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and Environmental Engineering

# **Energy balance: heat effects, solving coupled energy/mass balance equations**

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**CHE 540, Stoerzinger**

# 1<sup>st</sup> law (differential form)



- For closed system where no mass crosses system boundaries

$$dU = \delta Q - \delta W$$

- Change in internal energy equal to heat put in minus work performed by system ( $\delta$  from the fact that Q and W not exact differentials of a state function)

# Heat capacities



- If we specify any two properties of the system, then the state of the system is fully specified. In other words we can write

$$u = u(T, V), \quad u = u(P, V) \quad u = u(P, T)$$

chain rule:  $du = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV \rightarrow \text{const vol.}$

- Rewrite 1<sup>st</sup> law as quasistatic ( $dW = PdV$ ):  $du = \delta q - PdV \rightarrow \text{const vol.}$

$$\left(\frac{\partial u}{\partial T}\right)_V = \left(\frac{\partial q}{\partial T}\right)_V$$

- Any energy increase is due only to energy transfer as heat.
- Specific heat, constant V:

$$c_V \equiv \left(\frac{\partial u}{\partial T}\right)_V$$

## Heat capacities II



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$$\Delta G = \Delta H - T \Delta S$$

enthalpy =  $H$

- If we write  $H=H(T,P)$ , and consider a constant pressure process

$$C_p \equiv \left( \frac{\partial h}{\partial T} \right)_p$$

# Reaction under chemical equilibrium:



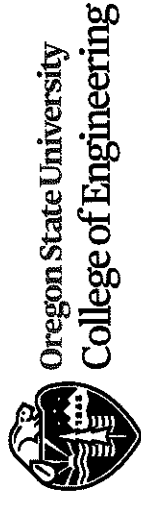
$$\left( \sum_P v_i z_i F \psi - \sum_R v_i z_i F \psi \right) + \left( \sum_P v_i \bar{V}_i P - \sum_R v_i \bar{V}_i P \right)$$

charge conserved atmospheric P in kg

$$+ \left( \sum_P v_i R T \ln a_i - \sum_R v_i R T \ln a_i \right) + \underbrace{\left( \sum_P v_i \mu_i^\circ - \sum_R v_i \mu_i^\circ \right)}_{\text{depends on } T, \text{ standard free energy change, } \Delta G^\circ} = 0$$

$$\boxed{\sum_P v_i \ln a_i - \sum_R v_i \ln a_i = - \frac{\Delta G^\circ}{R T}}$$

# Equilibrium constant



- Use log properties to rearrange and define  $K_a$ , equilibrium

constant:  $\prod_i a_i^{v_i}$  where

$$\frac{\prod_i a_i^{v_i}}{\prod_r a_i^{v_i}} = K_a$$

$$- \Delta G^0 / RT$$

$$K_a = e$$

# Outline



- Heat effects in reactors
  - Temperature affects reaction rates, and so will be coupled to the reactor volume design equations (performance equation)
- Approach: energy balance on reactor
  - Example: adiabatic reactor (no heat loss)
- Energy balance with heat exchangers
  - PFR (constant heat exchanger T)
- Heat exchangers with varying temperatures
  - Energy balance on fluid

# Designing non isothermal reactors

- Consider first order liquid phase reaction in a PFR:
- $$A \rightarrow B$$
- Reaction is exothermic and reactor operated adiabatically (no heat loss).
  - T increases with conversion down length of reactor
  - When T varies, k varies, impacting X
- Calculate PFR volume for X conversion and plot X, T profiles





