

## LECTURE 7

**NONISOTHERMAL OPERATION OF IDEAL REACTORS**  
**Continuous Flow Stirred Tank Reactor (CSTR)**

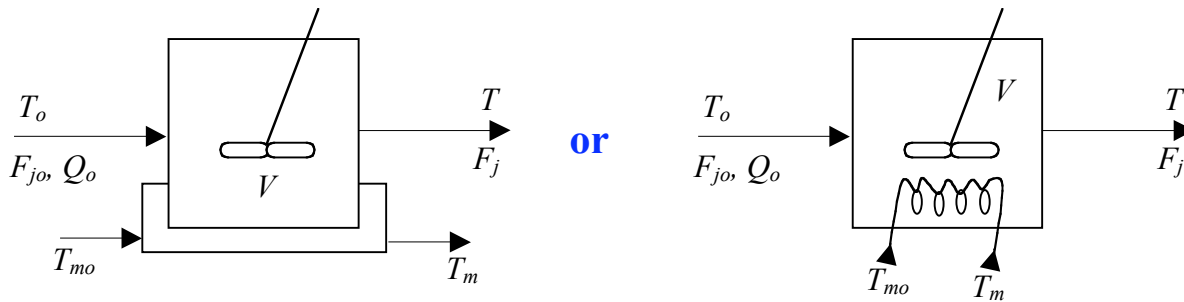


Figure 1: Schematic of CSTR with jacket and coil

**Assumptions:**

Homogeneous system

a) Single Reaction  $\sum_{j=1}^s \nu_j A_j = 0$

b) Steady state

A CSTR is always assumed perfectly mixed so that the concentration of every species is uniform throughout the reactor and equal to the concentration in the outflow. Due to assumption of perfect mixing the temperature,  $T$ , throughout the reactor is uniform and equal to the temperature of the outflow. The only difference between an “isothermal” CSTR treated previously and the general case treated now, is that now we do not necessarily assume that reactor temperature,  $T$ , and feed temperature,  $T_o$ , are equal.

A CSTR can be jacketed or equipped with a cooling (heating) coil.

Two basic types of problems arise:

1. Given feed composition and temperature, rate form and desired exit conversion and temperature find the necessary reactor size to get the desired production rate and find the necessary heat duty for the reactor.
2. Given feed conditions and flow rate and reactor size together with cooling or heating rates, determine the composition and temperature of the effluent stream.

To solve either of the above two problems we need to use both a species mass balance on the system and the energy balance.

Consider a **single reaction**

$$\sum_{j=1}^s \nu_j A_j = 0 \quad (1)$$

or



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Suppose the reaction is practically irreversible and the rate of reaction, which is a function of composition and temperature is given by:

$$r = \underbrace{k_o e^{-E/RT}}_{\text{Arrhenius Temperature}} \underbrace{C_A^\alpha C_B^\beta}_{\text{concentration dependence}} \left( \frac{\text{kmol}}{\text{m}^3 \text{ s}} \right) \quad (2)$$

Arrhenius  
Temperature  
Dependence of the rate

concentration dependence  
n-th order reaction  $n = \alpha + \beta$

For a single reaction we can always eliminate all concentrations in terms of conversion of the limiting reactant A (Lecture 1).

**For liquids**

$$C_j = C_{Ao} \left( M_{j/A} - \frac{v_j}{v_A} x_A \right); M_{j/A} = \frac{C_{jo}}{C_{Ao}}$$

**For gases**

$$C_j = C_{Ao} \left( \frac{M_{j/A} - \frac{v_j}{v_A} x_A}{1 + \varepsilon_A x_A} \right) \frac{T_o P}{TP_o}$$

where

$$\varepsilon_A = y_{Ao} \frac{\sum v_j}{(-v_A)}$$

In a CSTR we assume  $P_o = P = \text{const}$  i.e constant pressure.

The rate now becomes:

**For liquids**

$$r = k_o e^{-E/RT} C_{Ao}^{(\alpha+\beta)} (1 - x_A)^\alpha \left( M_{B/A} - \frac{b}{a} x_A \right)^\beta \quad (3a)$$

**For gases**

$$r = k_o e^{-E/RT} \left( \frac{T_o}{T} \right) C_{Ao}^{\alpha+\beta} (\alpha + \beta) \frac{(1 - x_A)^\alpha \left( M_{B/A} - \frac{b}{a} x_A \right)^\beta}{(1 + \varepsilon_A x_A)^{\alpha+\beta}} \quad (3b)$$

Recall that at steady state the basic conservation equation is:

$$(\text{Rate of input}) - (\text{Rate of output}) + (\text{Rate of generation by reaction}) = 0 \quad (4)$$

Apply equation (4) to mass of species A: (or to any species j)

$$F_{A_o} - F_A + v_A rV = 0; \quad F_{j_o} - F_j + v_j rV = 0$$

$$F_{A_o} x_A = arV = 0$$

$$C_{A_o} x_A = ar\tau \quad (5)$$

$$\dot{X} = rV \quad (5a)$$

where

$$\tau = \frac{V}{Q_o}$$

The energy balance of course cannot contain a generation term (in absence of nuclear reactions) and hence can be written as:

$$\sum_{j=1}^s F_{j_o} \tilde{H}_{j_o} - \sum_{j=1}^s F_j \tilde{H}_j + \dot{q} = 0 \quad (6)$$

$F_{j_o} \left( \frac{\text{kmol } j}{s} \right)$  - molar flow rate of species j in the feed

$F_j \left( \frac{\text{kmol } j}{s} \right)$  - molar flow rate of species j in the outflow

$\tilde{H}_j \left( \frac{J}{\text{kmol } j} \right)$  - virtual partial molal enthalpy of species j in the outflow mixture

$\tilde{H}_{j_o} \left( \frac{J}{\text{kmol } j} \right)$  - virtual partial molal enthalpy of species j in the feed

$\dot{q} \left( \frac{J}{s} \right)$  - rate of heat addition from the surroundings i.e from the jacket or coil to the reaction mixture in the reactor

The energy balance given by equation (6) is not general in the sense that the following assumptions have already been made in order to present it in that form:

**Assumptions involved in deriving eq (6):**

1. Potential energy changes are negligible with respect to internal energy changes.
2. Kinetic energy changes are negligible with respect to internal energy changes.
3. There is no shaft work involved i.e the only work term is the expansion (flow) work.

The virtual partial molal enthalpy,  $\tilde{H}_j \left( \frac{J}{mol\ j} \right)$ , is defined by:

$$\dot{m}_{tot} \underline{H} = \sum_{j=1}^s F_j \tilde{H}_j$$

$\dot{m}_{tot} \left( \frac{kg}{s} \right)$  - mass flow rate of the mixture

$\underline{H} \left( \frac{J}{kg} \right)$  - enthalpy per unit mass of the mixture

In principle the virtual partial molal enthalpy can be evaluated by the following procedure (for gases):

$$\tilde{H}_j(T, P, y_j) = \Delta H_{fj}^\circ + \int_{T^\circ}^T C_{p,j}^* dT + [H_j(T, P) - H_j^*(T, P)] + [H_j(T, P, y_j) - H_j(T, P)]$$

$\Delta H_{fj}^\circ$  - standard enthalpy of formation for species  $j$  at the pressure  $P^\circ$  of standard state and temperature  $T^\circ$  (enthalpy of 1 kmole of pure  $j$  at  $T^\circ, P^\circ$ )

$\int_{T^\circ}^T C_{p,j}^* dT$  - change in enthalpy of species  $j$ , if it behaved as an ideal gas, due to change in temperature from standard state temperature  $T^\circ$  to the temperature of interest  $T$ .  $C_{p,j}^*$  is the specific heat of  $j$  in ideal gas state. In reality  $C_{p,j}^\circ$  data for real gases obtained at atmospheric or lower pressures can be used.

$\Delta H_{fj}^\circ + \int_{T^\circ}^T C_{p,j}^* dT = H_j^*(T, P^\circ)$  enthalpy per mol of  $j$  for pure  $j$ , if it behaved like an ideal gas, at  $T$  and  $P^\circ$ .

