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_i

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

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

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

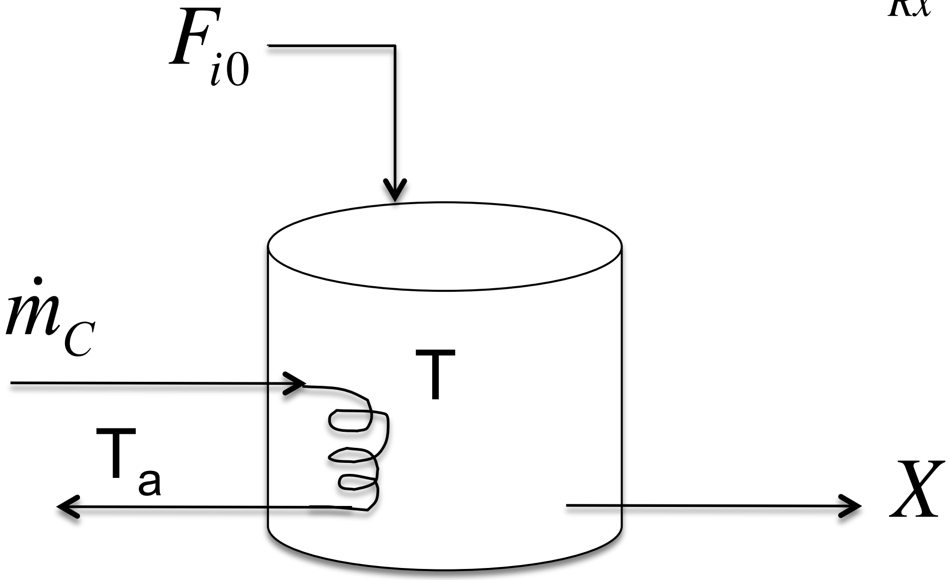
$$X = \frac{\sum \Theta_i \hat{C}_{P_i}\left(T - T_0\right)}{-\Delta H_{Rx}}$$

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

User Friendly Equations relate T, X, or F_i

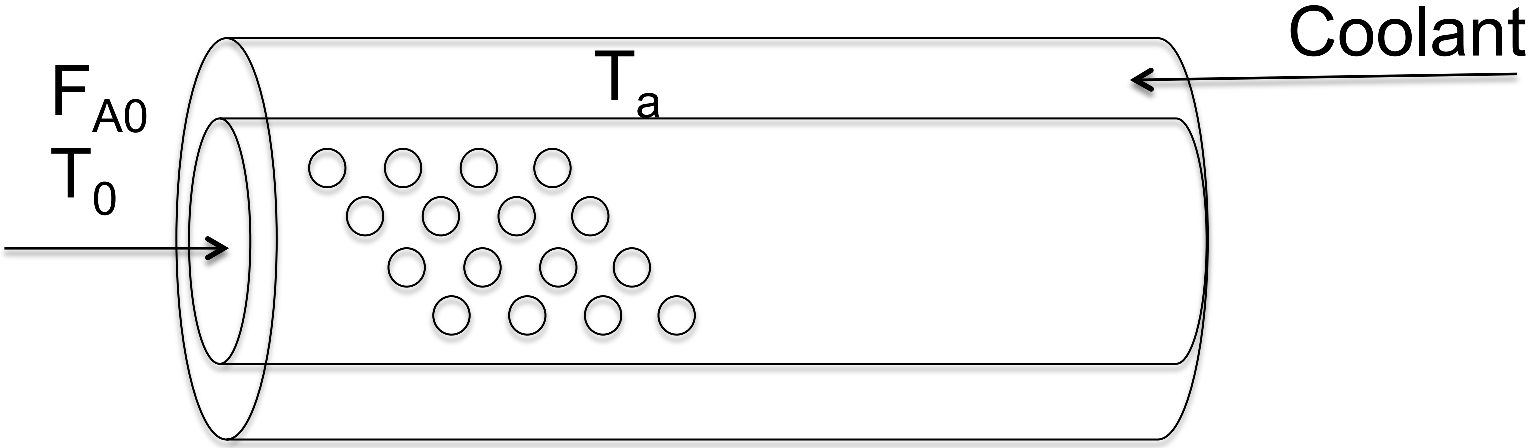
2. CSTR with heat exchanger, UA(T_a-T) and a large coolant flow rate:

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



User Friendly Equations relate T, X, or F_i

3. PFR/PBR with heat exchange:



3A. In terms of conversion, X

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

User Friendly Equations relate T, X, or F_i

3B. In terms of molar flow rates, F_i

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

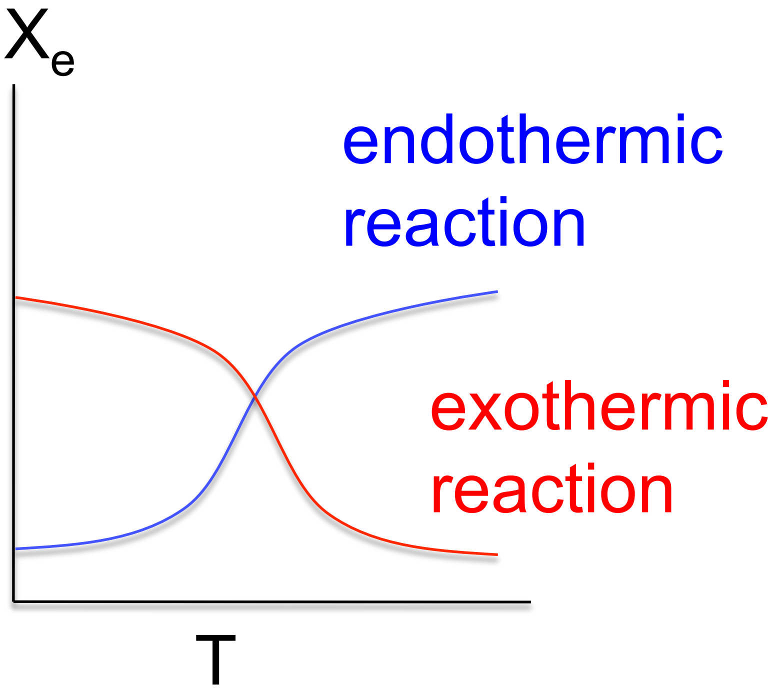
4. For multiple reactions

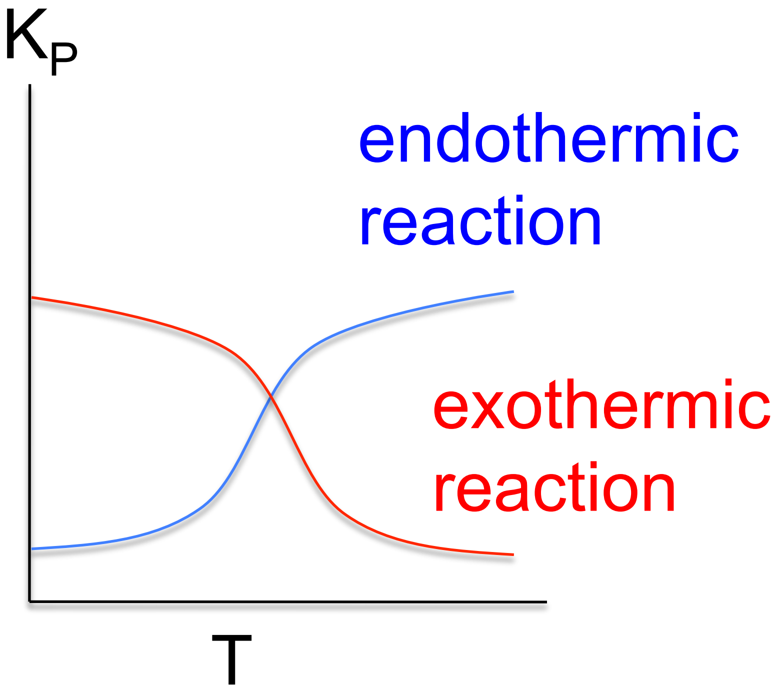
$$\frac{dT}{dV} = \frac{\frac{Ua}{\rho_B}\left(T_a - T\right) + \sum r_{ij} \Delta H_{Rx_{ij}}}{\sum F_i C_{P_i}}$$