# The need for energy balance



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

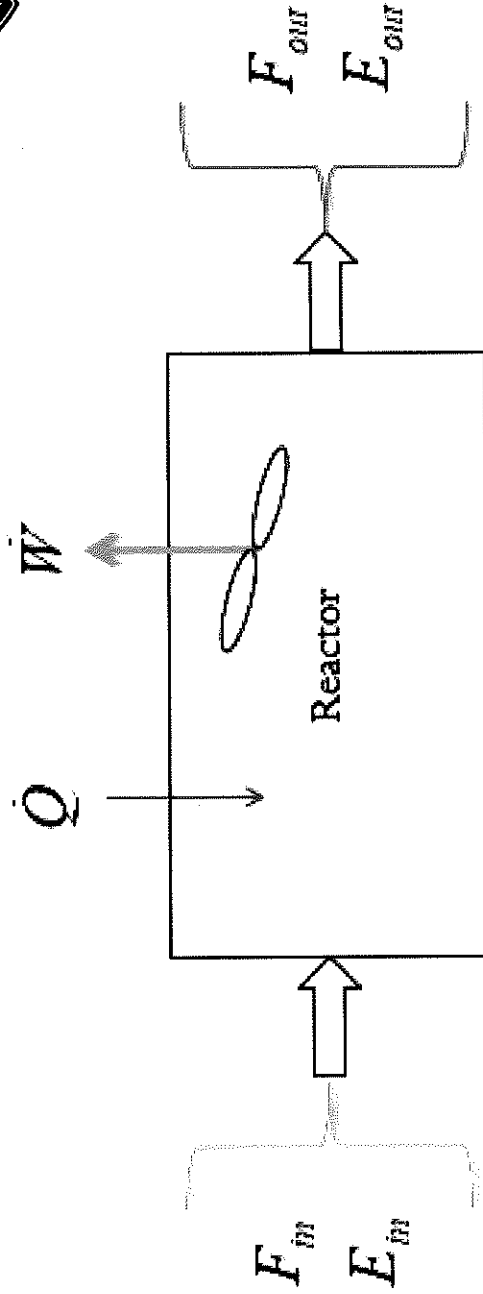
Rate Law:  $r_A = -k C_A = -k \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] C_A$  Arrhenius

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

Combine:  $\frac{dX}{dV} = \frac{k \exp \left[ \frac{E}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right] C_{A0}(1-X)}{F_{A0}}$

- We need another relationship between X and T (or T and V) to solve. Use energy balance!

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$$\left[ \begin{array}{l} \text{Rate of} \\ \text{accumulation} \\ \text{of energy} \\ \text{within the} \\ \text{system} \end{array} \right] = \left[ \begin{array}{l} \text{Rate of flow of} \\ \text{heat to the} \\ \text{system from} \\ \text{the} \\ \text{surroundings} \end{array} \right] - \left[ \begin{array}{l} \text{Rate of work} \\ \text{done by the} \\ \text{system on the} \\ \text{surroundings} \end{array} \right] + \left[ \begin{array}{l} \text{Rate of energy} \\ \text{added to the} \\ \text{system by mass} \\ \text{flow into the} \\ \text{system} \end{array} \right] - \left[ \begin{array}{l} \text{Rate of energy} \\ \text{leaving system} \\ \text{by mass flow} \\ \text{out of the} \\ \text{system} \end{array} \right]$$

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$$\hat{\frac{dE_{\text{sys}}}{dt}} = \dot{Q} - \dot{W} + \dot{F}_{\text{in}} E_{\text{in}} - \dot{F}_{\text{out}} E_{\text{out}}$$

(J/s)                      (J/s)                      (J/s)                      (J/s)

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# Adiabatic energy balance



- For equal heat capacities of products ( $C_{pB}$ ) and reactants ( $C_{pA}$ ), and constant heat of reaction ( $\Delta H_{RX}^0$ )

$$T = T_0 + \frac{-\Delta^* H_{rxn}^0}{C_{p,r}} \times$$

$$\Delta H_{rxn}(T) = \Delta H_{rxn}(T_{ref}) + \sum \nu_i C_{p,i} (T - T_{ref})$$

# Approach



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1. Replace  $U_i$  by  $U_i = H_i - PV_i$
2. Express  $H_i$  in terms of heat capacities
3. Express  $F_i$  in terms of either conversion or rates of reaction
4. Define  $\Delta H_{Rx}$
5. Define  $\Delta C_p$