Since enthalpy of an ideal gas does not depend on pressure this is also the enthalpy per kmol of  $j$ , if it were an ideal gas, at  $T$  and  $P$ ,  $H_j^*(T, P)$ .

$H_j(T, P) - H_j^*(T, P) =$  pressure correction factor i.e the difference between the enthalpy of  $j$  being a real gas at  $T, P$ , ( $H_j(T, P)$ ) and enthalpy of  $j$  being an ideal gas at  $T, P$  ( $H_j^*(T, P)$ ).

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Frequently the pressure correction is read off appropriate charts and is given by:

$$\tilde{H}_j(T, P) - \tilde{H}_j^*(T, P) = -T_{cj} \left( \frac{\tilde{H}_{j}^* - \tilde{H}_j}{T_{cj}} \right)_{T_r, P_r}$$

Where

$T_{cj}$  – critical temperature of species  $j$ .

$\left( \frac{\tilde{H}_{j}^* - \tilde{H}_j}{T_{cj}} \right)$  is the correction read off the charts at appropriate reduced temperature  $T_r = \frac{T}{T_{cj}}$  and

reduced pressure  $P_r = \frac{P}{P_{cj}}$

$P_{cj}$  – critical pressure of species  $j$ .

Finally

$\tilde{H}_j(T, P, y_j) - \tilde{H}_j(T, P) = \pi_j$  is the correction factor which accounts for the nonideality of the mixture.

For liquids (in a first approximation)

$$\tilde{H}_j = \Delta \tilde{H}_{f_j} + \int_{T^o}^T C_{pj} dT + \pi_j$$

Here we will assume:

**Gases:**

- ideal mixtures  $\pi_j = 0$
- ideal gas behavior  $\tilde{H} = \tilde{H}_j^*$

**Liquids:**

- ideal mixture  $\pi_j = 0$

Now the energy balance of eq (6) based on the above assumption can be written as

$$\sum_{j=1}^s F_{j0} \int_{T_o}^T C_{p_j} dT + \Delta H_{r_T} \dot{X} = \dot{q} \quad (7a)$$

$$\sum_{j=1}^s F_j \int_{T_o}^T C_{p_j} dT + \Delta H_{r_{T_o}} \dot{X} = \dot{q} \quad (7b)$$

where

$$\Delta H_{r_T} = \sum_{j=1}^s v_j \Delta H_{f_j^o} + \sum_{j=1}^s v_j \int_{T_o}^T C_{p_j} dT$$

is the heat of reaction at temperature  $T$ .

Finally, in preliminary reactor design we assume that the heat of reaction does not vary much with temperature

$$\Delta H_r \approx \text{const} \approx \Delta H_{r_{T_o}} \approx \Delta H_{r_T}$$

and that some mean value of the specific heat can be used

$$\int_{T_o}^T C_{p_j} dT = \bar{C}_{p_j} (T - T_o)$$

Equations (7) can then be written as:

$$\sum_{j=1}^s F_{j0} \bar{C}_{p_j} (T - T_o) + \Delta H_r \dot{X} = \dot{q}$$

or

$$\rho C_p Q (T_o - T) + (-\Delta H_r) \dot{X} + \dot{q} = 0 \quad (8)$$

where

$$\dot{X} = \frac{F_{A0} x_A}{(-v_A)} = \frac{C_{A0} Q_o x_A}{(-v_A)}$$

$$\Delta H_{r_A} = \frac{\Delta H_r}{(-v_A)}$$

$\Delta H_r$  - heat of reaction for the stoichiometry as written

$\Delta H_{r_A}$  - heat of reaction per mole of A.

$$\rho C_p Q (T_o - T) + (-\Delta H_{r_A}) C_{A0} Q_o x_A + \dot{q} = 0 \quad (9)$$

or

$$\rho C_p Q (T_o - T) + (-\Delta H_r) rV + \dot{q} = 0 \quad (9a)$$

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This final form of the energy balance resulting from all of the above assumptions can be interpreted as a “heat balance” i.e as rate of input of sensible heat by the flowing stream minus rate of output of sensible heat by exit stream plus heat generated by reaction plus heat added from the surroundings must add to zero.

In addition we now need an energy balance on the jacket or coil and a constitutive relationship for heat transfer rate,  $\dot{q}$ .

For a jacket at steady state (assuming that the jacket is well mixed too)

$$\rho_m Q_m \underline{C}_{p_m} (T_{m_o} - T_m) - \dot{q} = 0 \quad (10)$$

$\rho_m, Q_m, \underline{C}_{p_m}$  - are density, volumetric flow rate and mean specific heat of the fluid flowing through the jacket.

$T_{m_o}$  - inlet jacket temperature.

$T_m$  - exit jacket temperature.

Let

$$\dot{q} = UA(T_m - T) \quad (11)$$

$$U \left( \frac{J}{m^3 \text{ } ^\circ C s} \right) - \text{overall heat transfer coefficient.}$$

$A \text{ (m}^2\text{)}$  – area for heat transfer between reactor and jacket.

From eq (10)

$$T_m = \frac{T_{m_o} + \kappa_m T}{1 + \kappa_m} \quad (12)$$

where

$$\kappa_m = \frac{UA}{\rho_m \underline{C}_{p_m} Q_m}$$

For a coil with plug flow of heating/cooling medium:

$$\frac{dT_m}{dz} = \kappa_m (T - T_m) \quad (13)$$

$$z = 0, T_m = T_{m_o} \quad (13a)$$

$z$  = fractional length of the coil.

$$T_m(z) = T + e^{-\kappa_m z} (T_{m_o} - T) \quad (14)$$

For an n-th order irreversible reaction G(T) always has a sigmoidal shape and at high temperatures tends to a horizontal asymptote  $C_{A_o}$ .

Finally, in dimensionalized form the two equations that have to be solved simultaneously are:

$$C_{A_o} x_A = ar\tau \quad (15)$$

$$T_o - T + \tilde{\beta}_A ar\tau - \omega(T - T_{m_o}) = 0 \quad (16)$$

where r is given by equation (3) and

$$\tilde{\beta}_A = \left( \frac{-\Delta H_{r_A}}{\rho C_p} \right)$$

$$\omega = \frac{\kappa}{1 + \kappa_m} = \frac{UA}{\rho_m C_{p_m} Q_m + UA} \frac{\rho_m C_{p_m} Q_m}{\rho C_p Q} \quad \text{for a jacketed reactor}$$

$$\omega = \frac{\kappa}{\kappa_m} (1 - e^{-\kappa_m}) \quad \text{for a reactor with coil}$$

$$\kappa_m = \frac{UA}{\rho_m C_{p_m} Q_m} \quad \kappa = \frac{UA}{\rho C_p Q}$$


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When we deal with problems of type 1, to find reactor size for given feed and product stream conditions we use directly eq (15).

$$\tau = \frac{V}{Q_o} = \frac{C_{A_o} x_A}{ar} = \frac{C_{A_o} x_A}{-R_A}$$

Then calculate the desired heating or cooling rate from eq (16)

$$-\dot{q} = \rho C_p Q (T_o - T) + (-\Delta H_{r_A}) arV$$

When we deal with problems of type 2 and try to find the operating conditions for a given reactor, then we must solve eqs (15) and (16) simultaneously by trial and error for  $x_A$  and T.

Sometimes we can solve explicitly for  $x_A$  from eq (15) in terms of temperature  $x_A = x_A(T)$ .

Substituting this relationship into eq (16) we get



$$T_o - T + \tilde{\beta}_A ar_T \tau - \omega(T - T_{m_o}) = 0$$

$r_T$  indicates that the rate is now a function of temperature only since  $r(x_A, T) = r(x_A(T), T)$

$$\underbrace{\frac{1 + \omega}{\tilde{\beta}_A} T - \frac{T_o + \omega T_{m_o}}{\tilde{\beta}_A}}_{L(T)} = \underbrace{ar_T \tau}_{G(T)} = C_{A_o} x_A \quad (15)$$

Reactor operating temperature is given by the intersection of the straight line  $L(T)$  and curvilinear function  $G(T)$ .

