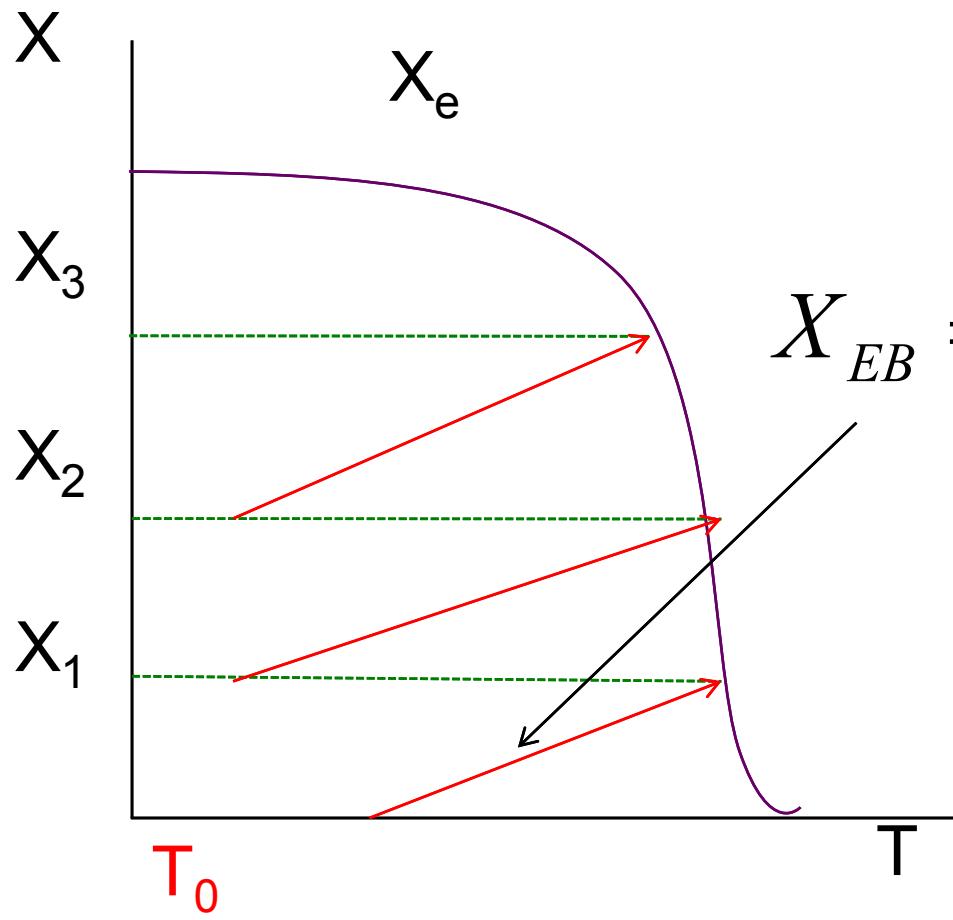
Adiabatic Equilibrium temperature ( $T_{\text{adia}}$ ) and conversion ( $X_{\text{e adia}}$ )