5. Co-Current Balance

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

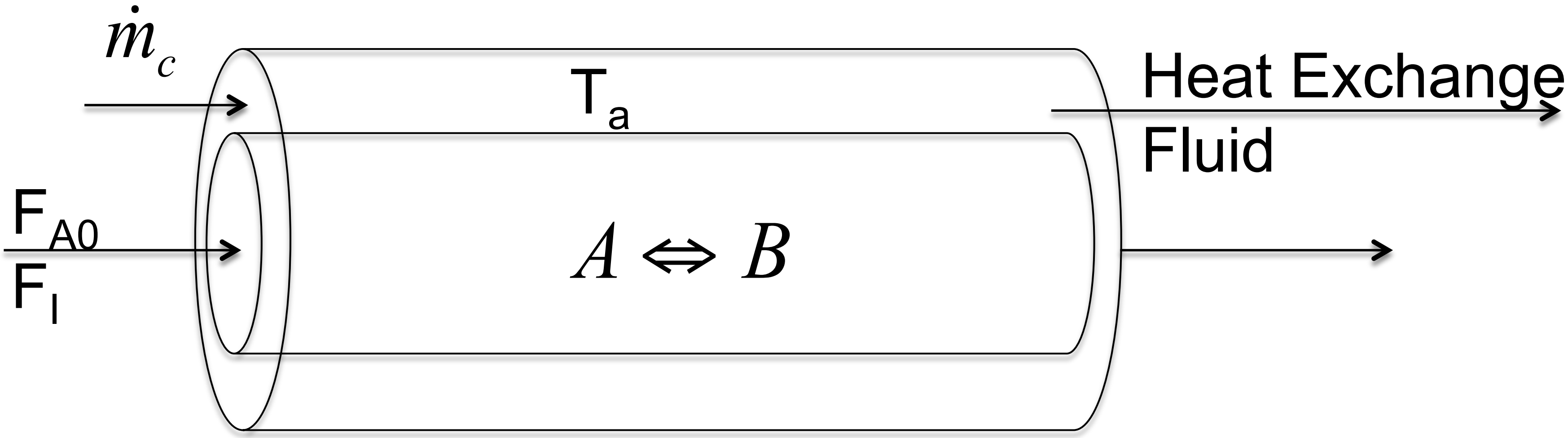
Reversible Reactions





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 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: 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

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

$$W = \rho_b V$$

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

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

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

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

Note: Nomenclature change for 5th edition p ≡ y

$$F_T = F_{T0}$$

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

$$W = \rho V$$

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

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 ↔ B

3) Stoichiometry:
Gas Phase

$$v = v_0 \left(1+\varepsilon X\right)\frac{P_0}{P}\frac{T}{T_0}$$

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

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

$$(7) \quad \frac{dp}{dW} = \frac{-\alpha}{2p}\frac{F_T}{F_{T0}}\frac{T}{T_0} = \frac{-\alpha}{2p}\left(1+\varepsilon X\right)\frac{T}{T_0}$$

Reversible Reactions

Gas Phase Heat Effects

Example: PBR A ↔ B

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

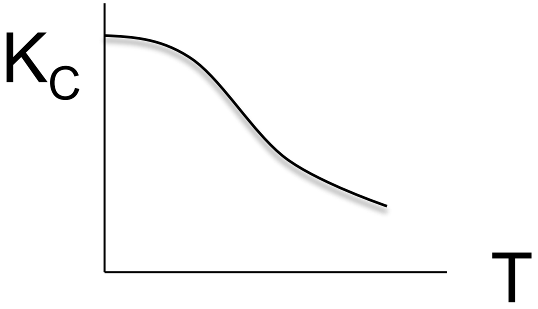
$$(8) \quad X_e = \frac{K_C}{1 + K_C}$$

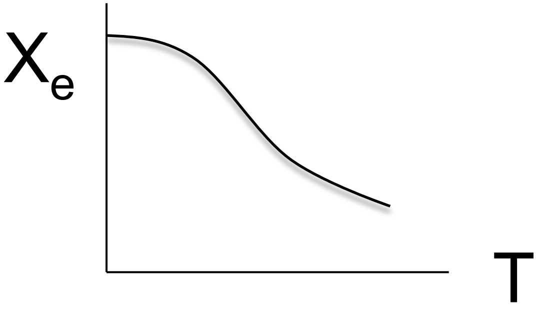
Reversible Reactions

Gas Phase Heat Effects

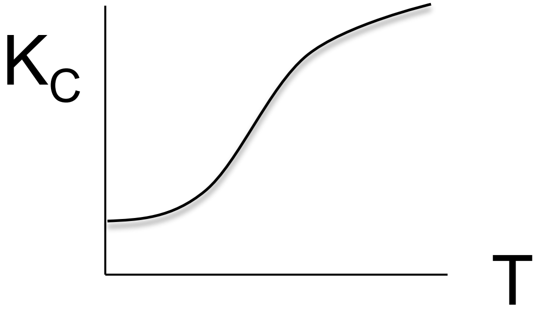
Example: PBR $A \leftrightarrow B$

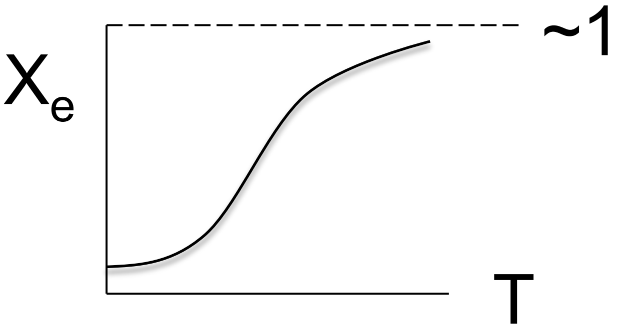
Exothermic Case:





Endothermic Case:





Reversible Reactions

Gas Phase Heat Effects

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

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

Case 1: Adiabatic and ΔC_P=0

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

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

Reversible Reactions

Gas Phase Heat Effects

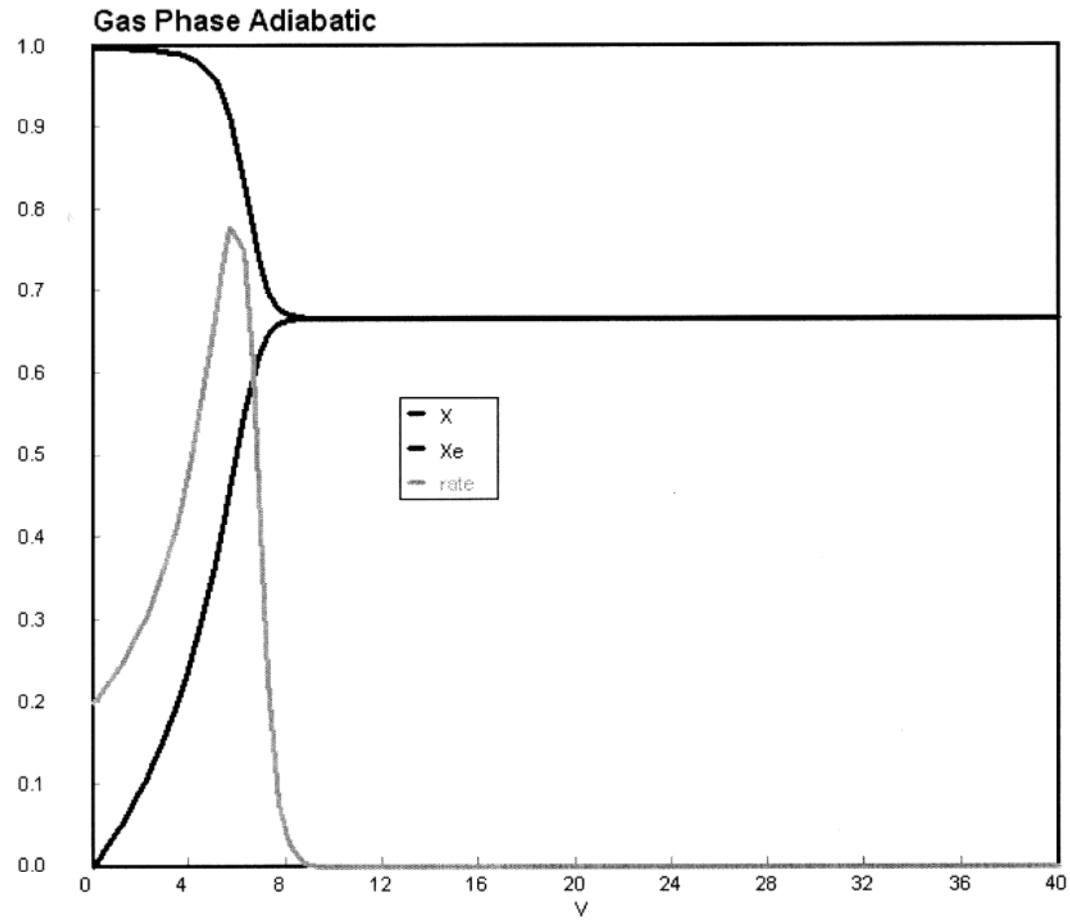
Case 3. Variable T_a Co-Current

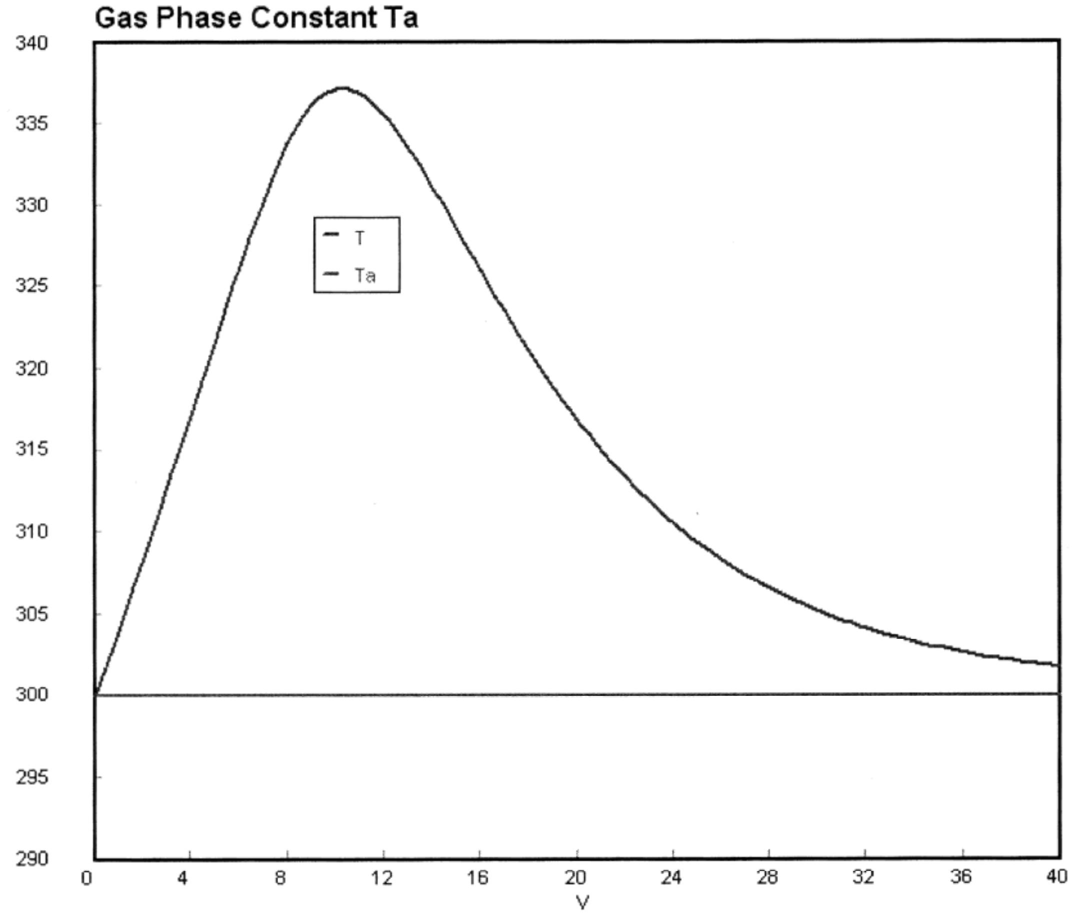
$$\frac{dT_a}{dV} = \frac{Ua\left(T - T_a\right)}{\dot{m}C_{P_{cool}}}, V = 0 \quad T_a = T_{ao} \qquad (17C)$$

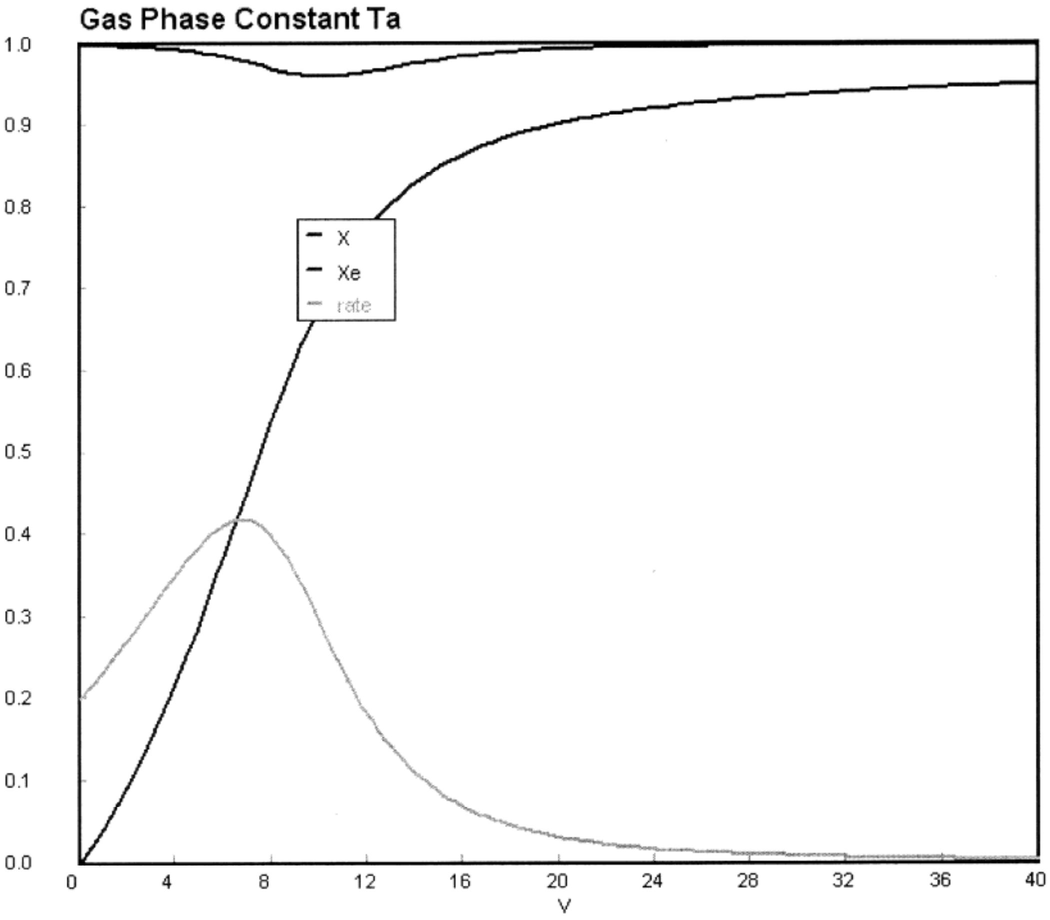
Case 4. Variable T_a Countercurrent

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

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


Gas Phase Adiabatic
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
4
8
12
16
20
24
28
32
36
40
V
X
Xe
rate


Gas Phase Constant Ta
340
335
330
325
320
315
310
305
300
295
290
0
4
8
12
16
20
24
28
32
36
40
V
T
Ta