For an n-th order irreversible reaction  $G(T)$  always has a sigmoidal shape and at high temperatures tends to a horizontal asymptote  $C_{A_o}$ .

For an endothermic reaction  $\Delta H_r > 0 \Rightarrow \tilde{\beta}_A < 0$  and line  $L$  has a negative slope.

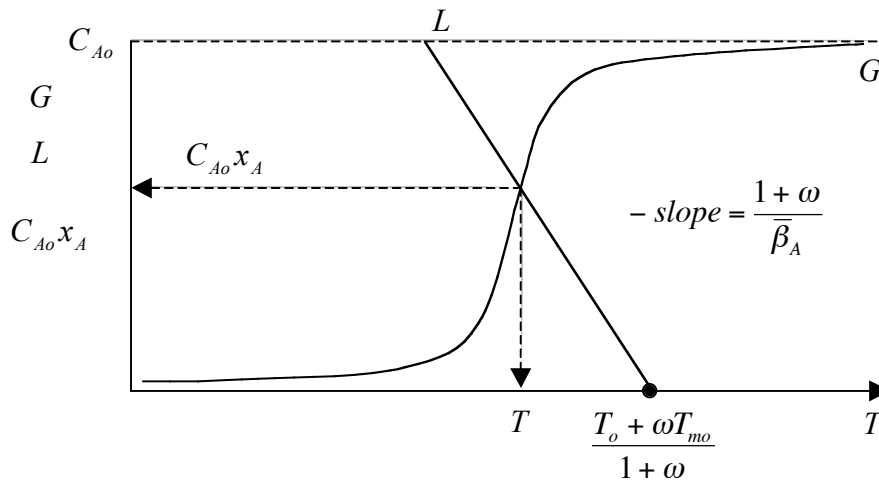


Figure 2: Operating point for an endothermic reaction in a CSTR.

Several conclusions can be reached for endothermic reactions:

- i)  $L$  &  $G$  can intersect at most once and for a given set of parameters only one steady state exists.
- ii) For a given reactor and flow rate, fixed  $\tau$ , given feed,  $T_o$  and heating medium feed temperature,  $T_{m_o}$ , and given heat transfer properties,  $\omega$ , the more endothermic the reaction, the larger  $|\tilde{\beta}_A|$  and the smaller the slope of the  $L$  line, therefore the lower the operating temperature and conversion.
- iii) For a fixed reaction, feed flow rate and composition and given reactor, fixed  $G$  curve, an increase in feed temperature moves the  $L$ -line to the right while its slope remains unchanged. Hence, the operating  $T$  and  $x_A$  are increased.

For an exothermic reaction  $\Delta H_r < 0$  and  $\tilde{\beta}_A > 0$ . The  $L$ -line has a positive slope.

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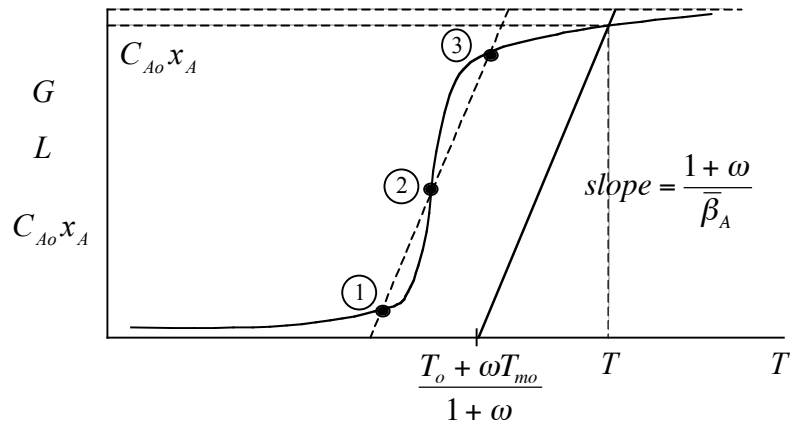


Figure 3: Operating point(s) for an exothermic reaction in a CSTR.

Several conclusions can be reached for exothermic reactions:

- L & G can intersect sometimes at more than one place and for a given set of conditions, more than one steady state may be possible.
- For fixed  $\tau$  and reaction, fixed G, an increase in the feed temperature moves the L line to the right increasing the operating T and  $x_A$ . An increase in coolant  $T_{m_o}$  has the same effect.
- For a fixed  $\tau$  and reaction, fixed G,  $\tilde{\beta}_A$ , an increase in heat removal, increase in  $\omega$ , rotates the L-line in the counterclockwise direction and moves the intercept at the abscissa to the left if  $T_o > T_{m_o}$  or to the right if  $T_{m_o} > T_o$ .

For exothermic reactions it is important to calculate the adiabatic temperature rise and the maximum adiabatic  $\Delta T$ .

From eq (16) with  $\omega \equiv 0$

$$(T - T_o)_{ad} = \tilde{\beta}_A C_{A_o} x_A \quad (18)$$

$$\Delta T_{ad, \max} = \tilde{\beta}_A C_{A_o} \quad (19)$$

Maximum fractional temperature rise is also called the Prater number,  $\beta$ .

$$\beta = \frac{\Delta T_{ad, \max}}{T_o} = \frac{\tilde{\beta}_A C_{A_o}}{T_o} \quad (20)$$

Now let us consider a number of simple illustrative examples.

### Example 1.

The following information is given.

Irreversible reaction  $A \rightarrow R$

$$-R_A = e^{25} e^{-20,000/RT} C_A \left( \frac{\text{mol}}{\text{L min}} \right)$$

$$C_{A_0} = 1 \left( \frac{\text{mol}}{\text{L}} \right) T_o = 350^\circ \text{K} = 77^\circ \text{C}$$

$$\Delta H_{R_A} = -100,000 \frac{\text{cal}}{\text{mol A}}$$

$$\rho C_p = 500 \left( \frac{\text{cal}}{\text{L}^\circ \text{C}} \right)$$

### CSTR

- a. **Isothermal**. Find reactor space time needed for  $x_A = 0.9$  at  $350^\circ \text{K}$  and heat to be removed.

$$\tau = \frac{C_{A_0} - C_A}{-R_A} = \frac{C_{A_0} x_A}{-R_A} = \frac{1 \times 0.9}{e^{25} e^{-\frac{20,000}{1.987 \times 300}}} = \frac{0.9}{0.0233}$$

$$\tau = 38.59 = 36 \text{ min}$$

$$\dot{q} = Q \rho C_p (T - T_o) + \dot{X} \Delta H_R$$

$$\dot{X} = F_{A_0} x_A = Q \rho C_{A_0} x_A (\Delta H_{R_A})$$

$$\dot{q} \left( \frac{\text{cal}}{\text{min}} \right) = Q \rho C_p (T - T_o) + Q C_{A_0} x_A (\Delta H_{R_A})$$

$$\frac{\dot{q}}{Q} \left( \frac{\text{cal}}{\text{L}} \right) = \rho C_p (T - T_o) + C_{A_0} x_A (\Delta H_{R_A}) = 1 \times 0.9 (-100,000) = -90,000 \text{ cal/L to be removed.}$$

Note that the reaction rate at  $350\text{K}$  is only  $0.0233 \left( \frac{\text{mol}}{\text{L min}} \right)$

- b. **Adiabatic**

Find  $\tau$  for  $x_A = 0.9$ .

$$Q \rho C_p (T - T_o) = (\Delta H_{R_A}) Q C_{A_0} x_A$$

$$T = T_o + \frac{(-\Delta H_{R_A}) C_{A_0}}{\rho C_p} x_A$$

$$T = 350 + \frac{100,000 \times 1}{500} 0.9 = 530\text{K} (257^\circ \text{C})$$

