8. Steady-State Nonisothermal Reactor Design

- Energy Balance
  - Overview of User Friendly Energy Balance Equations
  - Manipulating the Energy Balance, ΔH_{Rx}
- Reversible Reactions
- Adiabatic Reactions
- **Applications of the PFR/PBR User Friendly Energy Balance Equations**
- **Interstage Cooling/Heating**
- **Evaluating the Heat Exchanger Term**
- Multiple Steady States
- Multiple Reactions with Heat Effects

※ Review I

- **Ex 8-3 Liq.-phase isomerization reaction, p 490**

  - Normal butane, C_4H_{10}, isomerized in PFR

  - Adiabatically, liquid phase, high pressure

  - $k_1 = 31.1\ h^{-1}$ **at 360 K**
  - $\Delta H^\circ_{Rx} = -6{,}900$ **J/mol n-butane,** $E = 65.7$ **kJ/mol**
  - $K_C = 3.03$ **at 60°C,** $C_{A0} = 9.3\ mol/dm^3 = 9.3\ kmol/m^3$
  - $C_{P\text{n-B}} = 141$ **J/mol K,** $C_{P\text{i-B}} = 141$ **J/mol K**
  - $C_{P\text{n-P}} = 161$ **J/mol K**

  ☞ V_{CSTR}, V_{PFR} **= ? Processing 100,000 gal/day (163 kmol/h) at 70% conversion of mixture 90 mol % n-butane and 10 mol % i-pentane (inert),** $T_0 = 330$ **K**

※ Review II

○ **Ex 8-3 Liq.-phase isomerization reaction 2**

Sol)

$$n-\mathrm{C_4H_{10}} \Leftrightarrow i-\mathrm{C_4H_{10}}$$

$$\mathrm{A} \Leftrightarrow \mathrm{B}$$

- Mole balance

$$F_{\mathrm{A0}}\frac{dX}{dV} = -r_{\mathrm{A}}$$

- Rate law

$$-r_{\mathrm{A}} = k\left(C_{\mathrm{A}} - \frac{C_{\mathrm{B}}}{K_C}\right)$$

$$k = k(T_1)e^{\left[\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)\right]} \qquad K_C = K_C(T_2)e^{\left[\frac{\Delta H_{Rx}^{0}}{R}\left(\frac{1}{T_2}-\frac{1}{T}\right)\right]}$$

※ Review III

○ **Ex 8-3 Liq.-phase isomerization reaction 3**

Sol)

- Stoichiometry (liquid phase, $v = v_0$)

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

$$C_B = C_{A0}X$$

- Combine

$$-r_A = kC_{A0}\left[1 - \left(1 + \frac{1}{K_C}\right)X\right]$$

- Integration

$$V = \int_0^X \frac{F_{A0}}{-r_A}dX$$

※ Review IV

○ **Ex 8-3 Liq.-phase isomerization reaction 4**

Sol)

- Energy balance

$$\dot{Q}-\dot{W}_s-F_{A0}\sum_{i=1}^{n}\Theta_i C_{Pi}\left[T-T_{i0}\right]-\left[\Delta H_{RX}^{o}(T_R)+\Delta C_P\left(T-T_R\right)\right]F_{A0}X=0$$

Given conditions

$$\text{Adiabatic}: \ Q=0$$

$$\text{No work}: \ \dot{W}=0$$

$$\Delta C_P=C_{P_B}-C_{P_A}=141-141=0$$

- Rearrangement

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

※ Review V

- **Ex 8-3 Liq.-phase isomerization reaction 5**
  - **Parameter evaluation**

$$\Sigma\Theta_i C_{P_i} = C_{P_A} + \Theta_I C_{P_I} = \left(141 + \frac{0.1}{0.9}161\right) \text{J/mol}\cdot\text{K}$$

$$= 159 \text{ J/mol}\cdot\text{K}$$

$$T = 330 + \frac{-(-6900)}{159}X$$

$$\boxed{T = 330 + 43.4X}$$

  - **Substituti**

$$k = 31.1 \exp\left[\frac{65{,}700}{8.31}\left(\frac{1}{360} - \frac{1}{T}\right)\right](h^{-1})$$

$$\boxed{k = 31.1 \exp\left[7906\left(\frac{T-360}{360T}\right)\right](h^{-1})}$$

※ Review VI

- **Ex 8-3 Liq.-phase isomerization reaction 6**

- Substituting for activation energy

$$k = 31.1 \exp\left[\frac{65{,}700}{8.31}\left(\frac{1}{360} - \frac{1}{T}\right)\right](h^{-1})$$

$$\boxed{k = 31.1 \exp\left[7906\left(\frac{T-360}{360T}\right)\right](h^{-1})}$$

- Substituting for heat of reaction

$$K_C = 3.03 \exp\left[\frac{-6900}{8.31}\left(\frac{1}{333} - \frac{1}{T}\right)\right]$$

$$\boxed{K_C = 3.03 \exp\left[-830.3\left(\frac{T-333}{333T}\right)\right]}$$

※ Review VII

○ **Ex 8-3 Liq.-phase isomerization reaction 7**

- Rate law

$$-r_A = kC_{A0}\left[1-\left(1+\frac{1}{K_C}\right)X\right]$$

- Equilibrium conversion $-r_A = 0$

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

(1) PFR solution

- Start with X = 0.2

(a) $T = 330 + 43.4(0.2) = 338.6\ \text{K}$

※ Review VIII

- ○ **Ex 8-3 Liq.-phase isomerization reaction 8**

(b) $$k = 31.1\ \exp\left[7906\left(\frac{338.6-360}{(360)(338.6)}\right)\right] = 31.1\ \exp(-1.388) = 7.76\ \mathrm{h}^{-1}$$

(c) $$K_C = 3.03\ \exp\left[-830.3\left(\frac{338.6-333}{(333)(338.6)}\right)\right] = 3.03e^{-0.0412} = 2.9$$

(d) $$X_e = \frac{2.9}{1+2.9} = 0.74$$

(e) $$-r_\mathrm{A} = \left(\frac{7.76}{\mathrm{h}}\right)(9.3)\frac{\mathrm{mol}}{\mathrm{dm}^3}\left[1-\left(1+\frac{1}{2.9}\right)(0.2)\right] = 52.8\ \frac{\mathrm{mol}}{\mathrm{dm}^3\cdot\mathrm{h}} = 52.8\ \frac{\mathrm{kmol}}{\mathrm{m}^3\cdot\mathrm{h}}$$

(f) $$\frac{F_{\mathrm{A0}}}{-r_\mathrm{A}} = \frac{(0.9\ \text{mol butane/mol total})(163.\ \text{kmol total/h})}{52.8\ \dfrac{\mathrm{kmol}}{\mathrm{m}^3\cdot\mathrm{h}}} = 2.78\ \mathrm{m}^3$$

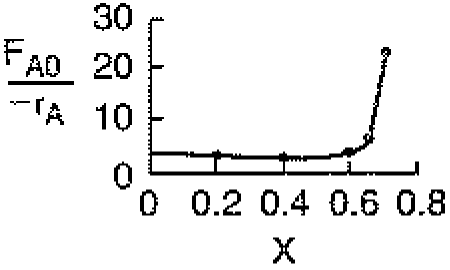
※ Review IX

○ Ex 8-3 Liq.-phase isomerization reaction 9

TABLE E8-3.1 HAND CALCULATION

X	T (K)	k (h^{-1})	K_C	X_e	$-r_A$($kmol/m^3 \cdot h$)	$\frac{F_{A0}}{-r_A}$ (m^3)
0	330	4.22	3.1	0.76	39.2	3.74
0.2	338.7	7.76	2.9	0.74	52.8	2.78
0.4	347.3	14.02	2.73	0.73	58.6	2.50
0.6	356.0	24.27	2.57	0.72	37.7	3.88
0.65	358.1	27.74	2.54	0.718	24.5	5.99
0.7	360.3	31.67	2.5	0.715	6.2	23.29

Make a Levenspiel plot as in Chapter 2.



