Temperature and Pressure Effects

Chapter 9

The reaction temperature and pressure also influence the progress of reactions, and it is the role of these variables that now consider.

We follow a three-step procedure:

- First, we must find how ==equilibrium composition==, rate of reaction, and product distribution are affected by changes in operating temperatures and pressures.

  This will allow us to determine the optimum temperature progression, and it is this that we strive to approximate with a real design.

- Second, chemical reactions are usually accompanied by ==heat effects==, and we must know how these will change the temperature of the reacting mixture.

  With this information we are able to propose a number of favorable reactor and heat exchange systems-those which closely approach the optimum.

- Finally, ==economic considerations== will select one of these favorable systems as the best.

    So, with the emphasis on finding the ==optimum conditions== and then seeing how best to approach them in actual design rather than determining what specific reactors will do

let us start with discussions of single reactions and follow this with the special considerations of multiple reactions.

SINGLE REACTIONS

- With single reactions we are concerned with conversion level and reactor stability.

- Questions of product distribution do not occur.

- Thermodynamics gives two important pieces of information, the first being the heat liberated or absorbed for a given extent of reaction, the

- second being the maximum possible conversion.
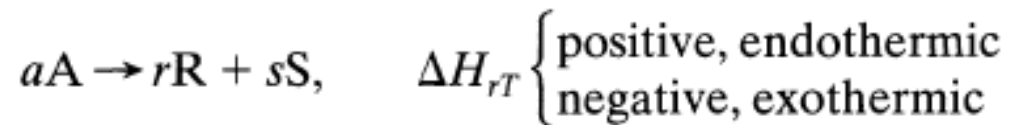
Heats of Reaction from Thermodynamics

- The heat liberated or absorbed during reaction at temperature T_2 depends on

- the nature of the reacting system, the amount of material reacting, and the

- temperature and pressure of the reacting system, and is calculated from the heat

- of reaction ΔH_r for the reaction in question.

- When this is not known, it can in most cases be calculated from known and tabulated thermochemical data on heats of formation ΔH_f or heats of combustion ΔH_c of the reacting materials.

- These are tabulated at some standard temperature, T_I usually 25°C.

- As a brief consider the reaction

$$aA \rightarrow rR + sS$$

- By convention we define the heat of reaction at temperature T as the heat transferred to the reacting system from the surroundings

- when a moles of A disappear to produce r moles of R and s moles of S with the system measured

- at the same temperature and pressure before and after the change.

- Thus

$$aA \rightarrow rR + sS, \qquad \Delta H_{rT} \begin{cases} \text{positive, endothermic} \\ \text{negative, exothermic} \end{cases}$$

- **Heats of Reaction and Temperature.** The first problem is to evaluate the heat of reaction at temperature T_2 knowing the heat of reaction at temperature T_1.

- This is found by the law of conservation of energy as follows:

$$\left(\begin{array}{c}\text{heat absorbed}\\\text{during reaction}\\\text{at temperature}\\T_2\end{array}\right) = \left(\begin{array}{c}\text{heat added to}\\\text{reactants to}\\\text{change their}\\\text{temperature}\\\text{from } T_2 \text{ to } T_1\end{array}\right) + \left(\begin{array}{c}\text{heat absorbed}\\\text{during reaction}\\\text{at temperature}\\T_1\end{array}\right) + \left(\begin{array}{c}\text{heat added to}\\\text{products to}\\\text{bring them}\\\text{back to } T_2\\\text{from } T_1\end{array}\right)$$

- In terms of enthalpies of reactants and products this becomes where subscripts 1 and 2 refer to quantities measured at temperatures T_1 and T_2, respectively. In terms of specific heats

$$\Delta H_{r2} = -(H_2 - H_1)_{\text{reactants}} + \Delta H_{r1} + (H_2 - H_1)_{\text{products}}$$
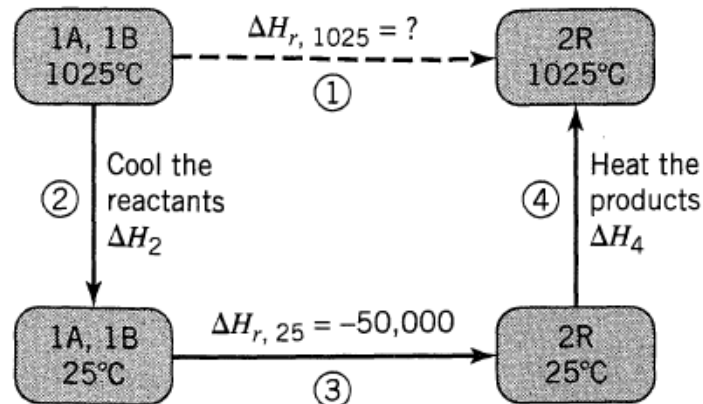
- In terms of specific heats