Gas Phase Constant Ta
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
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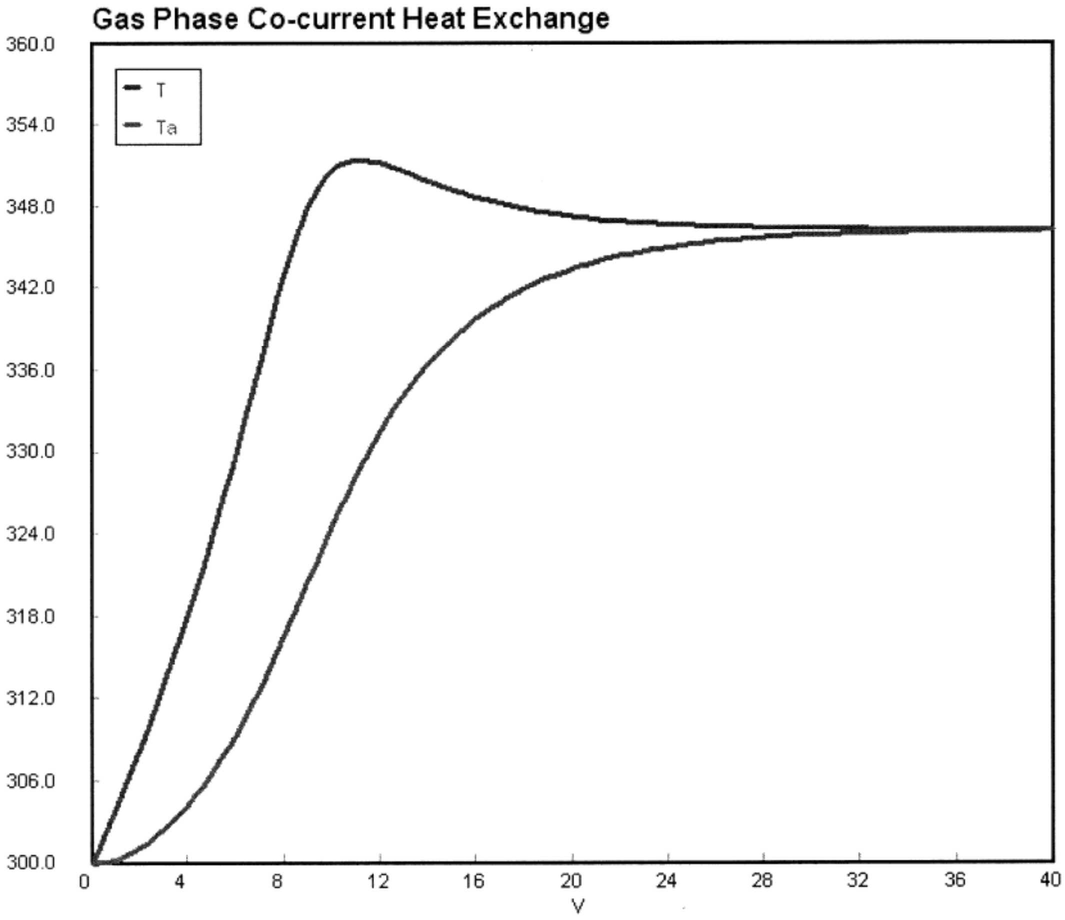
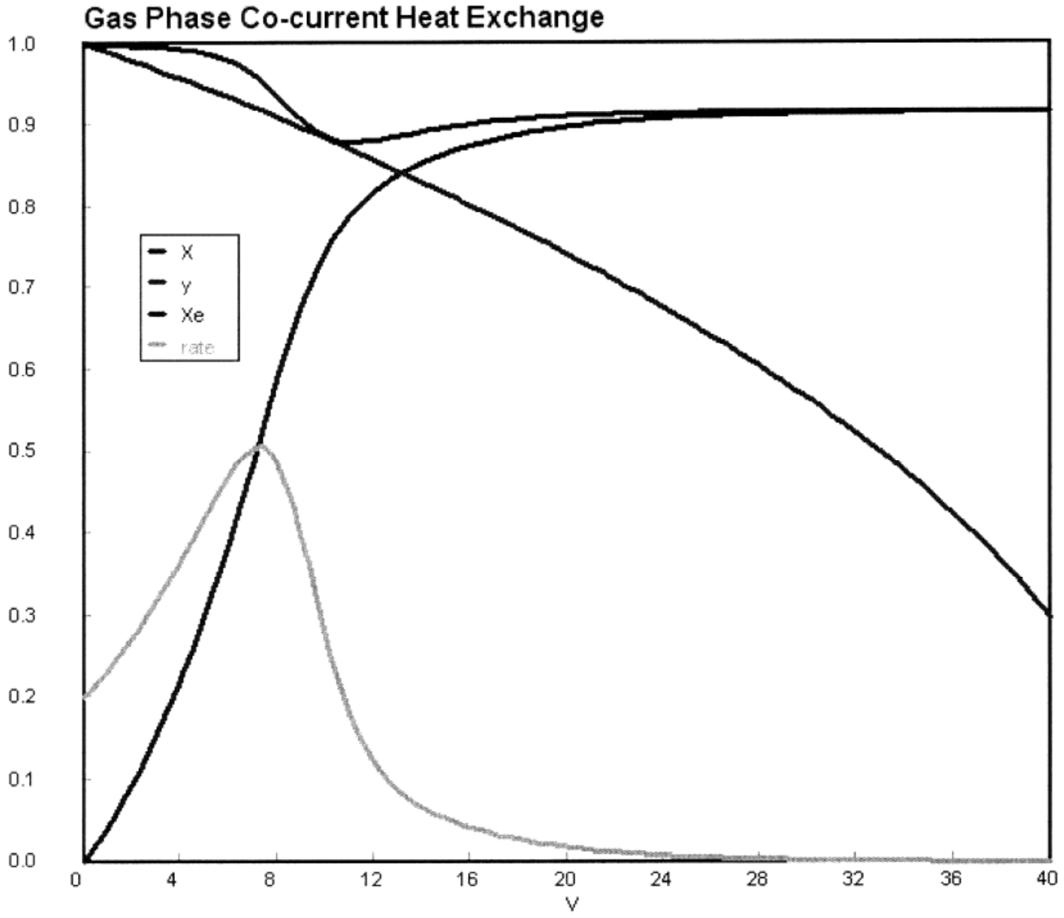
0
4
8
12
16
20
24
28
32
36
40
V
X
Xe
rate

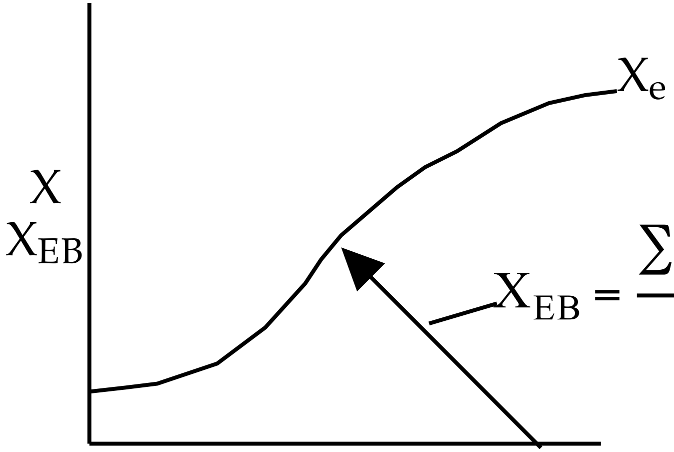

Gas Phase Co-current Heat Exchange
T
Ta
360.0
354.0
348.0
342.0
336.0
330.0
324.0
318.0
312.0
306.0
300.0
0
4
8
12
16
20
24
28
32
36
40
V


Gas Phase Co-current Heat Exchange
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
X
y
Xe
rate
0
4
8
12
16
20
24
28
32
36
40
V

Endothermic

PFR $A \rightleftarrows B$

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



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

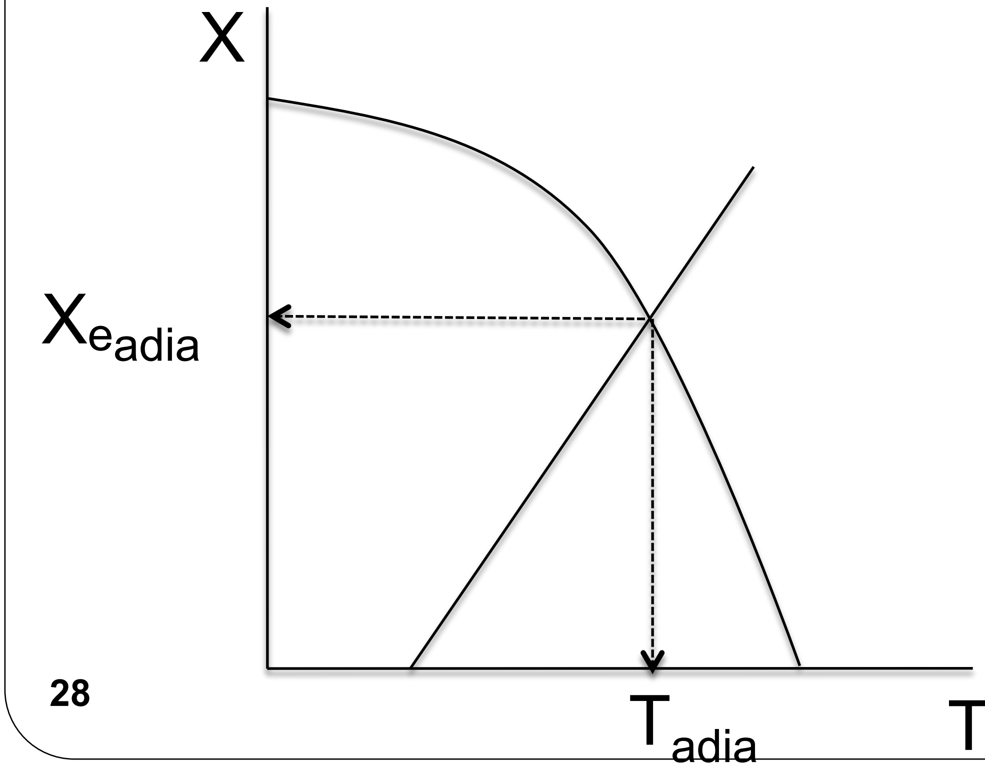
$$T = T_0 + \frac{\left(-\Delta H_{Rx}\right)X}{C_{P_A} + \Theta_I C_{P_I}}$$