※ Review X

- **Ex 8-3 Liq.-phase isomerization reaction 10**
  - **Calculation to get volume**

$$V = \int_0^{0.7} \frac{F_{A0}}{-r_A}\,dX = \int_0^{0.6} \frac{F_{A0}}{-r_A}\,dX + \int_{0.6}^{0.7} \frac{F_{A0}}{-r_A}\,dX$$

$$V = \frac{3}{8} \times \frac{0.6}{3}[3.74 + 3 \times 2.78 + 3 \times 2.50 + 3.88]\mathrm{m}^3 + \frac{1}{3} \times \frac{0.1}{2}[3.88 + 4 \times 5.99 + 23.29]\mathrm{m}^3$$

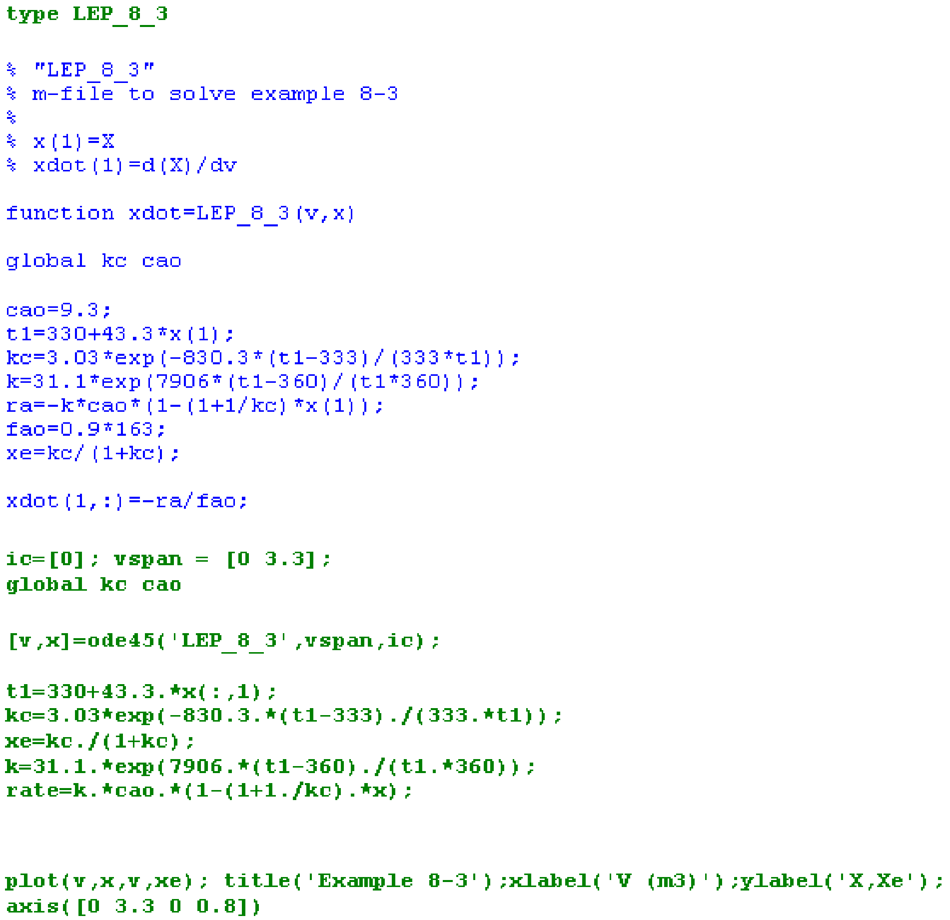
$$V = 1.75\ m^3 + 0.85\ \mathrm{m}^3$$

$$\boxed{V = 2.60\ m^3}$$

※ Review XI

- **Ex 8-3 Liq.-phase isomerization reaction 11**

  - Calculation to get volume with Matlab



```
type LEP_8_3

% "LEP_8_3"
% m-file to solve example 8-3
%
% x(1)=X
% xdot(1)=d(X)/dv

function xdot=LEP_8_3(v,x)

global kc cao

cao=9.3;
t1=330+43.3*x(1);
kc=3.03*exp(-830.3*(t1-333)/(333*t1));
k=31.1*exp(7906*(t1-360)/(t1*360));
ra=-k*cao*(1-(1+1/kc)*x(1));
fao=0.9*163;
xe=kc/(1+kc);

xdot(1,:)=-ra/fao;


ic=[0]; vspan = [0 3.3];
global kc cao

[v,x]=ode45('LEP_8_3',vspan,ic);

t1=330+43.3.*x(:,1);
kc=3.03*exp(-830.3.*(t1-333)./(333.*t1));
xe=kc./(1+kc);
k=31.1.*exp(7906.*(t1-360)./(t1.*360));
rate=k.*cao.*(1-(1+1./kc).*x);



plot(v,x,v,xe); title('Example 8-3');xlabel('V (m3)');ylabel('X,Xe');
axis([0 3.3 0 0.8])
```

※ Review XII

- ○ **Ex 8-3 Liq.-phase isomerization reaction 12**

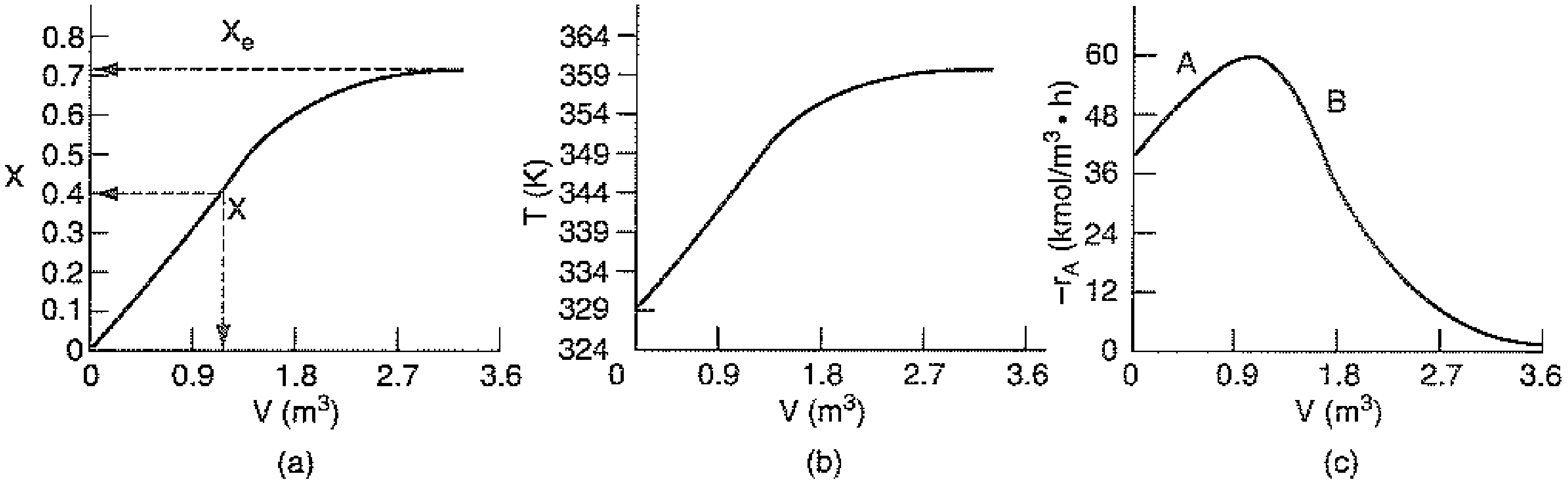


Figure E8-3.1 Conversion, temperature, and reaction rate profiles.

※ Review XIII

○ **Ex 8-3 Liq.-phase isomerization reaction 13**

- CSTR solution

Mole balance

$$V = \frac{F_{A0}X}{-r_A} \qquad V = \frac{F_{A0}X}{kC_{A0}\left[1-\left(1+\frac{1}{K_C}\right)\right]X}$$

Energy balance (for 40% conv.)

$$T = 330 + 43.4X$$

$$T = 330 + 43.4(0.4) = 347.3\text{K}$$

$$k = 14.02\ \text{h}^{-1}$$

$$K_C = 2.73$$

※ Review XIV

○ **Ex 8-3 Liq.-phase isomerization reaction 14**

- Calculation to get volume

$$-r_A = 58.6\ \text{kmol/m}^3\cdot\text{h}$$

$$V = \frac{(146.7\ \text{kmol butane/h})(0.4)}{58.6\ \text{kmol/m}^3\cdot\text{h}}$$

$$V = 1.0\ \text{m}^3$$

※ for PFR at X = 0.4, V = 1.15 m^3

※ Review XV

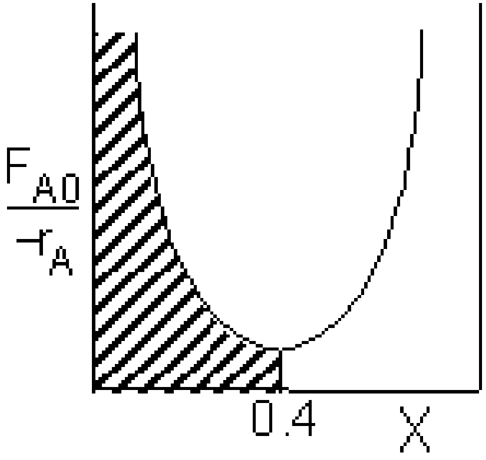
- **Ex 8-3 Liq.-phase isomerization reaction 15**