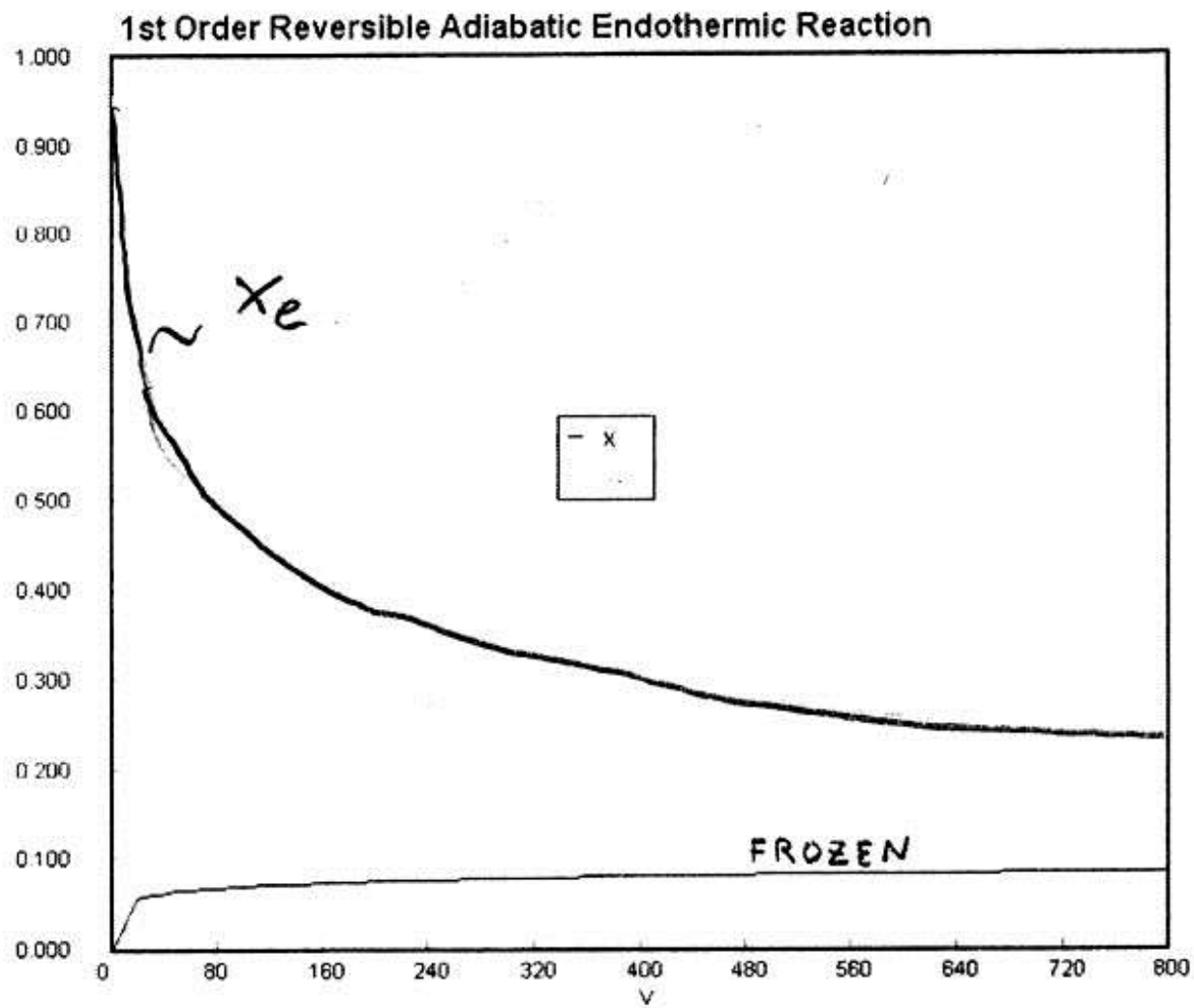
$$T = T_0 + \frac{(-\Delta H_{\text{RX}})X}{C_{\text{PA}}}$$