Adiabatic Equilibrium

Conversion on temperature

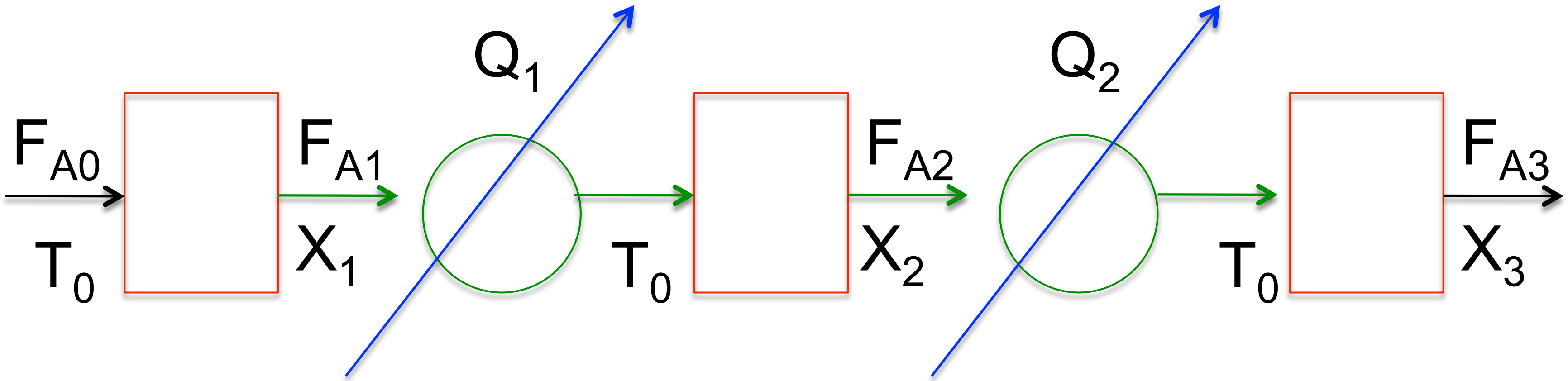
Exothermic ΔH is negative

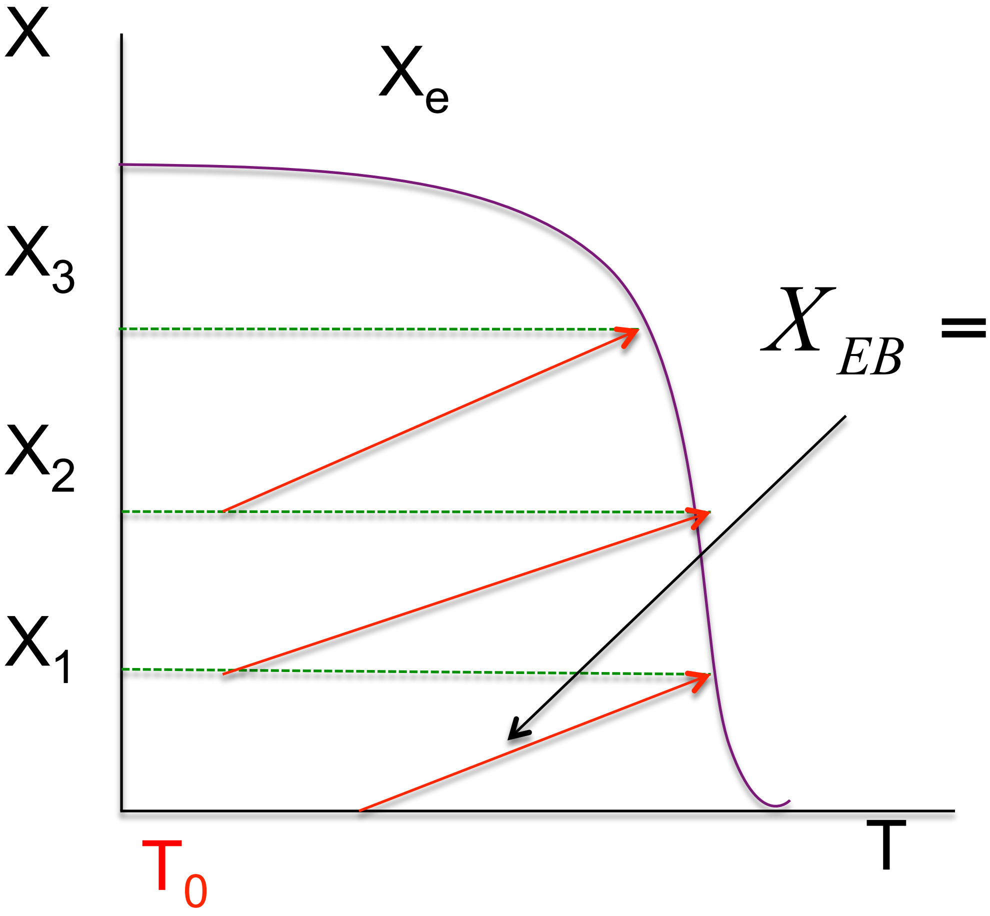
Adiabatic Equilibrium temperature (T_{adia}) and conversion (Xe_{adia})



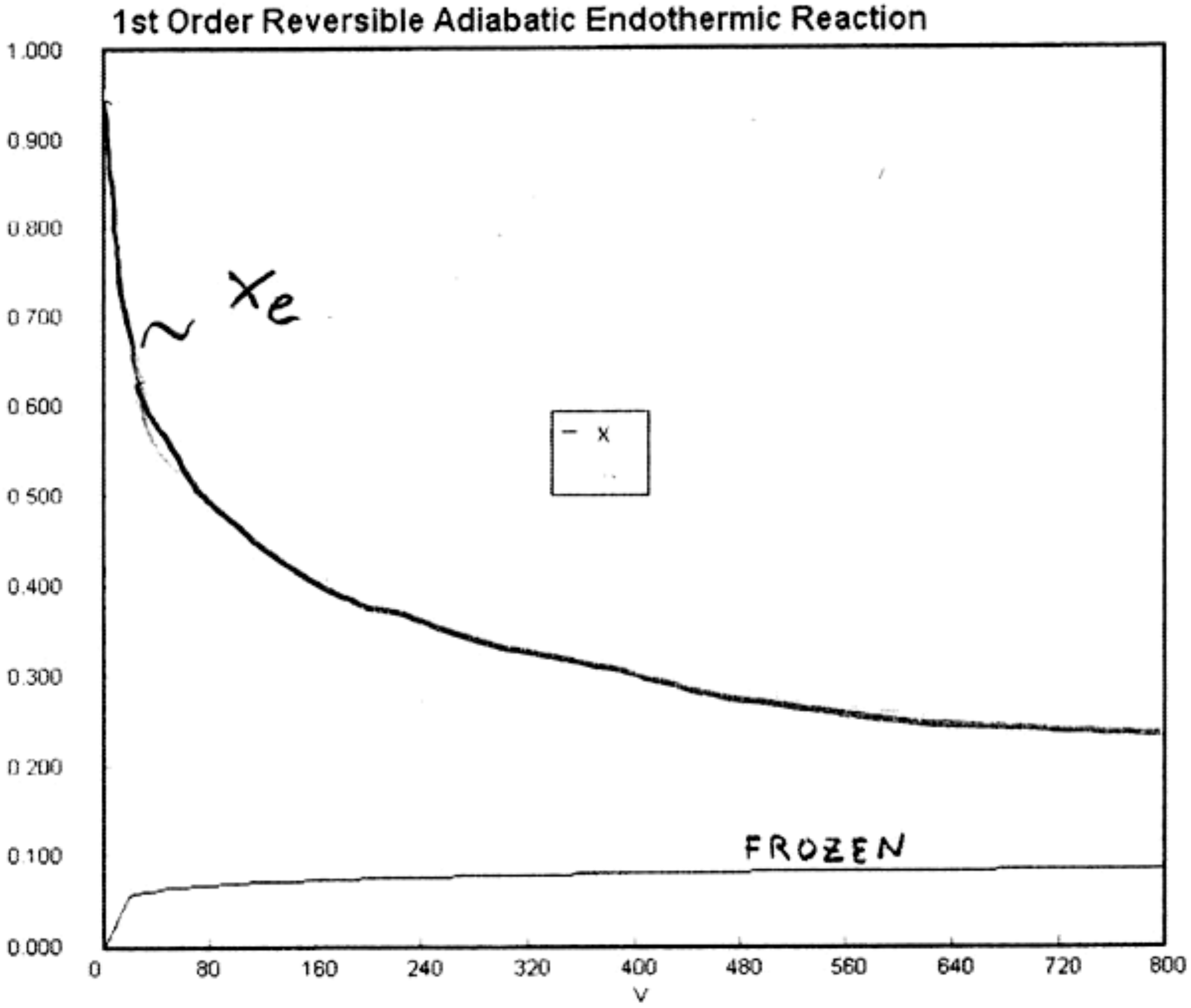
$$T = T_0 + \frac{(-\Delta H_{Rx})X}{C_{PA}}$$