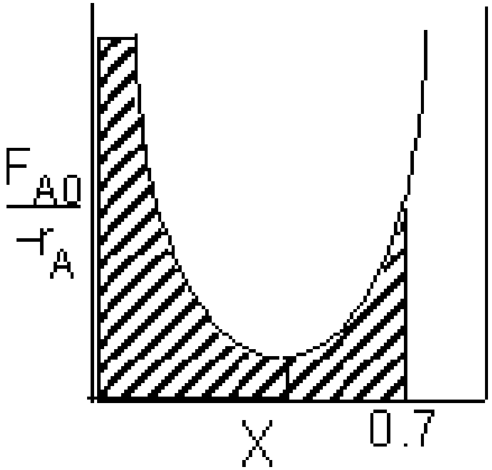
- Reactor Sizing

CSTR: $V_1 = \left(\frac{F_{Ao}}{-r_{A1}}\right)X_1$ $\qquad V_2 = \left(\frac{F_{Ao}}{-r_{A2}}\right)(X_2 - X_1)$

PFR: $V_1 = \int_0^{X_1}\left(\frac{F_{Ao}}{-r_A}\right)dX$ $\qquad V_2 = \int_{X_1}^{X_2}\left(\frac{F_{Ao}}{-r_A}\right)dX$

- PFR: Shaded area is the volume

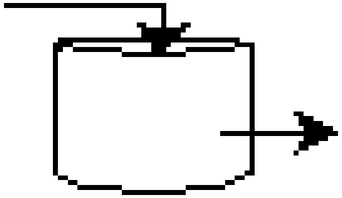


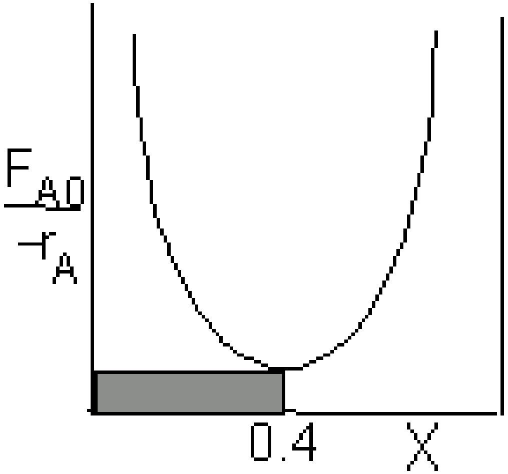


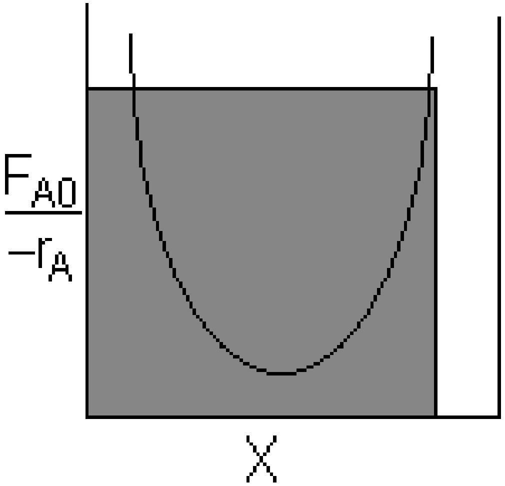
※ Review XVI

○ **Ex 8-3 Liq.-phase isomerization reaction 16**

- CSTR: Shaded area is the volume



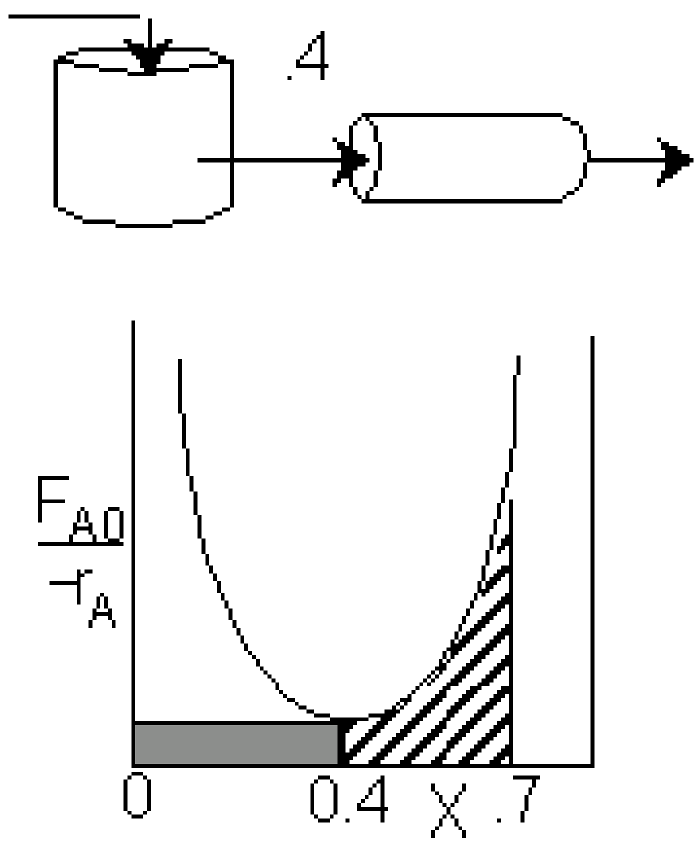


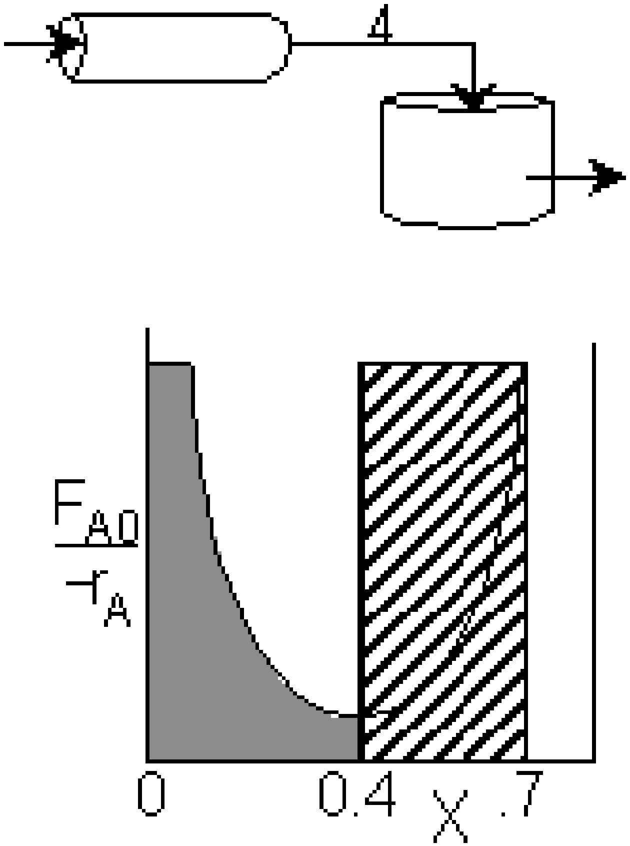


※ Review XVII

- **Ex 8-3 Liq.-phase isomerization reaction 17**

  - CSTR: Shaded area is the volume

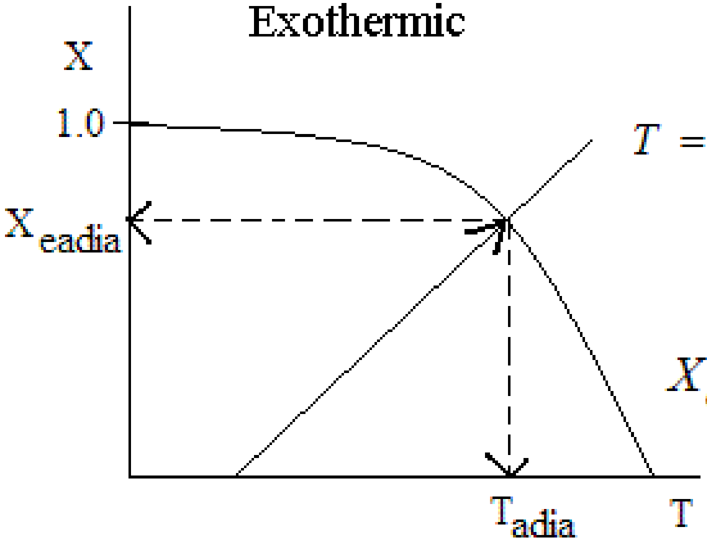




4. Reversible Reactions IV

○ **Adiabatic Equilibrium**

- **Conversion on Temperature**
- **Exothermic ΔH is negative**
- **Adiabatic Equilibrium temperature (T_{adia}) and conversion ($X_{e,adia}$)**