$$X_{\text{e}} = \frac{K_{\text{C}}}{1 + K_{\text{C}}}$$





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

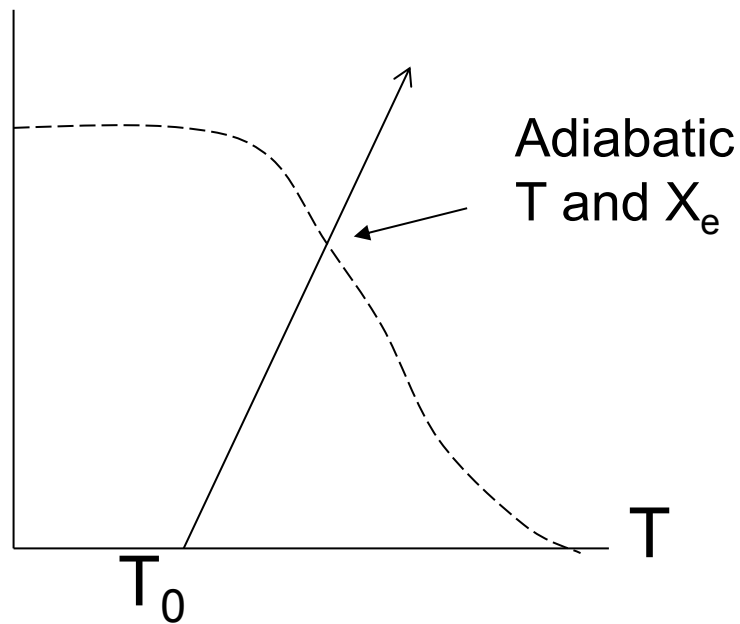


# Gas Flow Heat Effects

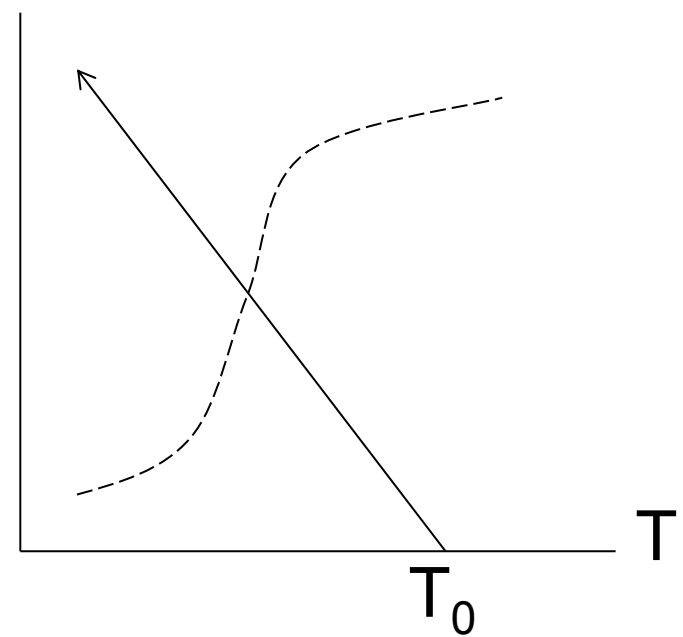
## Trends:

Adiabatic

X **exothermic**



X **endothermic**



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



# Effects of Inerts in the Feed

## PFR Adiabatic



1. Irreversible  $A \rightarrow B$  Liquid Phase, Keep  $F_{A0}$  Constant

A. First order

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

Constant density liquid

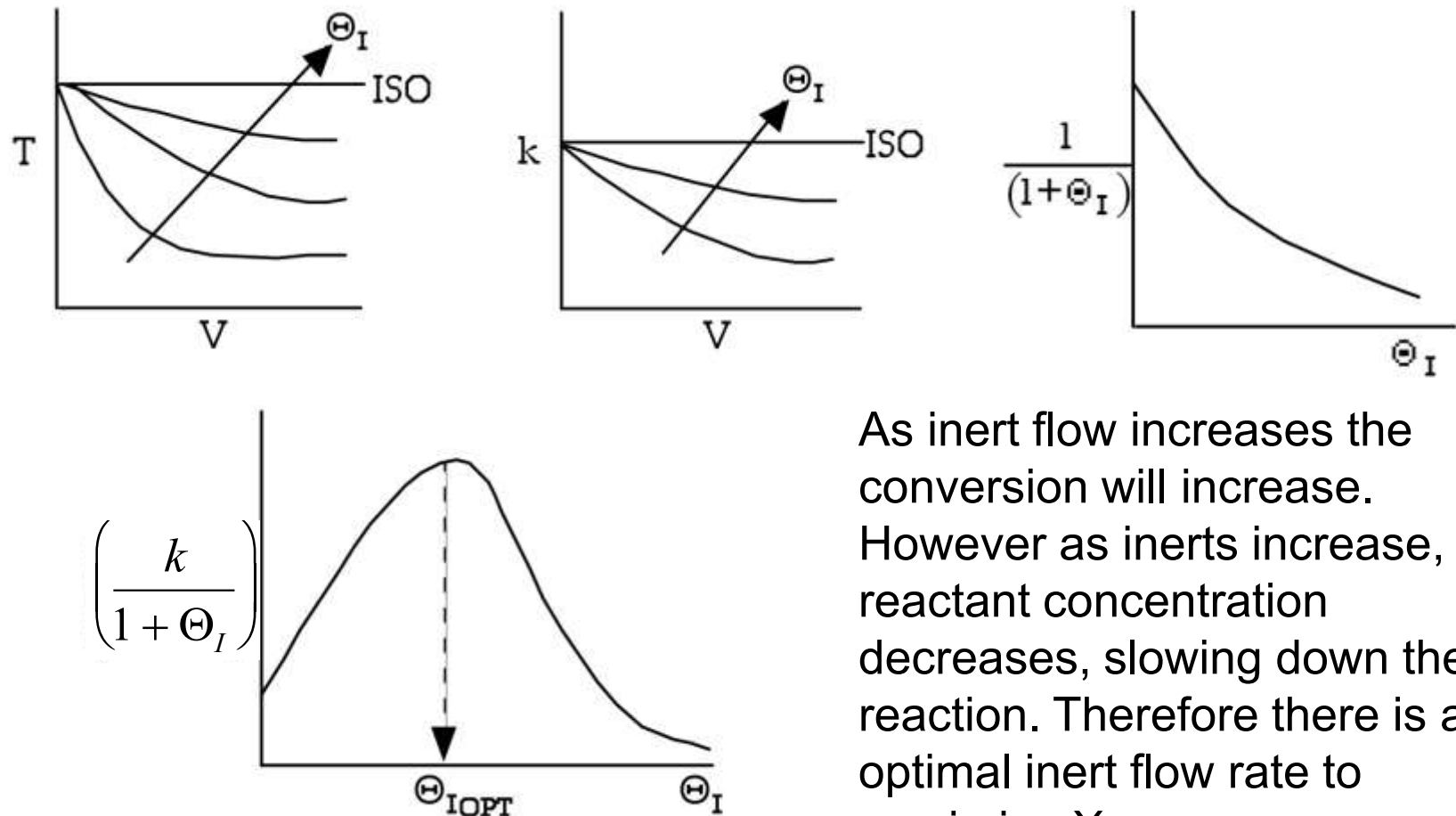
$v_0$  = volumetric flow rate without inert