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


F_{A0}
T_0
F_{A1}
X_1
Q_1
T_0
F_{A2}
X_2
Q_2
T_0
F_{A3}
X_3



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

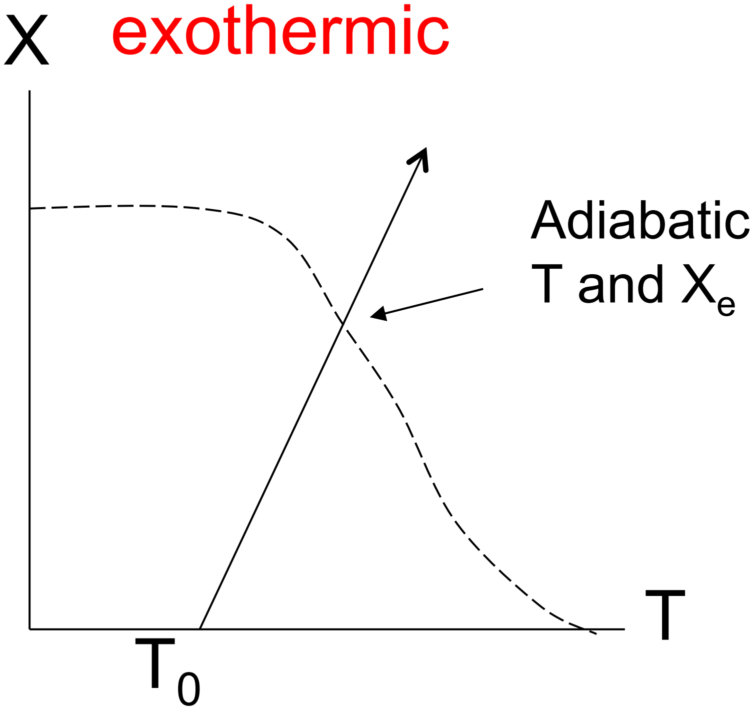


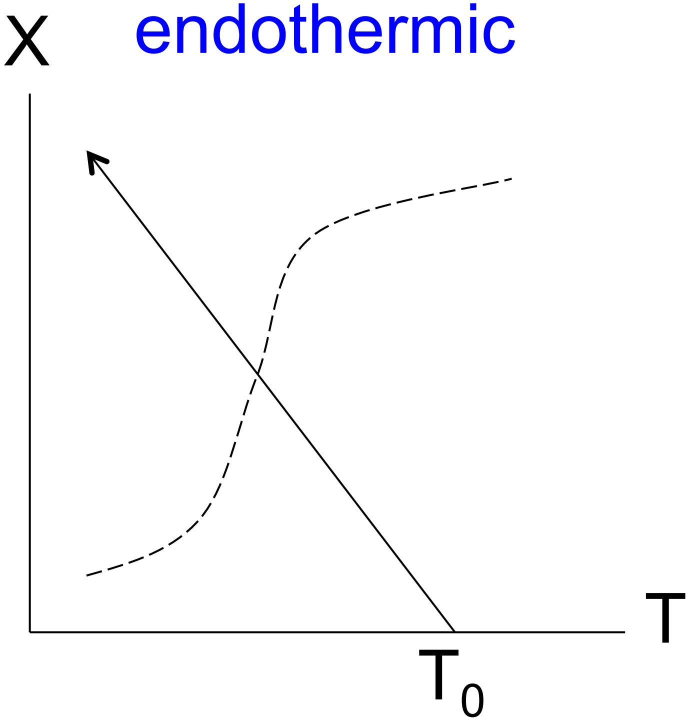
1st Order Reversible Adiabatic Endothermic Reaction

Gas Flow Heat Effects

Trends:

Adiabatic


exothermic


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 → 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

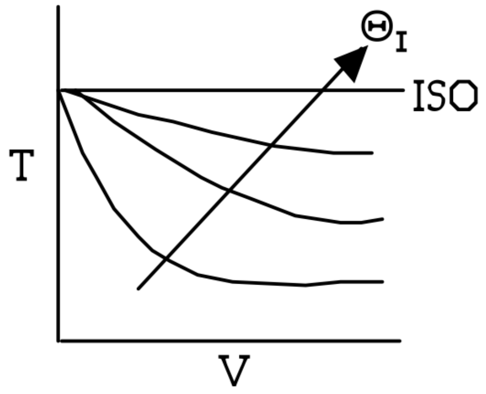
υ_0 = volumetric flow rate without inert

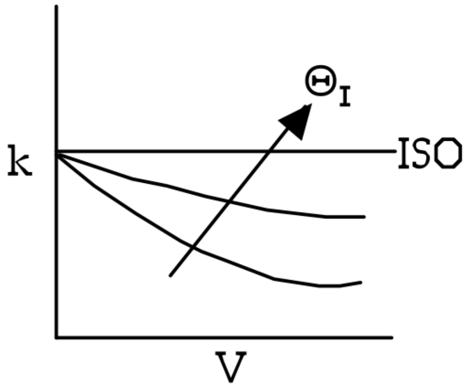
$$\upsilon = \upsilon_0\left(\frac{F_{A0}+F_I}{F_{A0}}\right) = \upsilon_0(1+\Theta_I)$$

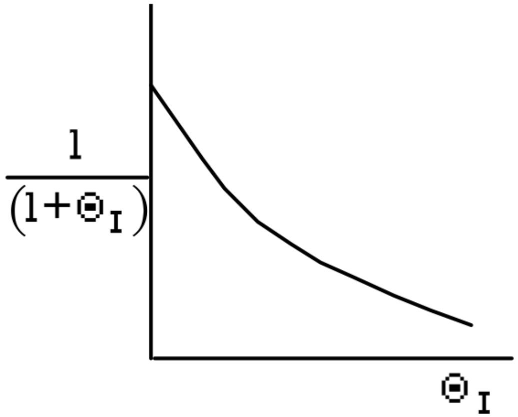
$$\frac{dX}{dV} = \frac{k(1-X)}{\upsilon_0(1+\Theta_I)}$$