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

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

4. Reversible Reactions V

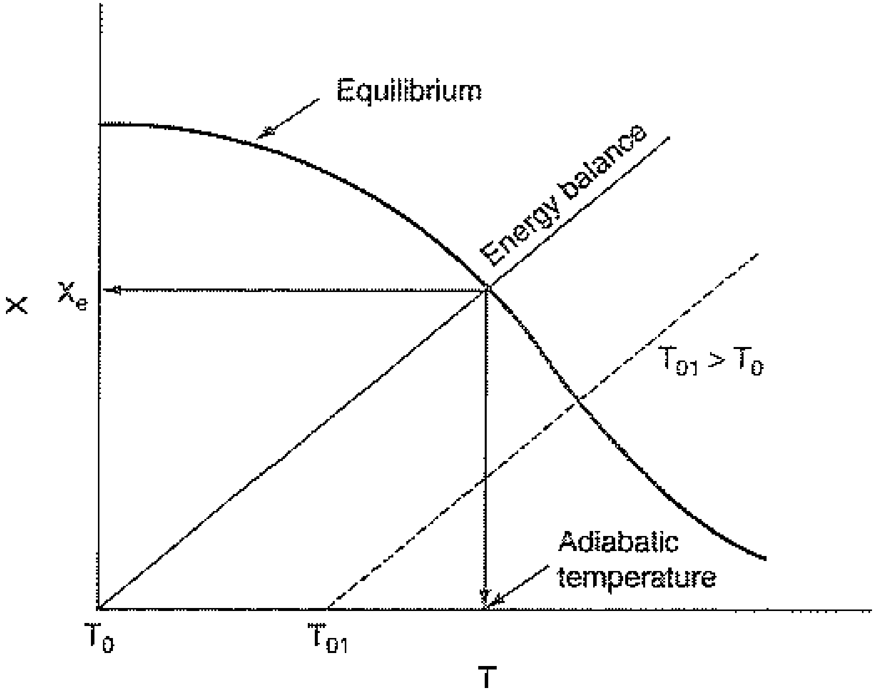
○ **Exothermic Adiabatic Equilibrium**

- Determine maximum conversion

$$X_{EB} = \frac{\sum \Theta_i C_{P_i} \left(T - T_0\right)}{-\Delta H_{RX}}$$

- **entering temp. T_0 to T_{01}**

  ☞ **parallel shift**



4. Reversible Reactions VI

- **Ex 8-6, Calculating the adiabatic equilibrium T, p 513**

  - An elementary solid-catalyzed liquid-phase

$$A \Leftrightarrow B$$

  - ΔH°_{A}**(298 K) = -40,000 cal/mol**
  - ΔH°_{B}**(298 K) = -60,000 cal/mol**
  - K_C **= 100,000 at 298 K**
  - C_{PA} **= 50 cal/mol K,** C_{PB} **= 50 cal/mol K**

(a) $X_e = f(T)$**?**

(b) at 300 K, pure A fed, X_e**, T = ?**

4. Reversible Reactions VII

- **Ex 8-6, Calculating the adiabatic equilibrium T 2**

Sol)

- Rate law

$$-r_A = k\left(C_A - \frac{C_B}{K_e}\right)$$

- Equilibrium: -r_A = 0

$$C_{Ae} = \frac{C_{Be}}{K_e}$$

- Sotichiometry: (v = v_0)

$$C_{A0}(1 - X_e) = \frac{C_{A0}X_e}{K_e}$$

- Solving for X

$$\boxed{X_e = \frac{K_e(T)}{1 + K_e(T)}}$$

4. Reversible Reactions VII

- **Ex 8-6, Calculating the adiabatic equilibrium T 3**
  - **Equilibrium constant: calculate ΔC_P then $K_e(T)$**

$$\Delta C_P = C_{P_\mathrm{B}} - C_{P_\mathrm{A}} = 50 - 50 = 0$$

  - **Equilibrium constant with T**

$$K_e(T) = K_e(T_1)\exp\left[\frac{\Delta H^0_{\mathrm{Rx}}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

$$\Delta H^0_{\mathrm{Rx}} = H^0_\mathrm{B} - H^0_\mathrm{A} = -20{,}000 \text{ cal/mol}$$

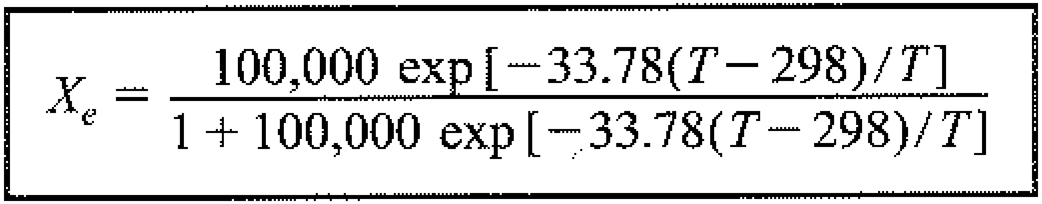
$$K_e(T) = 100{,}000 \exp\left[\frac{-20{,}000}{1.987}\left(\frac{1}{298} - \frac{1}{T}\right)\right]$$

$$K_e = 100{,}000 \exp\left[-33.78\left(\frac{T-298}{T}\right)\right]$$

4. Reversible Reactions VIII

- **Ex 8-6, Calculating the adiabatic equilibrium T 4**

  - Equilibrium conversion



$$X_e = \frac{100{,}000 \exp[-33.78(T-298)/T]}{1+100{,}000 \exp[-33.78(T-298)/T]}$$

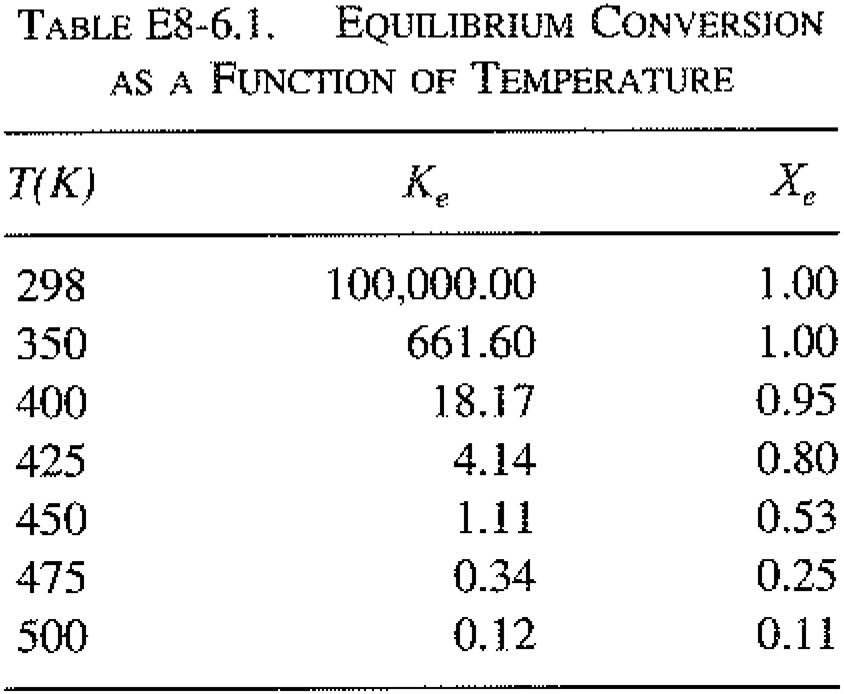


TABLE E8-6.1. EQUILIBRIUM CONVERSION AS A FUNCTION OF TEMPERATURE

$T(K)$	K_e	X_e
298	100,000.00	1.00
350	661.60	1.00
400	18.17	0.95
425	4.14	0.80
450	1.11	0.53
475	0.34	0.25
500	0.12	0.11