$$v = v_0 \left( \frac{F_{A0} + F_I}{F_{A0}} \right) = v_0 (1 + \Theta_I)$$

$$\frac{dX}{dV} = \frac{k(1-X)}{v_0(1+\Theta_I)}$$

# Endothermic

## First Order Irreversible

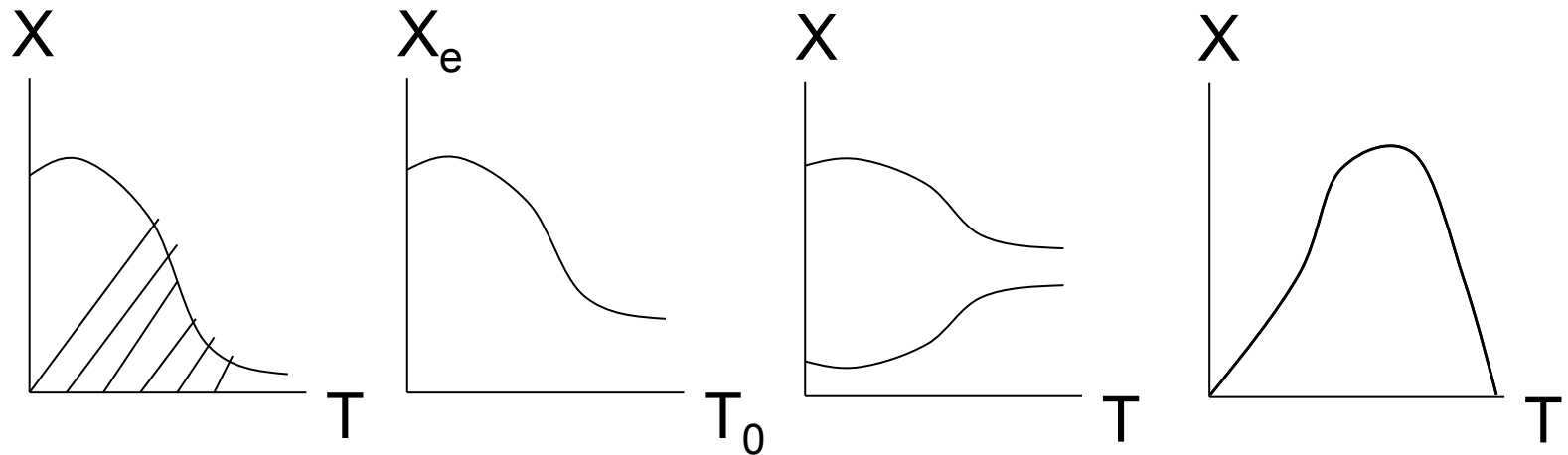


As inert flow increases the conversion will increase. However as inerts increase, reactant concentration decreases, slowing down the reaction. Therefore there is an optimal inert flow rate to maximize  $X$ .

# 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.

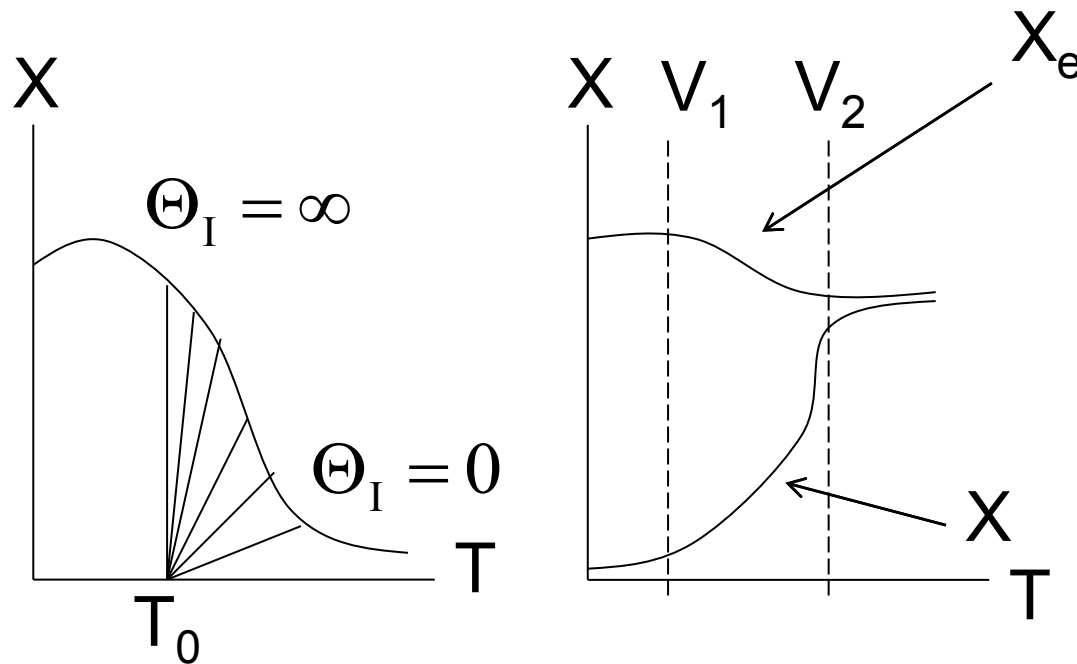


Therefore, for exothermic reactions there is an optimum inlet temperature, where  $X$  reaches  $X_{eq}$  right at the end of  $V$ . However, for endothermic reactions there is no temperature maximum and the  $X$  will continue to increase as  $T$  increases.