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$$\tau = \frac{C_{A0} - C_A}{-R_A} = \frac{C_{A0} x_A}{-R_A} = \frac{1 \times 0.9}{e^{25} e^{-20,000/1.987 \times 530}} = \frac{0.9}{407}$$

$$\tau = 2.21 \times 10^{-3} \text{ min} = 0.133 \text{ s}$$

Note that at 530K the reaction rate has increased by orders of magnitude to

$$-R_A = 407 \left( \frac{\text{mol}}{\text{Lmin}} \right)$$


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**Nonisothermal**

Find  $\tau, \dot{q}/Q$  given desired  $x_A = 0.9$  and desired  $T = 400\text{K}$ .

$$\tau = \frac{C_{A0} x_A}{-R_A} = \frac{0.9}{e^{25} e^{-\frac{20,000}{1.987 \times 400}}} = \frac{0.9}{0.849} = 1.06 \text{ (min)}$$

$$\begin{aligned} \frac{\dot{q}}{Q} &= \rho C_p (T - T_o) + C_{A0} x_A (-\Delta H_{R_A}) \\ &= 500(400 - 350) + (-90,000) \\ &= 25,000 - 90,000 = -65,000 \text{ cal/L} \end{aligned}$$

Note the value of the rate which is

$$-R_A = 0.849 \left( \frac{\text{kmol}}{\text{c min}} \right)$$

**Example 2**

A well stirred bench scale reactor (CSTR) is used for a first order exothermic reaction  $A \rightarrow R$  (practically irreversible) under the following conditions:

$$\tau = 1.0 \text{ (min)}$$

$$C_{A0} = 1.0 \text{ (mol/liter)} ; T_o = 350\text{K}$$

$$T_{mo} = 350\text{K} ; \omega = 1.0 = \frac{UA}{\rho_m C_{pm} Q_m + UA} \cdot \frac{\rho_m C_{pm} Q_m}{\rho C_p Q}$$

$$\tilde{\beta}_A = 200 \left( \frac{\text{K lit}}{\text{mol}} \right) = \frac{(-\Delta H_{R_A})}{\rho C_p}$$

$$r = e^{25} e^{-\frac{20,000}{RT}} C_A \left( \frac{\text{mol}}{\text{lit min}} \right)$$

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- Find the operating temperature and exit conversion.
- How many steady states are possible under these conditions?
- What is the maximum adiabatic temperature rise?
- How would you change some of the operating conditions ( $T_{mo}$ ,  $T_o$ ,  $\omega$ ) in order to operate at a unique steady state of high conversion.
- What start up program should one use in order to have the reactor settle in the steady state of high conversion?

**Solution**

Solve simultaneously eqs (15) & (16)

$$C_{Ao}x_A = ar\tau = k_0 e^{-E/RT} C_{Ao} (1 - x_A)\tau \quad (15)$$

$$k_0 = e^{25} \quad E = 20,000 \text{ cal/mol}$$

$$\frac{1 + \omega}{\tilde{\beta}_A} T - \frac{T_o + \omega T_{mo}}{\tilde{\beta}_A} = ar\tau = k_0 e^{-E/RT} C_{Ao} (1 - x_A)\tau \quad (16)$$

Eliminate  $x_A$  from (15).

$$x_A = \frac{k_0 e^{-E/RT} \tau}{1 + k_0 e^{-E/RT} \tau}$$

Substitute into eq (16)

$$\underbrace{\frac{1 + \omega}{\tilde{\beta}_A} T - \frac{T_o + \omega T_{mo}}{\tilde{\beta}_A}}_L = \underbrace{\frac{k_0 e^{-E/RT} \tau C_{Ao}}{1 + k_0 e^{-E/RT} \tau}}_G$$

Substitute in the values of parameters:

$$\frac{1+1}{200} T - \frac{350 + 1 \times 350}{200} = \frac{\exp\left\{-\frac{20,000}{1.9877T}\right\}}{1 + \exp\left\{25 - \frac{20,000}{1.987T}\right\}} \times 1 \times 1$$

$$0.01T - 3.5 = \frac{\exp\left\{25 - \frac{20,000}{1.987T}\right\}}{1 + \exp\left\{25 - \frac{20,000}{1.987T}\right\}} \quad (*)$$

Solve \* by trial and error for T. Then obtain the corresponding conversion by:

$$x_A = \frac{\exp\left\{25 - \frac{20,000}{1.987T}\right\}}{1 + \exp\left\{25 - \frac{20,000}{1.987T}\right\}} \quad (**)$$

We can also represent equation (\*) graphically as shown below:

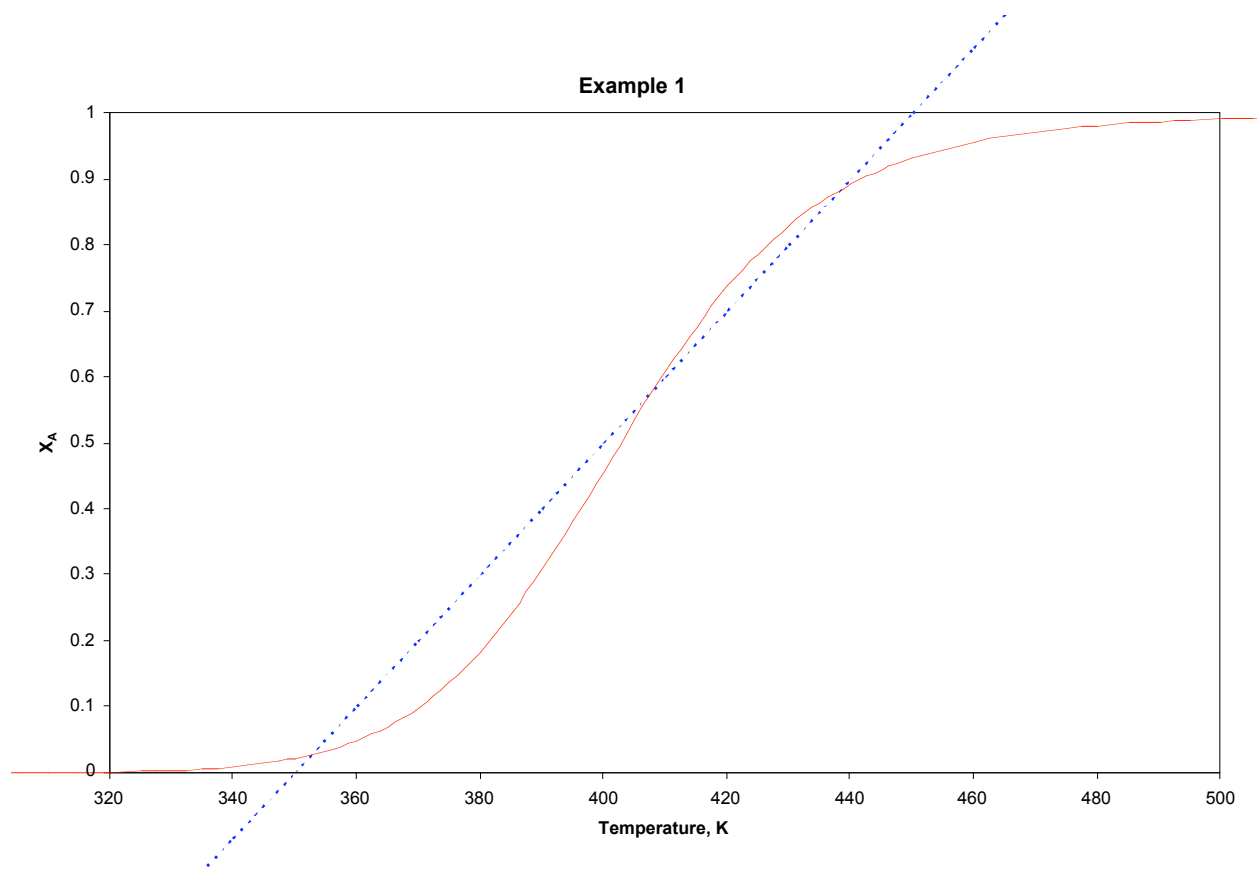


Figure 4: Operating points for the CSTR of Example 2.