4. Reversible Reactions IX

- **Ex 8-6, Calculating the adiabatic equilibrium T 5**

  - Energy balance

$$X_{\mathrm{EB}} = \frac{\sum \Theta_i C_{p_i}(T - T_0)}{-\Delta H_{\mathrm{Rx}}} = \frac{C_{P_{\mathrm{A}}}(T - T_0)}{-\Delta H_{\mathrm{Rx}}}$$

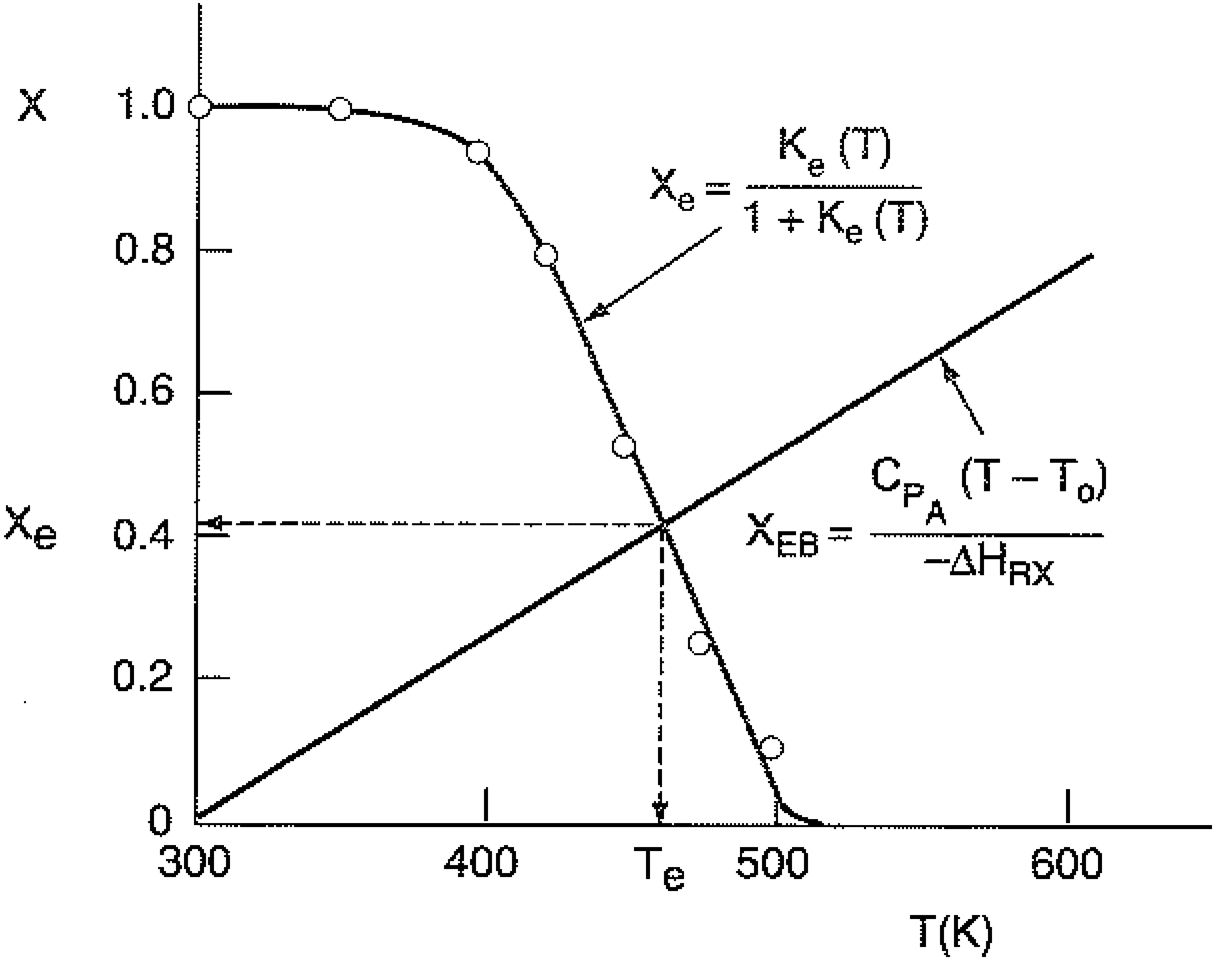
$$\boxed{X_{\mathrm{EB}} = \frac{50(T - 300)}{20{,}000} = 2.5 \times 10^{-3}(T - 300)}$$

T (K)	300	400	500	600
X_{EB}	0	0.25	0.50	0.75

$$X_e = 0.42 \quad T_e = 465 \text{ K}$$

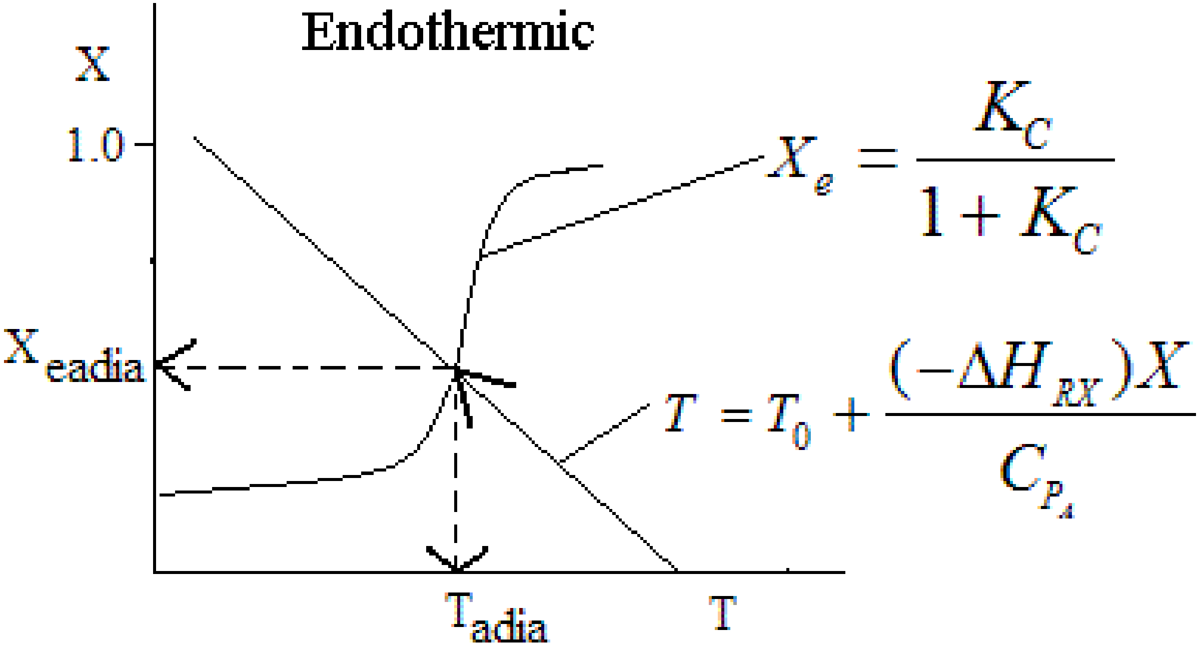
4. Reversible Reactions X

- **Ex 8-6, Calculating the adiabatic equilibrium T 6**



4. Reversible Reactions V

- **Adiabatic Equilibrium**
  - **<u>Endothermic</u> ΔH is positive**
  - **Adiabatic Equilibrium temperature (T_{adia}) and conversion ($X_{e,adia}$)**



※ Self Test

○ **Liquid phase reaction follows an elementary rate law**

$$A \rightleftarrows B$$

- The reaction is to be carried out in a PFR

(a) CRE algorithm, sketch the temperature as a function of conversion for an adiabatic endothermic reaction and an adiabatic exothermic reaction

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

- Rate Law $$-r_A = k\left[C_A - C_B/K_C\right]$$

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

$$C_B = C_{A0}X$$

※ Self Test

(a) CRE algorithm,

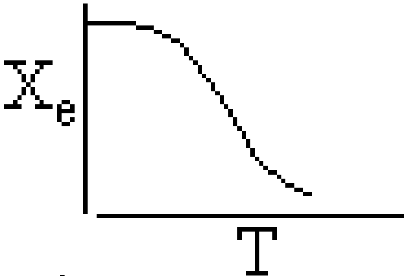
- Combine

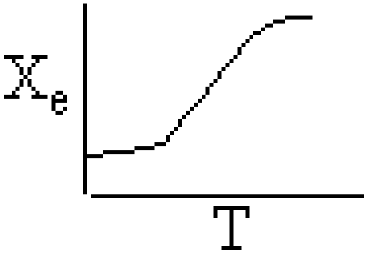
$$-r_A = kC_A\left[1-\left(1+\frac{1}{K_C}\right)X\right]$$

at equilibrium $-r_A = 0$

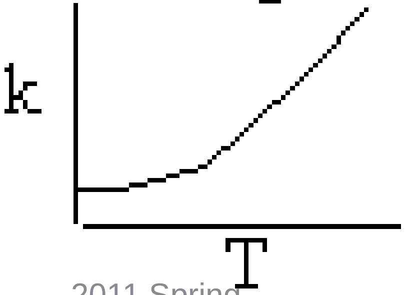
$$K_C = K_C(T_1)\exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_1}-\frac{1}{T}\right)\right]$$