# Gas Phase Heat Effects

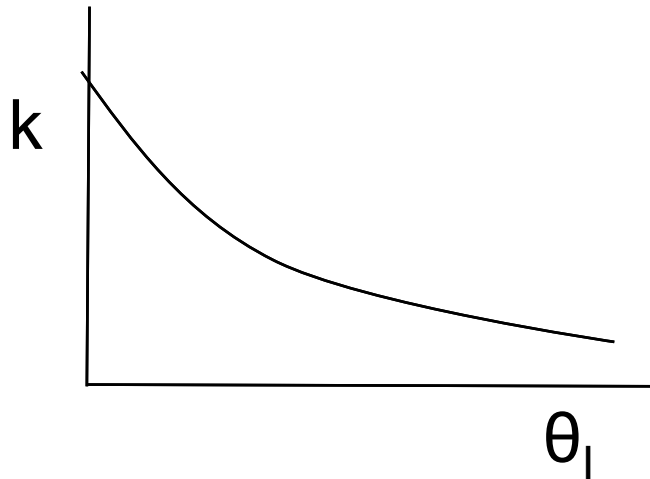
Effect of adding inerts

Adiabatic:



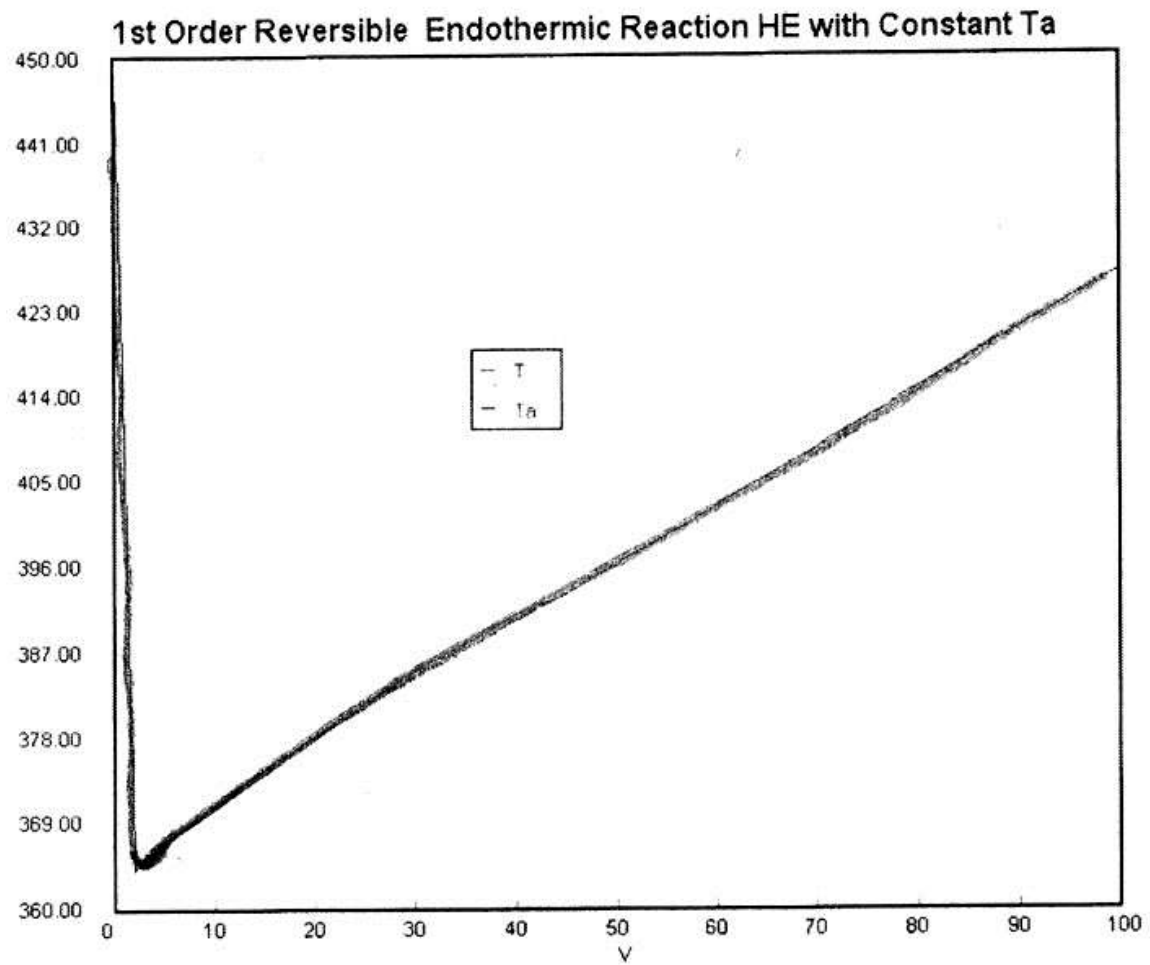
$$X = \frac{(T - T_0)[C_{pA} + \theta_I C_{pI}]}{-\Delta H_{Rx}}$$