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Figure 5 on next page shows the dramatic temperature excursions that the reactor can experience during start-up before it settles to a steady state.

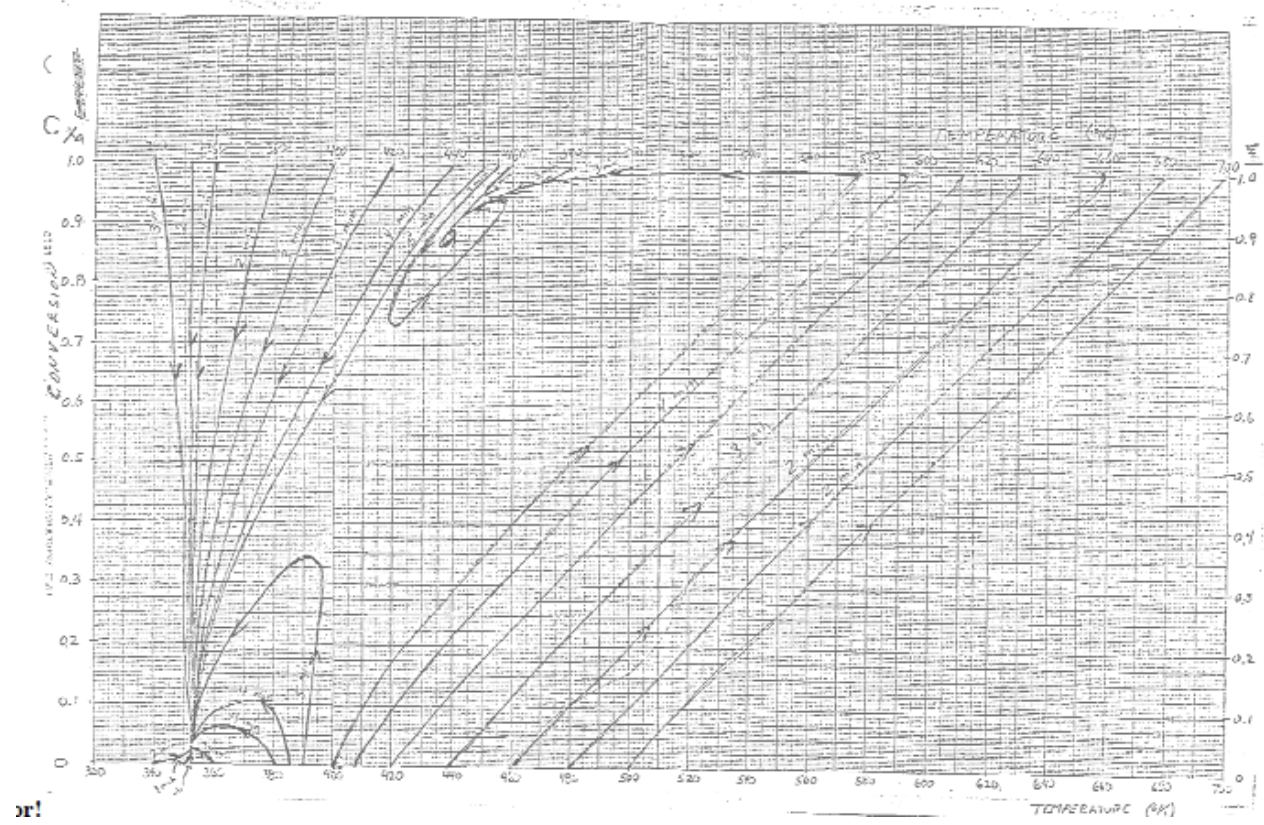


Figure 5. Transient operation of a CSTR for example 2

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a) There are three intersections of the L and G line indicating 3 possible steady states.

$$(1) \quad \begin{cases} T = 353K \\ x_A = 0.03 \end{cases}$$

$$(2) \quad \begin{cases} T = 408K \\ x_A = 0.576 \end{cases}$$

$$(3) \quad \begin{cases} T = 439K \\ x_A = 0.886 \end{cases}$$

b) Three steady states are possible.

$$c) \quad \Delta T_{admax} = \tilde{\beta}_A C_{Ao} = 200 \times 1 = 200 K$$

$$T_{admax} = T_o + \Delta T_{admax} = 550 K!$$

d) Increase  $T_o$  or  $T_{mo}$  to bypass the lower bump in the curve. Increase  $\omega$  if possible.

e) See attached Figure 5.

### Reversible Reactions

For reversible reactions the effect of temperature on equilibrium must be considered.

For endothermic reactions,  $\Delta H_r > 0$ , equilibrium conversion increases with increased temperature.

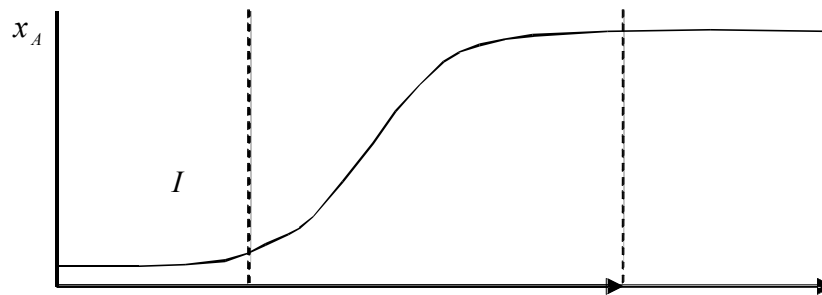


Figure 6: Equilibrium conversion as function of temperature for endothermic reactions.

In region III the reaction can be considered practically irreversible. In region II  $x_{Ae}$  rises with increase in T.

For endothermic reactions the maximum permissible temperature is always the optimal temperature for maximizing conversion or production rate from a given CSTR.



The net rate of an endothermic reaction at fixed composition always increases with increased temperature.

$$r = k_{10} e^{-E_1/RT} \prod_{j=1}^s C_j^{\alpha_j} - k_{20} e^{-E_2/RT} \prod_{j=1}^s C_j^{\beta_j}$$

since  $E_1 > E_2$

For exothermic reactions,  $\Delta H_r < 0$ , equilibrium conversion decreases with increased temperature.

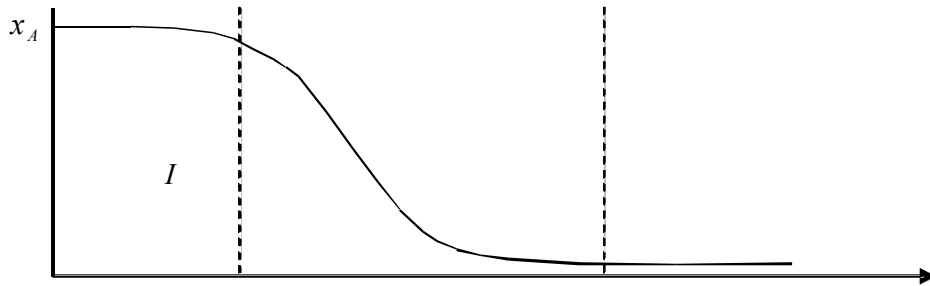


Figure 7: Equilibrium conversion as function of temperature for exothermic reactions.

Again in region I the reaction is practically irreversible. In region II it is reversible.

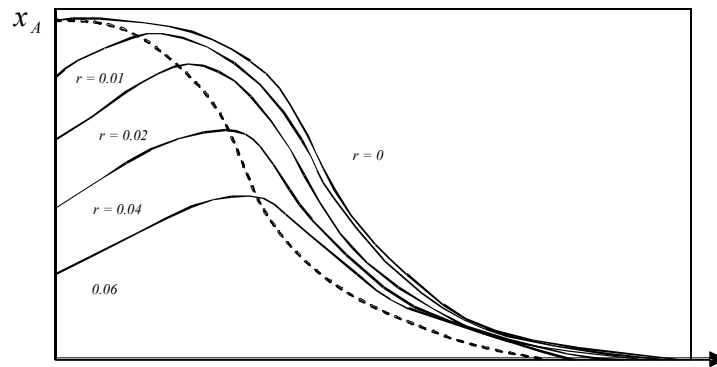


Figure 8: Conversion temperature relation at fixed rates for exothermic reactions.