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





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

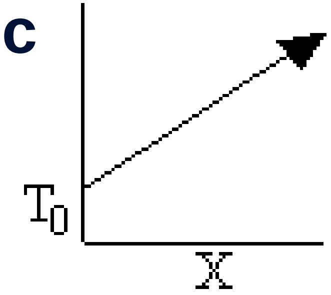


※ Self Test

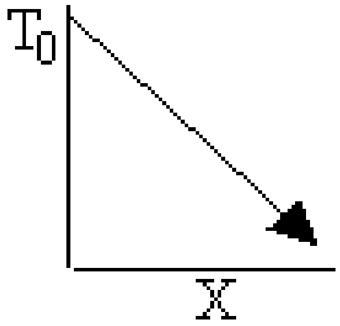
(b) Write the adiabatic energy balance

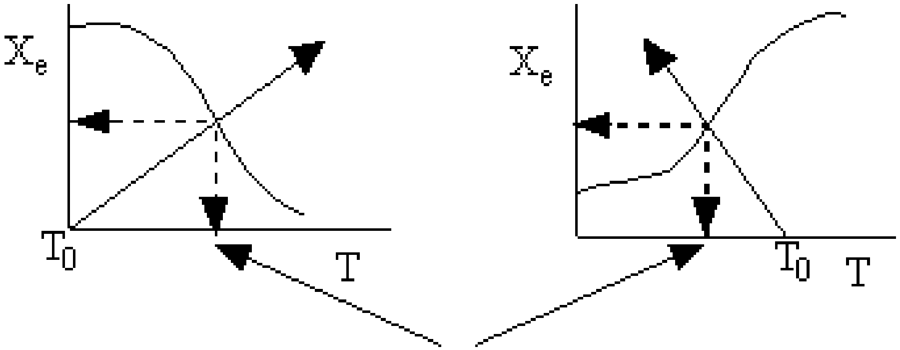
$$\boxed{T = T_0 + \frac{-\Delta H_{Rx}}{C_{P_A}} X}$$

- Exothermic



Endothermic



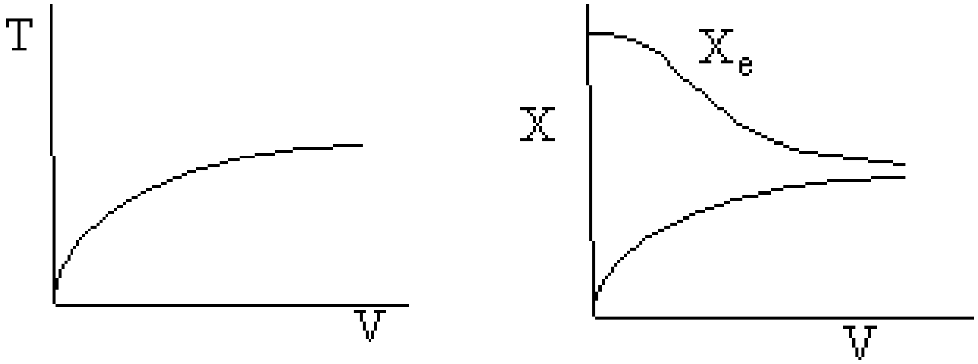


Adiabatic Equilibrium Temperature and Conversion

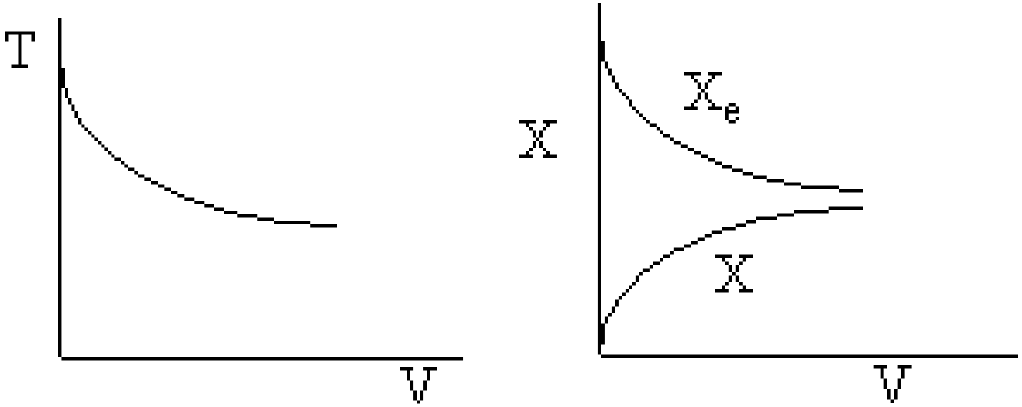
※ Self Test

(c) Adiabatic Temperature and Conversion Profiles

- Exothermic



- Endothermic



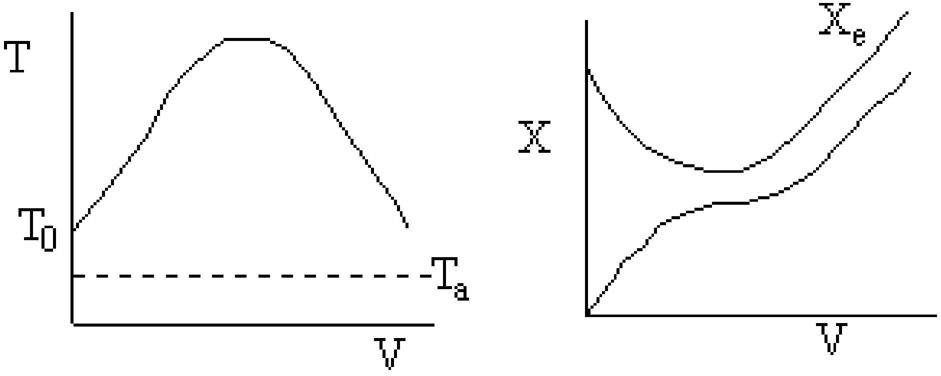
※ Self Test

(d) Energy Balance with Heat Exchange

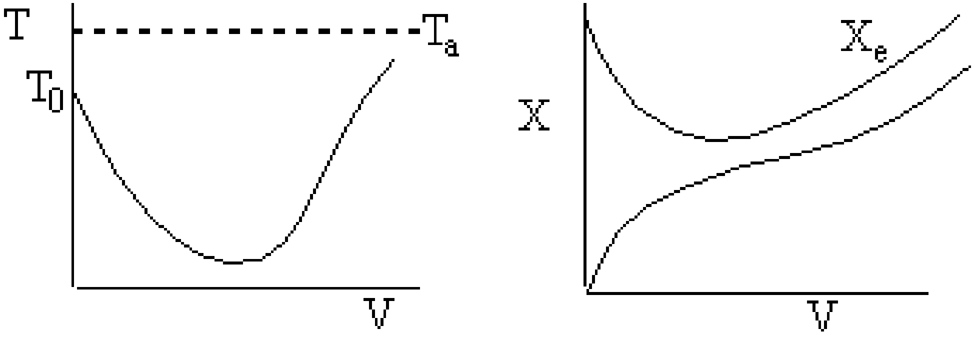
$$\frac{dT}{dV} = \frac{Ua(T_a - T) + (-r_A)(-\Delta H_{Rx})}{\sum F_i C_{P_i}}$$