# Optimal Temperature Progression

## = highest $-r_{A,ave}$ = smallest $V_{reactor}$



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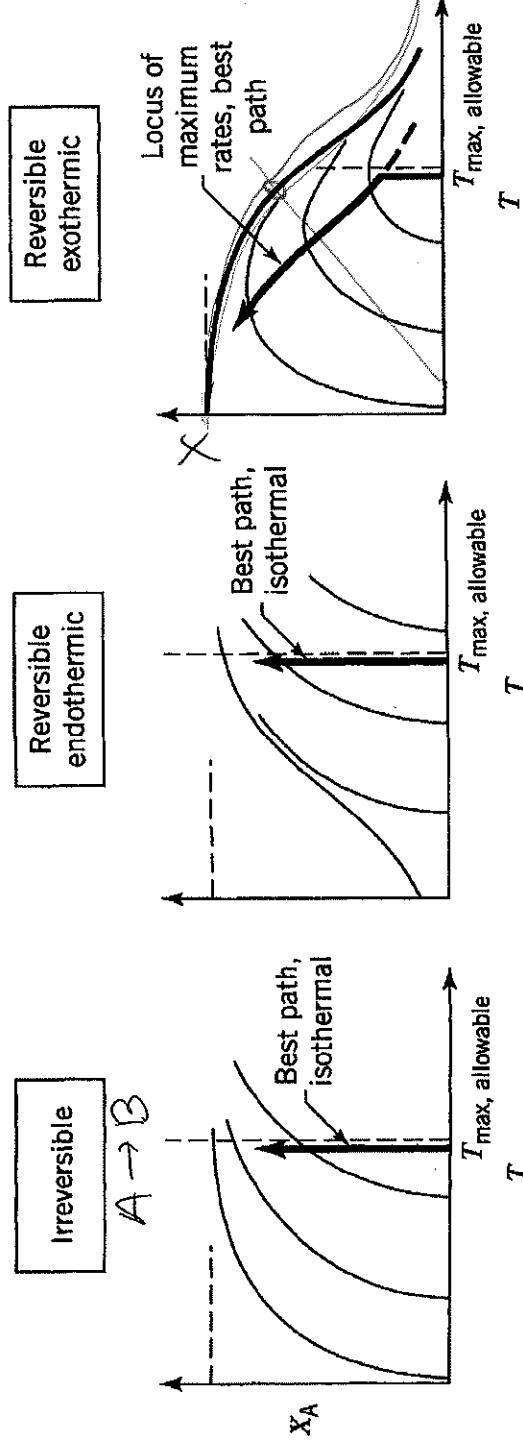


Figure 9.5 Operating lines for minimum reactor size.

Optimal T progression is ideal that we attempt to approach with reactor design (unrealistic)

# Calculating adiabatic equilibrium T

- Consider elementary liquid phase reaction



Make plot of equilibrium conversion as a function of T.

- Determine adiabatic equilibrium T and X when pure A fed into reactor at 300 K.
- What is CSTR volume to achieve 90% adiabatic equilibrium conversion for  $v_0 = 5 \text{ dm}^3/\text{min}$ ?

**What do we need?**  $A \xrightleftharpoons[k]{B}$



$$H_A^\circ(298K) = -40,000 \text{ cal/mol}$$

$$H_B^\circ(298K) = -60,000 \text{ cal/mol}$$

$$C_{pA} = C_{pB} = 50 \text{ cal/mol K}$$

$$K_e(298K) = 100,000$$

$$k = 10^{-3} \exp \left( \frac{E}{R} \left( \frac{1}{298} - \frac{1}{T} \right) \right) [\text{min}^{-1}]$$

$$E = 10,000 \frac{\text{cal}}{\text{mol}}$$

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

1. Rate law:

$$\text{2. Equilibrium: } -r_A = 0 \quad K_e = \frac{C_{Be}}{C_{BAe}}$$

$$\text{3. Stoichiometry: } v = v_0 \quad C_A = C_{A0}(1-X)$$

$$C_B = C_{A0}(X)$$

$$-r_A = k C_{A0} \left( 1 - X - \frac{X}{K_e} \right)$$

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





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



4. Equilibrium constant  $\Delta C_p = C_{pB} - C_{pA} = 0$

$$K_e(T) = K_e(T_1) \exp \left[ \frac{\Delta H_{rxn}^0}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right) \right]$$