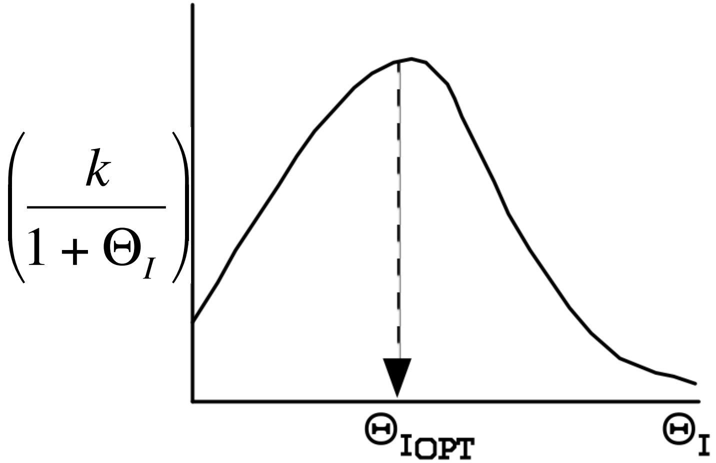
Endothermic

First Order Irreversible







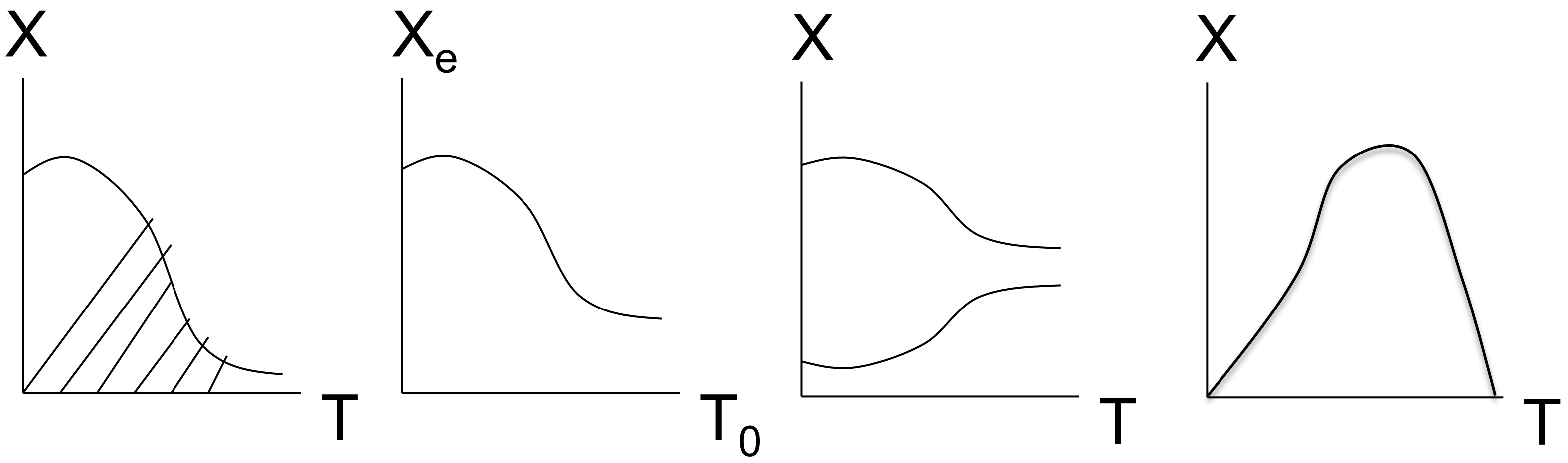


As inert flow increases the conversion will increase. However as inerts increase, reactant concentration decreases, slowing down the reaction. Therefore there is an optimal inert flow rate to maximize X.

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.

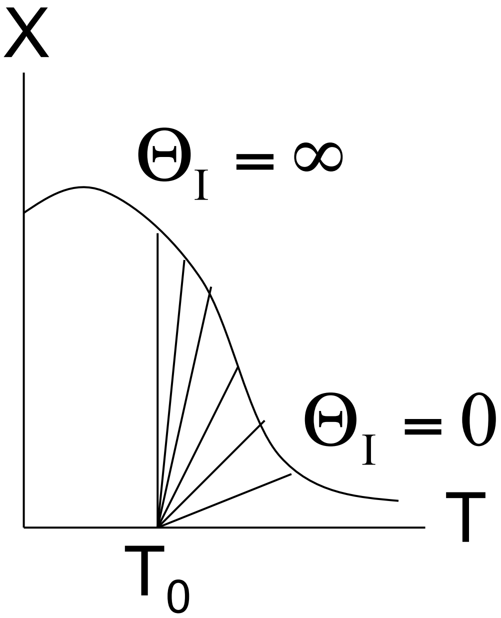


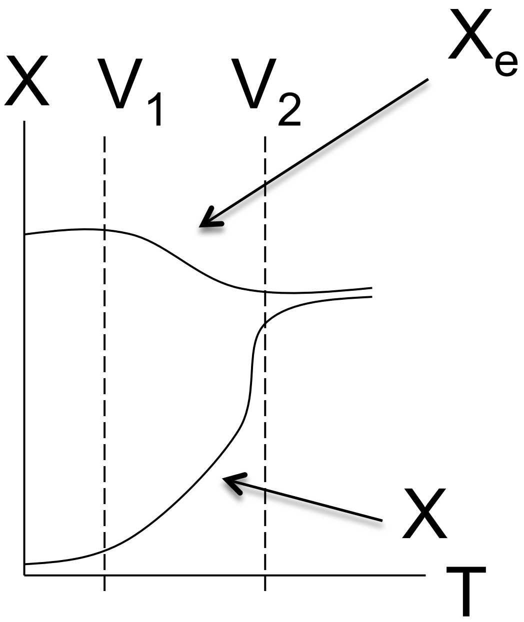
Therefore, for <u>exothermic</u> reactions there is an optimum inlet temperature, where X reaches X_{eq} right at the end of V. However, for <u>endothermic</u> reactions there is no temperature maximum and the X will continue to increase as T increases.

Gas Phase Heat Effects

Effect of adding inerts

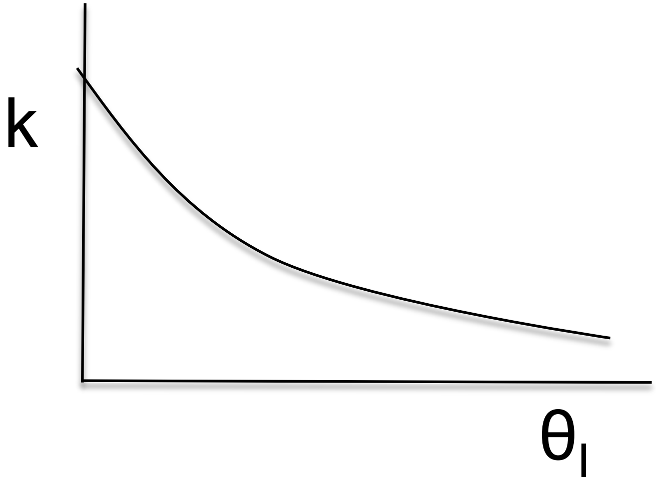
Adiabatic:





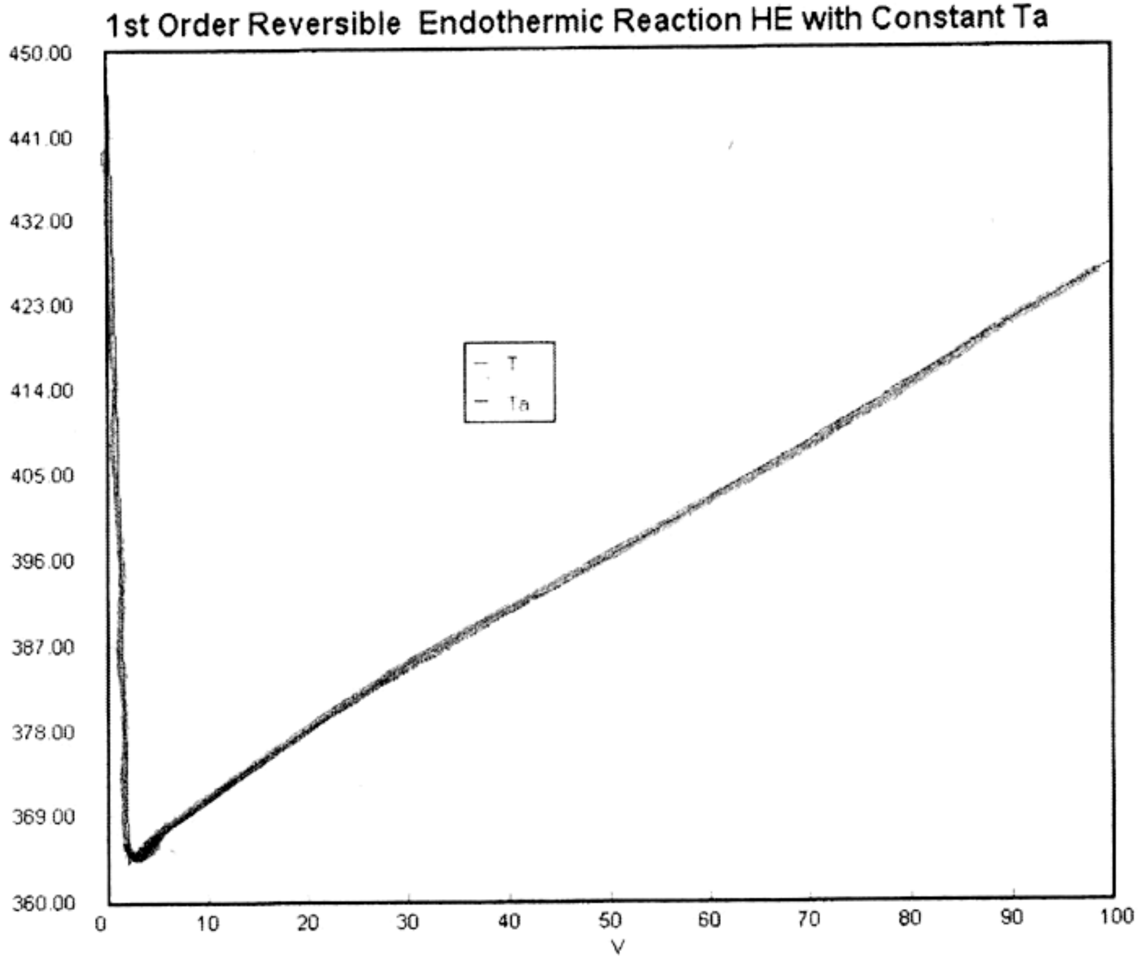
$$X = \frac{(T - T_0)\left[C_{pA} + \theta_I C_{pI}\right]}{-\Delta H_{Rx}}$$