(e) Constant Coolant Temperature T_a

- Exothermic



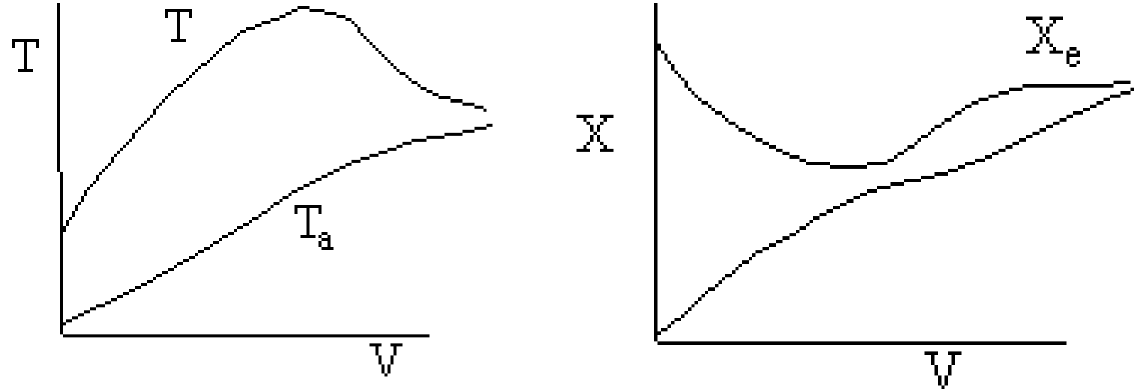
- Endothermic



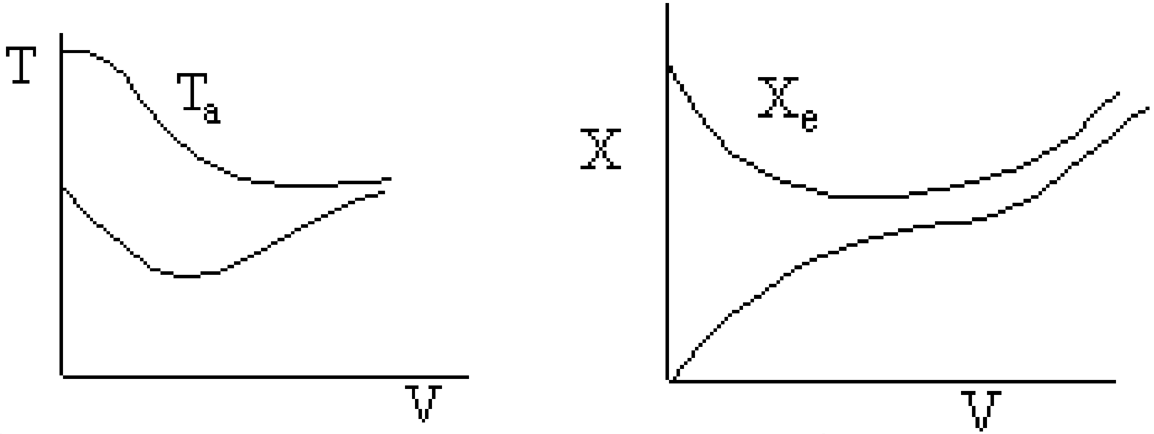
※ Self Test

(f) Variable Coolant Temperature T_a

- Exothermic

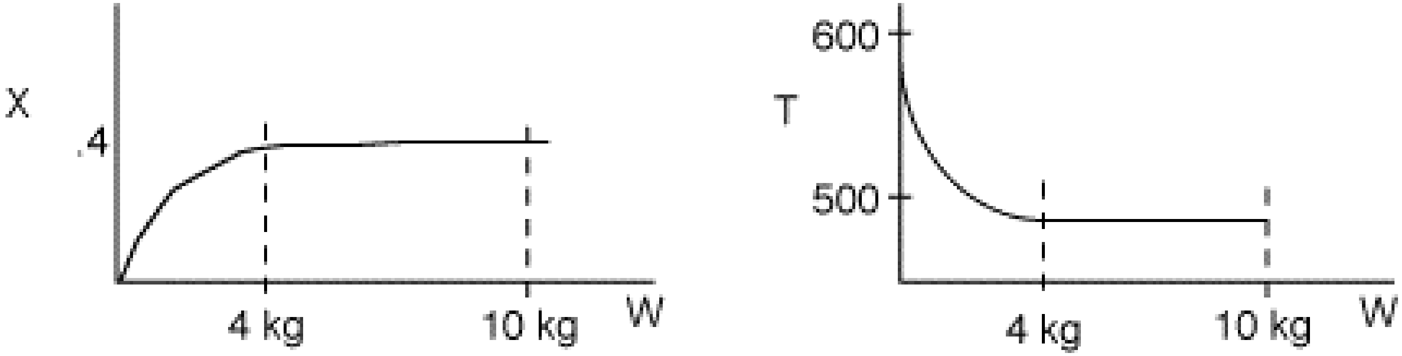


- Endothermic



※ Self Test 2

- Nonisothermal reactions
  - The elementary isomerization of A to B was carried out in a packed bed reactor. The following profiles were obtained



(a) The above profiles could represent an adiabatic system where the addition of inerts to the feed stream will increase conversion. [✓ T] or F

※ Self Test 2

- **Nonisothermal reactions**

(b) If the reaction is irreversible, a small decrease in the flow rate will produce a small increase in the conversion. [✓ T] **or** F

(c) If the reaction is reversible, a small decrease in the flow rate will produce a small increase in the conversion. T **or** [✓ F]

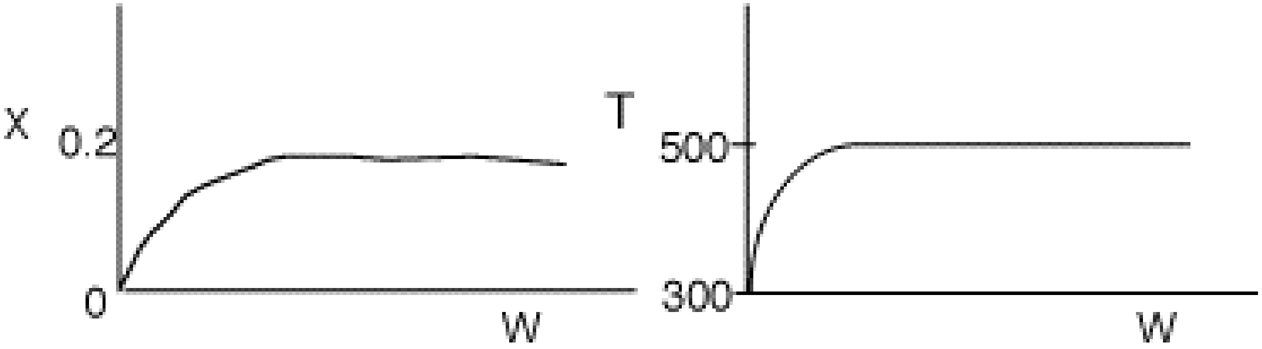
(d) An increase in the feed temperature will increase the conversion. [✓ T] **or** F

(e) A decrease in feed temperature will increase conversion. T **or** [✓ F]

※ Self Test 3

- **The elementary reaction in a packed bed reactor**

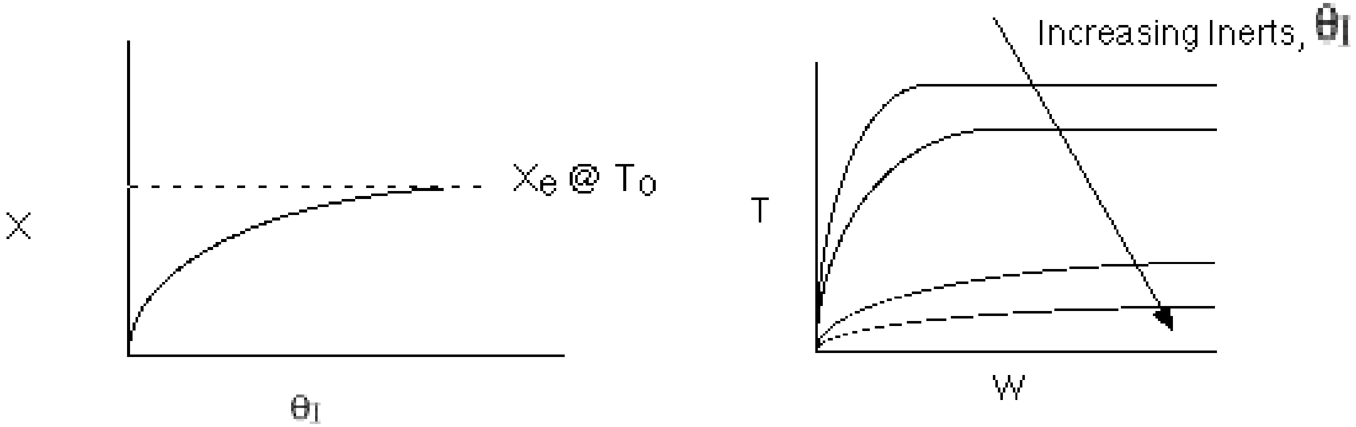
$$A + B \rightleftarrows C + D$$



(a) The above profiles could represent an adiabatic system where the addition of inerts will increase the conversion. [✓ T] or F