Now we notice that at fixed composition, fixed  $x_A$ , the net rate of reaction has a maximum at a certain temperature,  $T_m$ . Below that temperature the rate is lower and above it, it is lower. The reason for this is that  $E_1 < E_2$ .

On the above diagram we can pass a line - - - called the locus of maximum rates or a  $T_m$  line. For a given conversion the  $T_m$  line defines a temperature at which the rate is maximum and vice versa at every T the line defines an  $x_A$  which the rate is maximum.

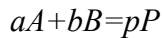
## LECTURE 7

We should always select  $T_o$ ,  $T_{mo}$ ,  $\omega$  in such a manner as to make sure that we operate on the  $T_m$  line.

The equation for the  $T_m$  line is obtained by

$$\frac{\partial r}{\partial T} = 0 \text{ from } \left. \frac{dx_A}{dT} \right|_r = 0$$

For example if we have a reversible reaction



and the rate is given by

$$r = k_{10} e^{-E_1/RT} C_A^\alpha C_B^\beta - k_{20} e^{-E_2/RT} C_P^\gamma$$

Assuming further that we deal with liquids and that  $C_{A0}$  and  $C_{B0}$  are given while  $C_{p0} = 0$

$$K_c = C_{A0}^{p-a-b} \frac{\left(\frac{P}{a} x_{Ae}\right)^p}{(1-x_{Ae})^a \left(\frac{C_{B0}}{C_{A0}} - \frac{b}{a} x_{Ae}\right)^b} \quad (\text{A})$$

Assuming an ideal solution

$$K_c = e^{\frac{-\Delta G_r^\circ}{RT}} \quad (\text{B})$$

Using (A) and (B) we can calculate  $x_{Ae}$  as a function of temperature.

The given rate form, if it is to be viable in the vicinity of equilibrium, must satisfy the following constraint:

$$\left( \frac{C_P^\gamma}{C_A^\alpha C_B^\beta} \right)_{eq} = \frac{C_P^p}{C_A^a C_B^b}$$

The locus of maximum rates i.e the  $T_m$ -line can be obtained by  $\frac{\partial r}{\partial T} = 0$  which results in

$$T = T_m = \frac{(E_2 - E_1)/R}{\ln \left[ \frac{k_{20} E_2 C_{Ao}^{\gamma - \alpha - \beta} \left( \frac{p}{a} x_A \right)^\gamma}{k_{10} E_1 (1 - x_A)^\alpha \left( \frac{C_{Bo}}{C_{Ao}} - \frac{b}{a} x_A \right)^\beta} \right]} \quad (C)$$

For a desired conversion eq (C) gives the temperature  $T_m$  at which the rate is maximum. Substituting that conversion and temperature into the equation for the rate produces the maximum rate

### Example 3 - CSTR



$$\Delta G_{r,298}^\circ = 2,500 \text{ cal/mol}$$

$$\Delta H_{r,298}^\circ = -20,000 \text{ cal/mol} = \text{const}$$

$$\rho C_p = 2,000 \text{ (cal/lit)} = \text{const}$$

$$k_1 = \underbrace{5 \times 10^8}_{k_{10}} e^{-\frac{12,500}{RT}} \text{ (min}^{-1}\text{)}$$

$$C_{Ao} = 2 \left( \frac{\text{mol}}{\text{lit}} \right)$$

- f) Find the optimal size CSTR necessary to achieve a production rate of  $F_R = 100$  (mol/min) at  $x_A = 0.9$ . If the reactor is to be operated adiabatically find the necessary feed temperature.
- g) If the feed is available only a  $T = 298\text{K}$  how should one operate? Can one maintain the desired production rate and conversion?
- h) How should 2 CSTR's in series be operated to minimize the total reactor volume and keep  $F_R$  and  $x_A$  at desired levels. Feed is at  $298\text{K}$ ,  $T = 350\text{K}$  is not to be exceeded.

### Solution

Find equilibrium constant at  $298\text{K}$

$$K_{298} = \exp\left(\frac{-\Delta G_{r,298}^\circ}{RT}\right) = \exp\left(\frac{-2,500}{1.987 \times 298}\right) = 68.2$$

Find equilibrium constant as a function of temperature using Van't Hoff's equation

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{RT^2}$$

$$K_T = K_{298} e^{\frac{\Delta H_r}{R} \left( \frac{1}{298} - \frac{1}{T} \right)} = 1.461 \times 10^{-13} \exp\left(\frac{10.065}{T}\right)$$

Find equilibrium conversion variation with temperature:

$$x_{Ae} = \frac{K_T}{1 + K_T} = \frac{1.461 \times 10^{-13} \exp\left(\frac{10,065}{T}\right)}{1 + 1.461 \times 10^{-13} \exp\left(\frac{10,065}{T}\right)}$$

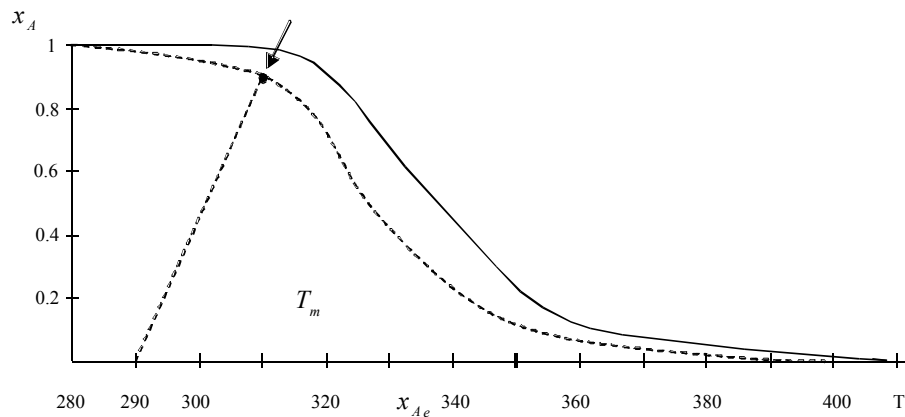
$T$	298	300	310	320	330	340	350	360	370	380
$x_{Ae}$	0.986	0.982	0.949	0.870	0.720	0.512	0.311	0.169	0.094	0.045

Find the locus of maximum rates

$$T_m = \frac{(E_2 - E_1)/R}{\ln\left[\frac{k_{20} E_2 x_A}{k_{10} E_1 (1 - x_A)}\right]} = \frac{10,065}{30.51 + \ln\left(\frac{x_A}{1 - x_A}\right)}$$

$x_A$	0.94	0.95	0.9	0.85	0.8	0.6	0.4	0.2	0.1	0.01
$T_m$	287	301	308	312	316	326	334	346	356	388

Plot the equilibrium line,  $x_{Ae}$ , and the locus of maximum rates,  $T_m$ , in order to graphically interpret some of the later results.



a. At  $x_A = 0.9$   $T = T_m = 308K$

The rate at the operating point is:

$$r = 5 \times 10^8 e^{-\frac{12,500}{1.987 \times 308}} \times 2(1 - 0.9) - 3.422 \times 10^{21} e^{-\frac{32,500}{1.987 \times 308}} \times 2 \times 0.9$$

$$r = 0.815 \left( \frac{\text{mol}}{\text{lit min}} \right)$$

From the design equation (balance on R)

$$V = \frac{F_R}{R_R} = \frac{F_R}{r} = \frac{100}{0.815} = 1227 \text{ (lit)} = 1.23 \text{ m}^3$$

$$V = 1.23 \text{ m}^3$$

For adiabatic operation

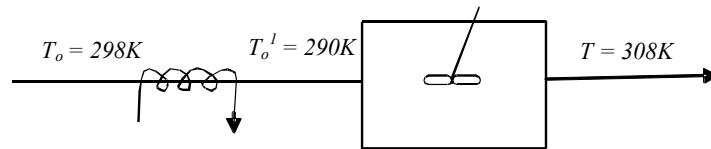
$$T_o - T + \tilde{\beta}_A (-V_A) r \tau = 0 \quad \tilde{\beta} = \frac{-\Delta H_{rA}}{\rho C_p} = 10$$

$$T_o = T - \tilde{\beta}_A C_{A_o} x_A = 308 - 10 \times 2 \times 0.9 = 290\text{K}$$