# Exothermic Adiabatic

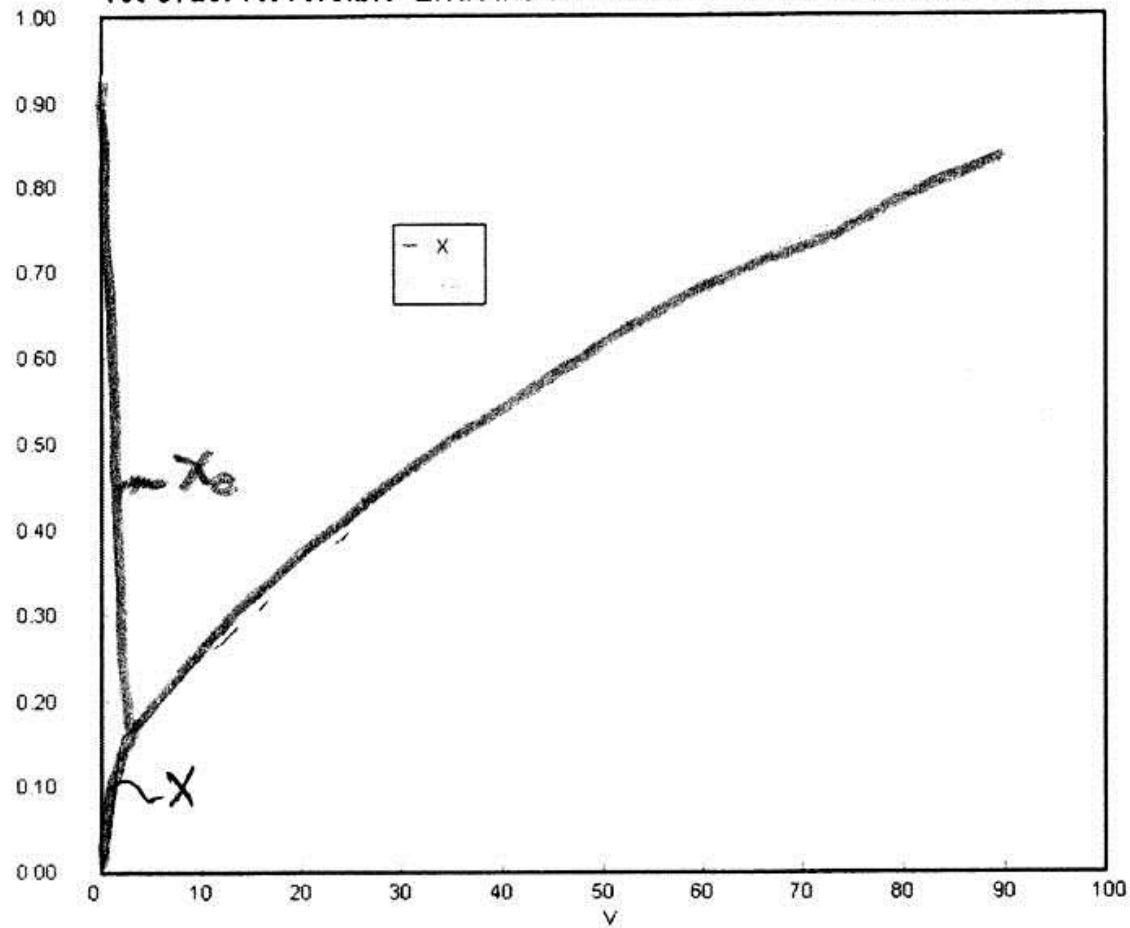


As  $\theta_I$  increase,  $T$  decrease and

$$\frac{dX}{dV} = \frac{k}{v_0(H\theta_I)}$$

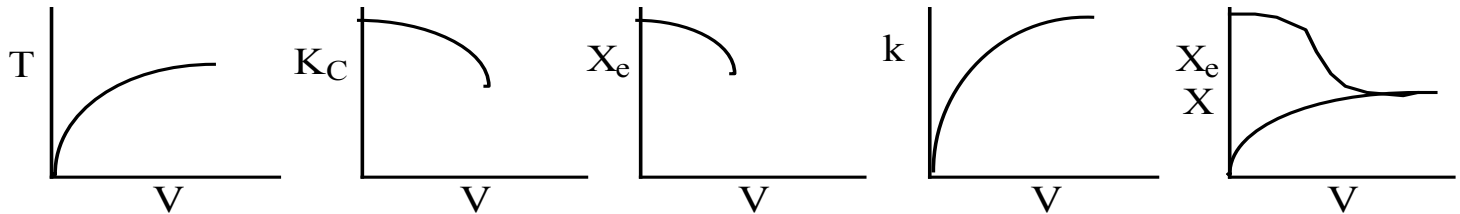


1st Order Reversible Endothermic Reaction HE with Constant  $T_a$