※ Self Test 3

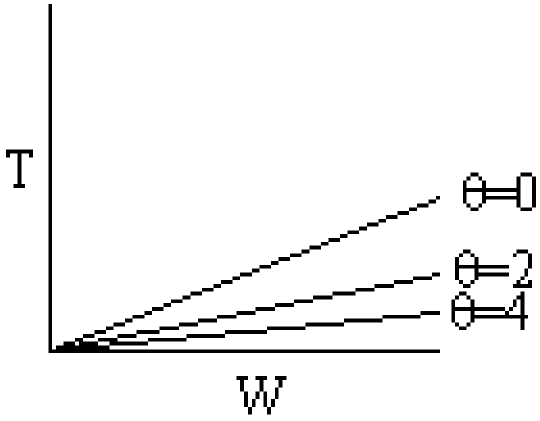
- ○ The elementary reaction in a packed bed reactor 2
  - Case 1 - Rapid Reaction: Equilibrium reached even at isothermal temperature, T_o

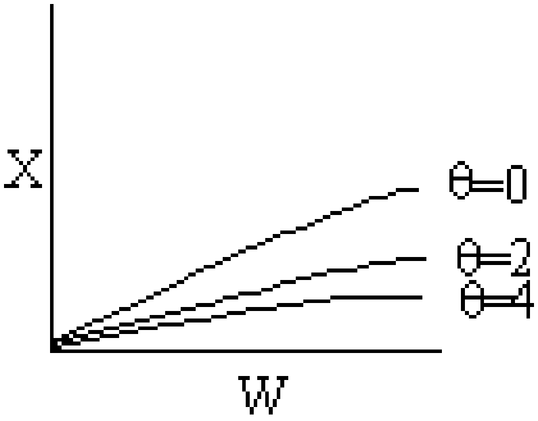


  - Inerts ↑, exit temperature↓, ⇒ equilibrium conversion and the exit conversion ↑
  - As more and more inerts continue to be added, the reactor approaches isothermal condition, T_o

※ Self Test 3

- The elementary reaction in a packed bed reactor 3
  - Case 2 - Slow Reaction: Equilibrium not achieved at isothermal temperature, T_o





※ Self Test 3

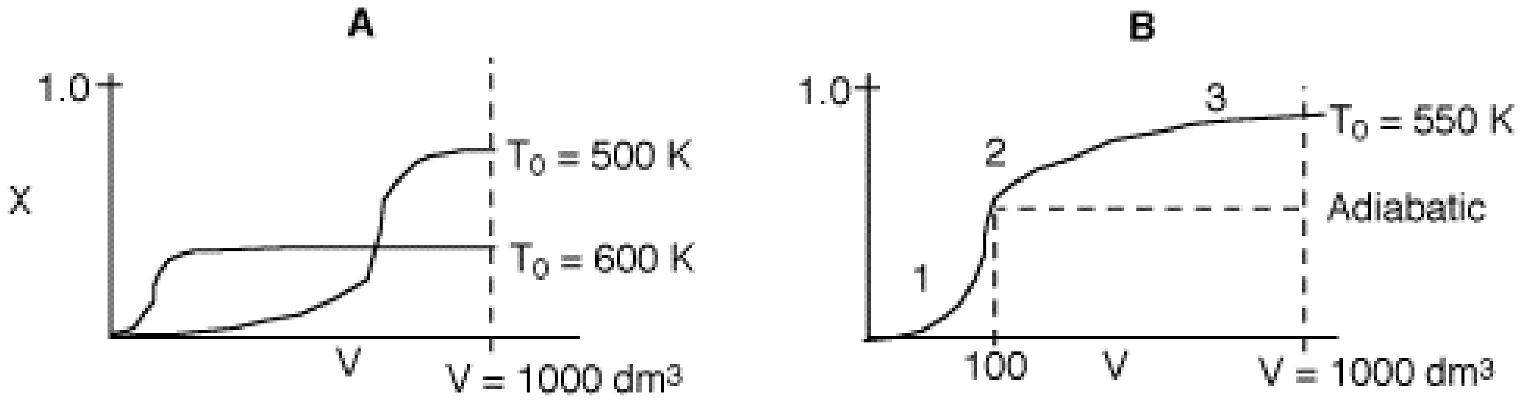
○ The elementary reaction in a packed bed reactor 4

(b) The above profiles could represent a system where decreasing the flow rate will increase the conversion. [✓ T] or F

(c) The above profiles could represent a system where if the feed temperature is increased, one cannot tell from the above profiles whether or not the conversion will increase or decrease. [✓ T] or F

※ Self Test 4

- Two PFR's (A and B) for the same reaction



(a) Is the reaction exothermic or endothermic?

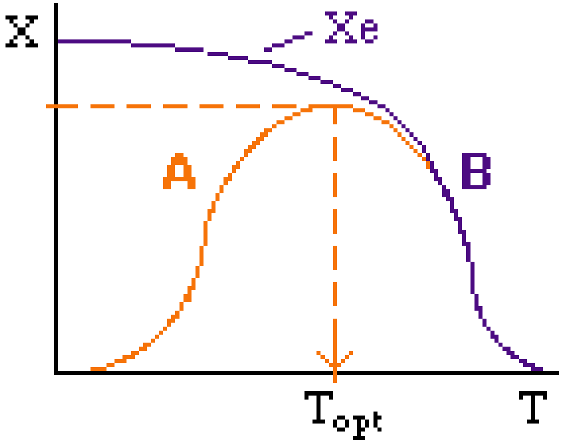
(b) Is the reaction reversible or irreversible?

7. Interstage Cooling/Heating I

○ **Fixed Volume Exothermic Reactor**

- Curve A

- **reaction rate slow**
- **as temperature increases rate increases and therefore conversion increases.**

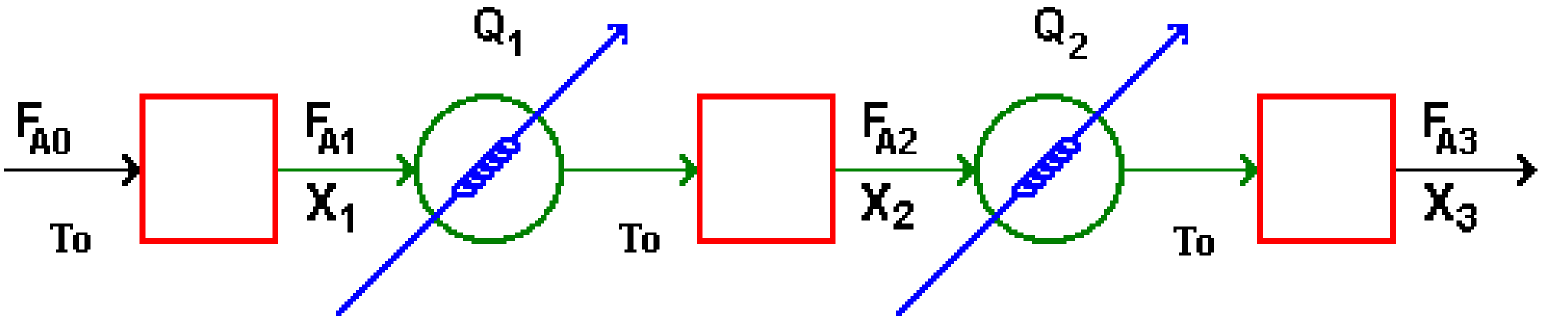


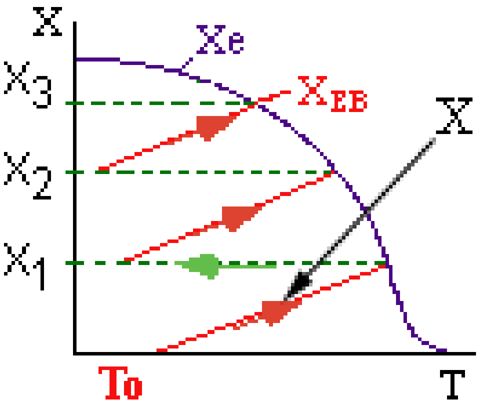
- Curve B

- **reaction rate very rapid**
- **virtual equilibrium reached in reaction conversion dictated by equilibrium conversion**

7. Interstage Cooling/Heating II

- Interstage Cooling:





$$X = \frac{\sum \theta_i C_{Pi}(T - T_o)}{-\Delta H_{RX}}$$