For adiabatic operation the feed temperature would have to be 290K. The same result is obtained graphically (--- adiabatic line).

b. If the feed is available only at 298K we could do one of the following:

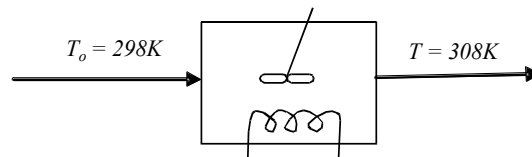
i) Cool the feed from 298K to 290K and operate adiabatically



$$-\dot{q} = Q \rho C_p (T_o - T_o^1) = \frac{F_R}{C_{A_o} x_A} \rho C_p (T_o - T_o^1)$$

$$-\dot{q} = \frac{100}{2 \times 0.9} \times 2000 (298 - 290) = 8.889 \times 10^5 \left( \frac{\text{cal}}{\text{min}} \right)$$

ii) Introduce the feed at 298K and cool the reactor



$$-\dot{q} = Q \rho C_p (T_o - T) + (-\Delta H_{rA}) C_{A_o} Q x_A$$

$$-\dot{q} = \frac{F_R}{C_{A_o} x_A} \rho C_p (T_o - T) + (-\Delta H_r) F_R$$

$$-\dot{q} = 100 \left[ \frac{2000}{2 \times 0.9} (298 - 308) + 20,000 \right] = 8.889 \times 10^5 \frac{\text{cal}}{\text{min}}$$

## LECTURE 7

The cooling rate requirement is the same, as it should be as there is no work term in the energy balance. But it is easier to remove heat from the higher reactor temperature.

iii) Operate adiabatically with the new feed temperature while maintaining the previous feed

$$\text{rate } F_{A_o} = \left(\frac{100}{0.9}\right); F_{A_o} x_A = F_R$$

$$Q_o = \frac{F_{A_o}}{C_{A_o}} = \frac{100}{1.8}$$

Now we must find the new operating point by a simultaneous solution of the species and energy balance.

$$C_{A_o} x_A = r \tau$$

$$T_o - T + \tilde{\beta} \tau r = 0$$

Since we need adiabatic operation by combining the above two equations we get the relationship between conversion and temperature

$$T = T_o + \tilde{\beta} r \tau = T_o + \tilde{\beta} C_{A_o} x_A$$

$$T = 298 + 10 \times 2 x_A = 20 [14.9 + x_A]$$

Substituting into the first equation we get:

$$2 x_A = \left[ 5 \times 10^8 e^{-\frac{12,500}{1.987 \times 20 [14.9 + x_A]}} \times 2 (1 - x_A) - 3.4 \times 10^{21} e^{-\frac{32,500}{1.987 \times 20 (14.9 + x_A)}} \right] \frac{1227 \times 1.8}{100}$$

$$11.043 \left\{ 10^9 (1 - x_A) e^{-\frac{314.5}{14.9 + x_A}} - 6.8 \times 10^{21} x_A e^{-\frac{817.8}{14.9 + x_A}} \right\} - x_A = 0$$

By trial and error

$x_A = 0.88$	$T = 315.6 = 316 K$
--------------	---------------------

The purity (conversion) has been reduced somewhat from the required 90%.

The production rate now is  $F_R$  and rate is  $r$ .

## LECTURE 7

$$r = 5 \times 10^8 e^{-\frac{12,500}{1.987 \times 315.6}} 2(1-0.88) - 3.4 \times 10^{21} e^{-\frac{32,500}{1.987 \times 315.6}} 2 \times 0.88$$

$$r = 0.0786 \left( \frac{\text{mol}}{\text{lit min}} \right)$$

$$F_R = F_{A_o} x_A = \frac{100}{0.9} \times 0.88 = 97.8 \left( \frac{\text{mol}}{\text{min}} \right)$$

and production rate has dropped very little.

- iii) We could operate the reactor adiabatically with the new feed temperature and maintain (via a controller) fixed exit composition at  $x_A = 0.9$  which would require adjusting the feed rate.

Now

$$T = T_o + \tilde{\beta}_A C_{A_o} x_A = 298 + 20 \times 1.8 = 316K$$

$$x_A = 0.9$$

The new rate is:

$$r = 5 \times 10^8 e^{-\frac{12,500}{1.987 \times 316}} \times 2(1-0.9) - 3.4 \times 10^{21} e^{-\frac{32,500}{1.987 \times 316}} \times 2 \times 0.9$$

$$r = 0.023 \left( \frac{\text{mol}}{\text{lit min}} \right)$$

Which is much smaller than the maximum rate.

The production rate now drops to

$$F_R = r V = 0.023 \times 1227 = 28.2 \left( \frac{\text{mol}}{\text{min}} \right)$$

This is too high a penalty to pay for maintaining purity i.e. keeping  $x_A = 0.9$  constant!

C. For minimum total reactor size we must find the minimum of the following expression

$$\frac{\tau_1 + \tau_2}{C_{A_o}} = \frac{x_{A_1}}{r_{m_1}} + \frac{0.9 - x_{A_1}}{r_{m_f}}$$

$$r_{m_1} = 10^9 e^{\frac{12,500}{1.987 T_m}} (1 - x_{A_1}) - 6.8 \times 10^{21} e^{\frac{-32,500}{1.987 T_m}} x_{A_1}$$

$$\text{With } T_m = \frac{10,065}{30.51 + \ln\left(\frac{x_{A_1}}{1 - x_{A_1}}\right)}$$

$$r_{m_f} = 0.0818 \text{ (mol/lit min)}$$

By taking  $\frac{d}{d x_{A_1}} \left( \frac{\tau_1 + \tau_2}{C_{A_o}} \right) = 0$  one gets by trial and error

$$\begin{aligned} x_{A_1} &= 0.72 \\ T_{m_1} &= 320K \end{aligned} \quad r_{m_1} = 0.5 \left( \frac{\text{mol}}{\text{lit min}} \right)$$

The required volumes are:

For the first reactor

$$V_1 = \frac{F_{A_o} x_{A_1}}{r_{m_1}} = \frac{100 \cdot 0.72}{0.9 \cdot 0.5} = \underline{160 \text{ liters}}$$

For the second reactor

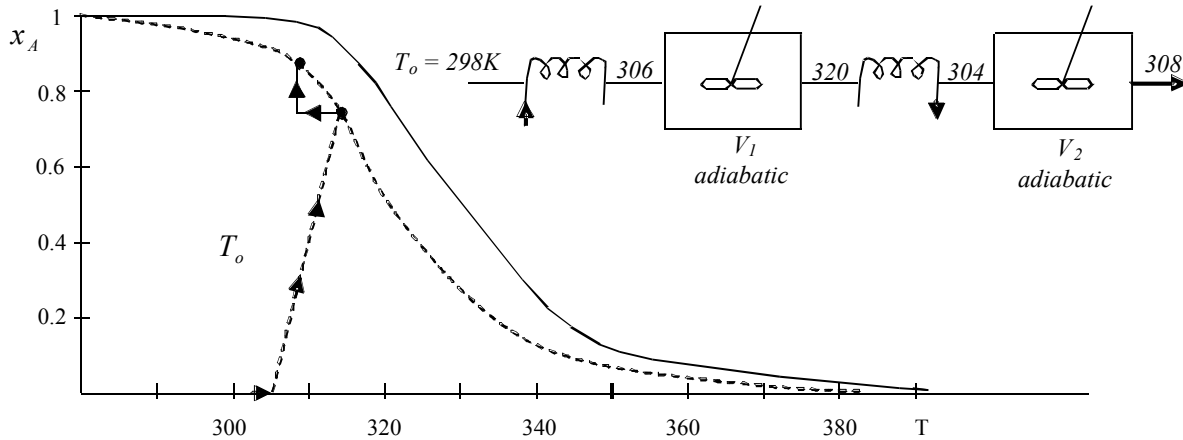
$$V_2 = \frac{F_{A_o} (x_{A_f} - x_{A_1})}{r_{m_f}} = \frac{100 (0.9 - 0.72)}{0.9 \cdot 0.0818} = \underline{244.5 \text{ lit}}$$