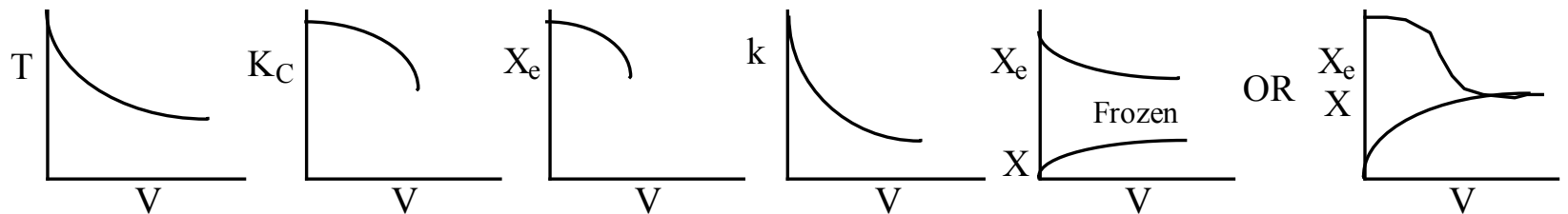


# Adiabatic

## Exothermic



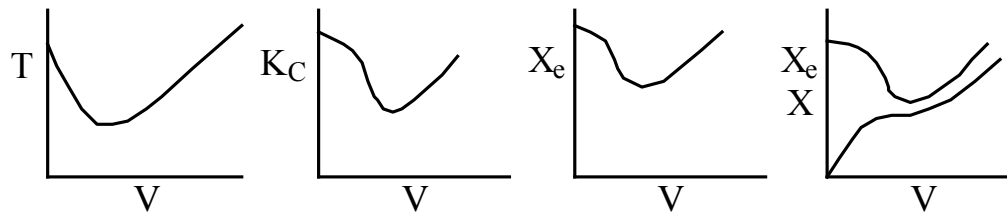
## Endothermic



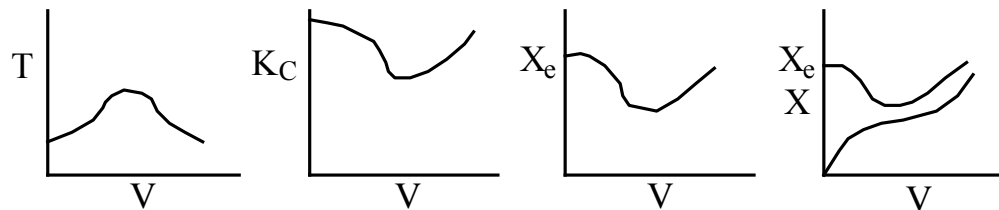


# Heat Exchange

Exothermic



Endothermic



End of Web Lecture 21  
End of Class Lecture 17