van't Hoff

$$\Delta H_{rxn}^0 = H_B^0 - H_A^0 = -20,000 \text{ cal/mol}$$

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



## 5. Equilibrium conversion from thermodynamics

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

## 6. Energy balance

$$X_{eb} = \frac{C_{PA}(T - T_0)}{-\Delta H_{rxn}^{\circ}}$$

$$T = T_0 + \frac{-\Delta H_{rxn}^{\circ}}{C_{PA}} X$$

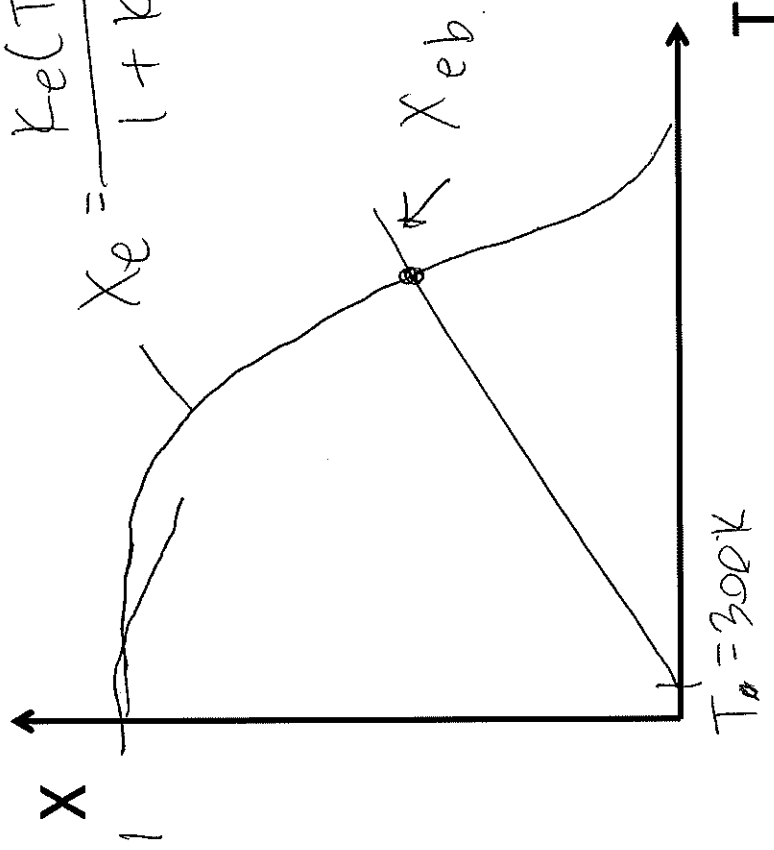
assuming  $\Delta H_{rxn}$  is  $T$  independent



$A \rightleftharpoons B$  exothermic

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

from mass  
balance



$$X_{eb} = \frac{C_{PA}(T - T_0)}{-\Delta H_{rxn}}$$

energy  
balance



```
1- clc
2-
3- % parameters
4- cp = 50; % per mol of A
5- dHr = -20000; % reaction enthalpy
6- Eact = 10000; % activation energy
7- R = 1.987; % cal/mol K
8- T = 300:600; % temperature
9- Tlength = length(T);
10- Xe = zeros(size(T));
11- Xeb = zeros(size(T));
12-
13- for ii = 1:Tlength
14-     k = 10^-3*exp(Eact/R*(1/298 - 1/T(ii)));
15-     Ke = 100000*exp(dHr/R*(1/298-1/T(ii)));
16-     Xe(1,ii) = Ke/(1+Ke);
17-     Xeb(1,ii) = cp*(T(ii)-298)/(-dHr);
18- end
19-
20- plot(T, Xe);
21- hold on
22- plot(T, Xeb);
23- [Ti,Xi] = polyxpoly(T, Xe, T, Xeb)
24-
```

Don't have to worry about little  $\frac{0.5}{K}$  or activation energy