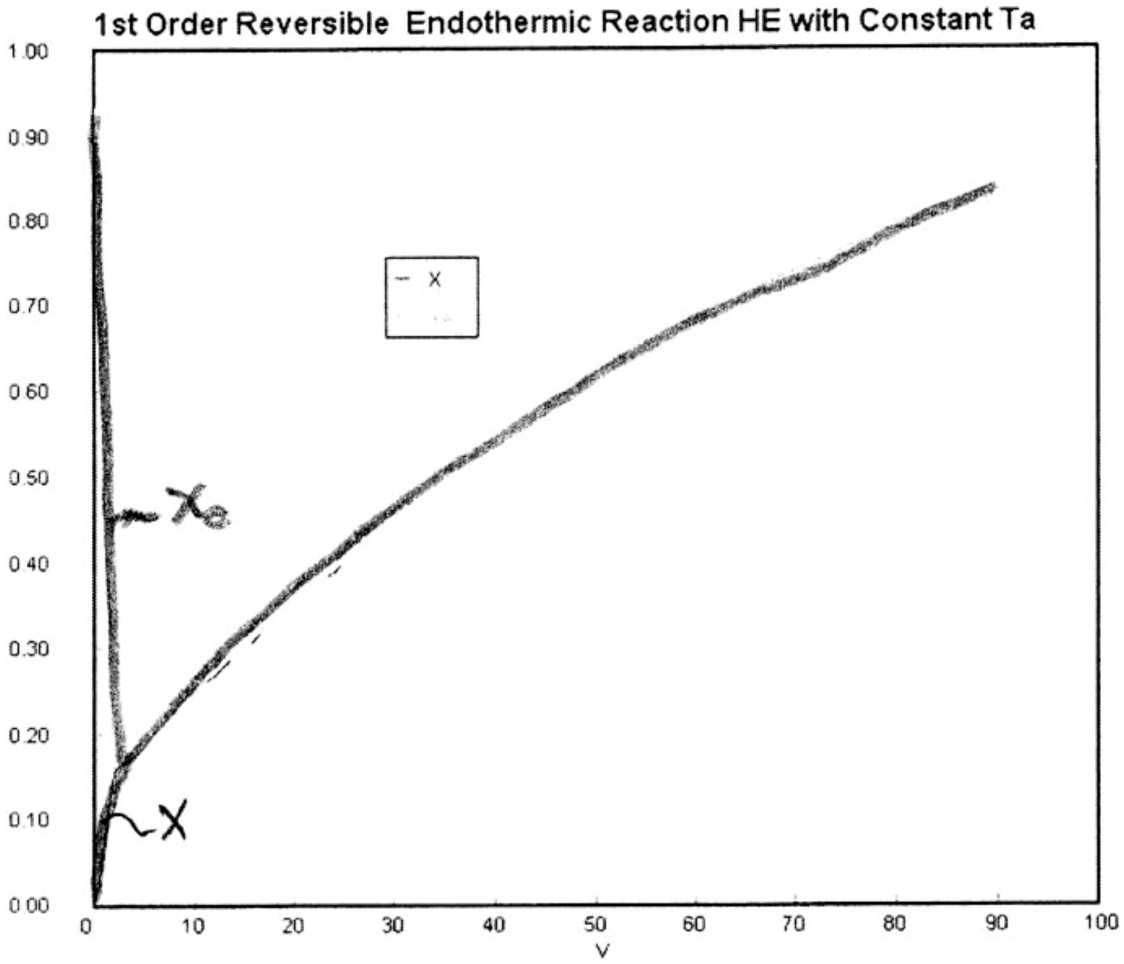
Exothermic Adiabatic



As θ_I increase, T decrease and

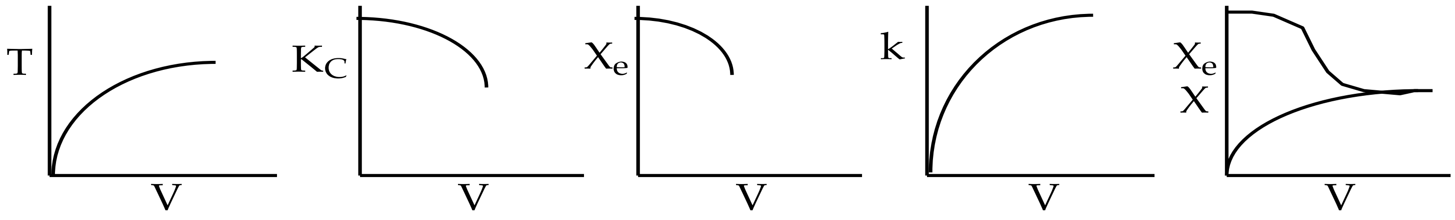
$$\frac{dX}{dV} = \frac{k}{\upsilon_0\left(H\theta_I\right)}$$


1st Order Reversible Endothermic Reaction HE with Constant Ta
450.00
441.00
432.00
423.00
414.00
405.00
396.00
387.00
378.00
369.00
360.00
0
10
20
30
40
50
60
70
80
90
100
V
T
Ta

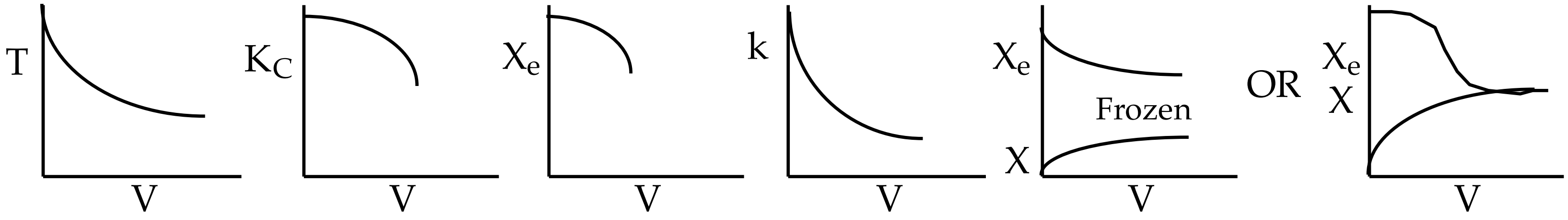

1st Order Reversible Endothermic Reaction HE with Constant Ta
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
10
20
30
40
50
60
70
80
90
100
V
X
X_e
X

Adiabatic

Exothermic

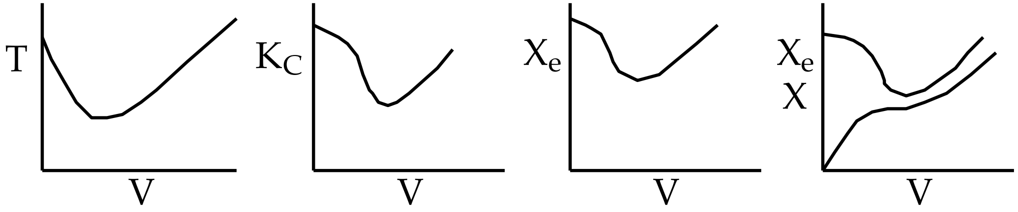


Endothermic

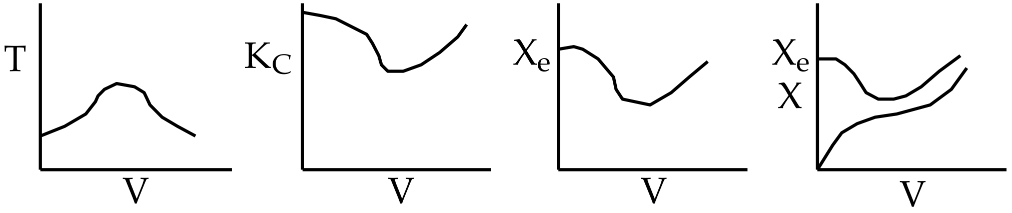


Heat Exchange

Exothermic



Endothermic



End of Web Lecture 21
End of Class Lecture 17