Total volume  $V = V_1 + V_2 = \underline{405 \text{ liters}}$

The graphical representation of the above system is shown below



## LECTURE 7



Preheat the feed from 298K to 305.6K  $\approx$  306K

$$\dot{q}_1 = Q \rho C_p (305.6 - 298) = \frac{100}{0.9 \times 2} \times 2000 (305.6 - 298) = 8.44 \times 10^5 \left( \frac{\text{cal}}{\text{min}} \right)$$

Cool the stream from 1<sup>st</sup> reactor to 304.4K  $\approx$  304

$$-\dot{q}_2 = Q \rho C_p \Delta T = \frac{700}{0.9 \times 2} \times 2000 (320 - 304.4) = 1.73 \times 10^6 \left( \frac{\text{cal}}{\text{min}} \right)$$

It should be noted that the above calculations can be made easier with a little analytical work to obtain an expression for the maximum rate as a function of conversion. This is done by substituting the  $T_m$  values

$$T_m = \frac{(E_2 - E_1)/R}{\ln \left[ \frac{k_{20} E_2 x_A}{k_{10} E_1 (1 - x_A)} \right]}$$

for temperature  $T$  in the rate expression

$$(-R_A)_m = r_m = k_{10} e^{-E_1/RT_m} C_{A_o} (1 - x_A) - k_{20} e^{-E_2/RT_m} C_{A_o} x_A$$

If we recall that  $e^{a \ln b} = e^{\ln b^a} = b^a$

We get:

$$r_m = \left( k_{10} \left( \frac{k_{10} E_1}{k_{20} E_2} \right)^{\frac{E_1}{E_2 - E_1}} - k_{20} \left( \frac{k_{10} E_1}{k_{20} E_2} \right)^{\frac{E_2}{E_2 - E_1}} \right) C_{A_o} \frac{(1 - x_A)^{\frac{E_2}{E_2 - E_1}}}{x_A^{\frac{E_1}{E_2 - E_1}}}$$

## LECTURE 7

In our particular example the above expression reduces to:

$$r_m = 3.22 (1 - x_A)^{1.625} x_A^{-0.625}$$


---

Another variation on the above problem is to have two equal size CSTRs in series. For maximum production rate then under conditions  $\tau_1 = \tau_2$  we must find  $x_{A_1}$  that satisfies

$$\frac{x_{A_1}}{r_{m_1}} = \frac{x_{A_2} - x_{A_1}}{r_{m_2}}$$

This happens at  $x_{A_1} = 0.75$  so  $V_1 = V_2 = 205$  liters

In summary the following types of problems may be encountered:

- I. Given  $V, Q, T_o, T_{m_o}, Q_m, \tilde{\beta}, \dot{q}$ , find  $x_A$  and  $T$ . This is equivalent to determining the performance of an existing reactor or of one that is contemplated by design engineers. In this case species mass balance and energy balance are solved simultaneously.
- II. Given  $T_o, T_{m_o}, \tilde{\beta}, F_R$  and  $x_A$  determine the required  $V$  and desired operating  $T$ .

This is the typical design problem.

- III. Production rate is specified. Exit conversion and temperature can be selected together with  $V$  in order to optimize some profit function.

This is also a typical design problem.

We have not touched here on two very important problems.

- transients in a CSTR
- control of a CSTR around an unstable steady state.

## LECTURE 7

**Extension to Multiple Reactions**

One should keep in mind that yields and selectivities can be affected dramatically by the choice of operating temperature when activation energies of various reactions are different.

The problems consist of

- Finding the optimum temperature for a desired product distribution irrespective of space time requirements.
- Finding an optimal temperature for a given reactor (given  $\tau$ ) which maximizes the production of the desired product.

The equations to be solved are given  $R$  independent reactions among  $S$  species

$$\sum_{j=1}^S v_{ij} A_j = 0 \quad i = 1, 2, \dots, R$$

$$F_{j0} - F_j + \sum v_{ij} r_i V = 0 \quad (1)$$

$$j = 1, 2, \dots, R$$

**or**

$$\sum_{i=1}^R v_{ij} [\dot{X}_i - r_i V] = 0$$

$$\boxed{\dot{X}_i - r_i V = 0 \quad \text{for } i = 1, 2, 3 \dots R} \quad (1a)$$

**and**

$$\sum_{j=1}^S (F_{j0} \tilde{H}_{j0} - F_j \tilde{H}_j) + \dot{q} = 0 \quad (2)$$

Equation (1) represents independent  $R$  species balances and eq (2) is the energy balance based on assumptions of

- no work other than flow work
- negligible changes in potential and kinetic energy

If we assume further c) ideal gas behavior d) ideal mixture

## LECTURE 7

$$\sum_{j=1}^s F_{jo} \left( \Delta H_{\sim fj} + \int_{T^0 \sim pj}^{T_o} C_{\sim pj} dT \right) - \sum_{j=1}^s F_j \left( \Delta H_{\sim fj} + \int_{T^0 \sim pj}^T C_{\sim pj} dT \right) + \dot{q} = 0$$

$$\sum_{j=1}^s F_{jo} \int_{T \sim pj}^{T_o} C_{\sim pj} dT - \sum_{j=1}^s \sum_{i=1}^R v_{ij} \left( \Delta H_{\sim fj} + \int_{T^0 \sim pj}^T C_{\sim pj} dT \right) r_i V + \dot{q} = 0$$


---

$$\sum_{j=1}^s F_{jo} \int_{T \sim pj}^{T_o} C_{\sim pj} dT - \sum_{i=1}^R v_{ij} \left( \Delta H_{\sim r_i} \right) r_i V + \dot{q} = 0 \quad (2a)$$


---

Where  $\Delta H_{r_i}$  is the heat of reaction of reaction  $i$  at temperature  $T$ .

If we further assume e) constant heats of reaction and f) constant mean specific heats we get

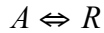
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$$\rho C_p Q (T_o - T) + \sum_{i=1}^R (-\Delta H_{r_i}) r_i V + \dot{q} = 0 \quad (2b)$$


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## PROBLEMS

A. Consider the following simple reaction



The reaction rate is given by:

$$\pi = k_1 C_A - k_2 C_R \quad (\text{mol/lit } s)$$

$$k_1 = \exp\left(7 - \frac{83,000}{RT}\right) \times 10^3 \quad (s^{-1})$$

$$k_2 = \exp\left(18 - \frac{167,400}{RT}\right) \times 10^3 \quad (s^{-1})$$

**Note:** the activation energies are given in (J/mol) use the value of the gas constant accordingly.

The heat of reaction is:

$$\Delta H_r = -80,000 \quad (J/mol)$$

Specific heat of the reaction mixture is:

$$C_{\sim p} = 40 \quad (J/mol K)$$

Assume that these are constant.

1. The above reaction occurs in the liquid phase. The pressure is high enough so that the liquid will not volatize in the permissible temperature operating range which is: 300 to 900K.

The feed conditions are:

$$Q_o = 100 \quad (\text{lit/s}); C_{A_o} = 1 \quad (\text{mol/lit}); T_o = 300K$$

You have a  $V = 100$  liters CSTR reactor. How would you operate this CSTR in order to maximize the production rate of  $R$ ?

- a) What is  $F_R$  (mol/s) -maximum production rate?
- b) What are  $x_A$  &  $T$  -operating conditions?
- c) What is the heat duty for the system?
- d) Sketch your system and location and heat duty of all heat exchangers, if any.