$$\Delta H_{r2} = \Delta H_{r1} + \int_{T_1}^{T_2} \nabla C_p \, dT$$

$$\nabla C_p = rC_{pR} + sC_{pS} - aC_{pA}$$

$$C_{pA} = \alpha_A + \beta_A T + \gamma_A T^2 \qquad\qquad \nabla\alpha = r\alpha_R + s\alpha_S - a\alpha_A$$

$$C_{pR} = \alpha_R + \beta_R T + \gamma_R T^2 \qquad\qquad \nabla\beta = r\beta_R + s\beta_S - a\beta_A$$
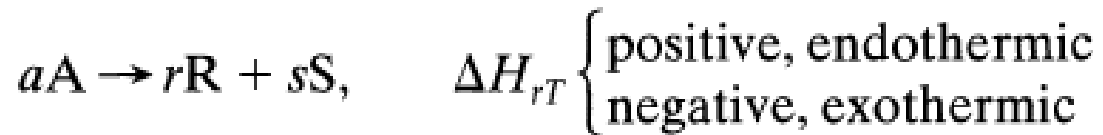
$$C_{pS} = \alpha_S + \beta_S T + \gamma_S T^2 \qquad\qquad \nabla\gamma = r\gamma_R + s\gamma_S - a\gamma_A$$

$$\Delta H_{r2} = \Delta H_{r1} + \int_{T_1}^{T_2} (\nabla\alpha + \nabla\beta T + \nabla\gamma T^2) \, dT$$

$$= \Delta H_{r1} + \nabla\alpha(T_2 - T_1) + \frac{\nabla\beta}{2}(T_2^2 - T_1^2) + \frac{\nabla\gamma}{3}(T_2^3 - T_1^3)$$

Equilibrium Constants from Thermodynamics

- From the second law of thermodynamics equilibrium constants, hence equilibrium compositions of reacting systems, may be calculated.

- We must remember, however, that real systems do not necessarily achieve this conversion; therefore, the conversions calculated from thermodynamics are only suggested attainable values.

- As a brief reminder, the standard free energy ΔG_O for the reaction of Eq at temperature T is defined as

$$a\mathrm{A} \rightarrow r\mathrm{R} + s\mathrm{S}, \qquad \Delta H_{rT} \begin{cases} \text{positive, endothermic} \\ \text{negative, exothermic} \end{cases}$$

Heats of Reaction and Temperature.

The first problem is to evaluate the heat of reaction at temperature T_2 knowing the heat of reaction at temperature T_1.

- This is found by the law of conservation of energy as follows:

$$\Delta G^\circ = rG_R^\circ + sG_S^\circ - aG_A^\circ = -\mathbf{R}T \ln K = -\mathbf{R}T \ln \frac{\left(\frac{f}{f^\circ}\right)_R^r \left(\frac{f}{f^\circ}\right)_S^s}{\left(\frac{f}{f^\circ}\right)_A^a}$$

- where f is the fugacity of the component at equilibrium conditions; f ^{O} is the fugacity of the component at the arbitrarily selected standard state at temperature T, the same one used in calculating ΔG_O ; Go is the standard free energy of a reacting component, tabulated for many compounds; and K is the thermodynamic equilibrium constant for the reaction. Standard states at given temperature are commonly chosen as follows:

- Gases-pure component at one atmosphere, at which pressure ideal gas behavior is closely approximated
- Solid-pure solid component at unit pressure
- Liquid-pure liquid at its vapor pressure
- Solute in liquid-1 molar solution; or at such dilute concentrations that the activity is unity.
- For convenience define

$$K_f = \frac{f_R^r f_S^s}{f_A^a}, \quad K_p = \frac{p_R^r p_S^s}{p_A^a}, \quad K_y = \frac{y_R^r y_S^s}{y_A^a}, \quad K_C = \frac{C_R^r C_S^s}{C_A^a}$$

$$\Delta n = r + s - a$$

At this low pressure the deviation from ideality invariably is small; hence fugacity and pressure are identical and $f^o = p^o = 1$ atm.
Thus

$$K = e^{-\Delta G^o / RT} = K_p \{p^o = 1 \text{ atm}\}^{-\Delta n}$$

$$f_i = p_i = y_i \pi = C_i \mathbf{R}T \qquad\qquad K_f = K_p$$

$$K = \frac{K_p}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}} = \frac{K_y \pi^{\Delta n}}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}} = \frac{K_c(\mathbf{R}T)^{\Delta n}}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}}$$

For a *solid component* taking part in a reaction, fugacity variations with pressure are small and can usually be ignored. Hence

$$\left(\frac{f}{f^\circ}\right)_{\text{solid component}} = 1$$

Equilibrium Conversion. The equilibrium composition, as governed by the equilibrium constant, changes with temperature, and from thermodynamics the rate of change is given by

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{\mathbf{R}T^2}$$

On integrating we see how the equilibrium constant changes with temperature.

When the heat of reaction ΔH, can be considered to be constant in the temperature interval, integration yields

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_r}{\mathbf{R}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

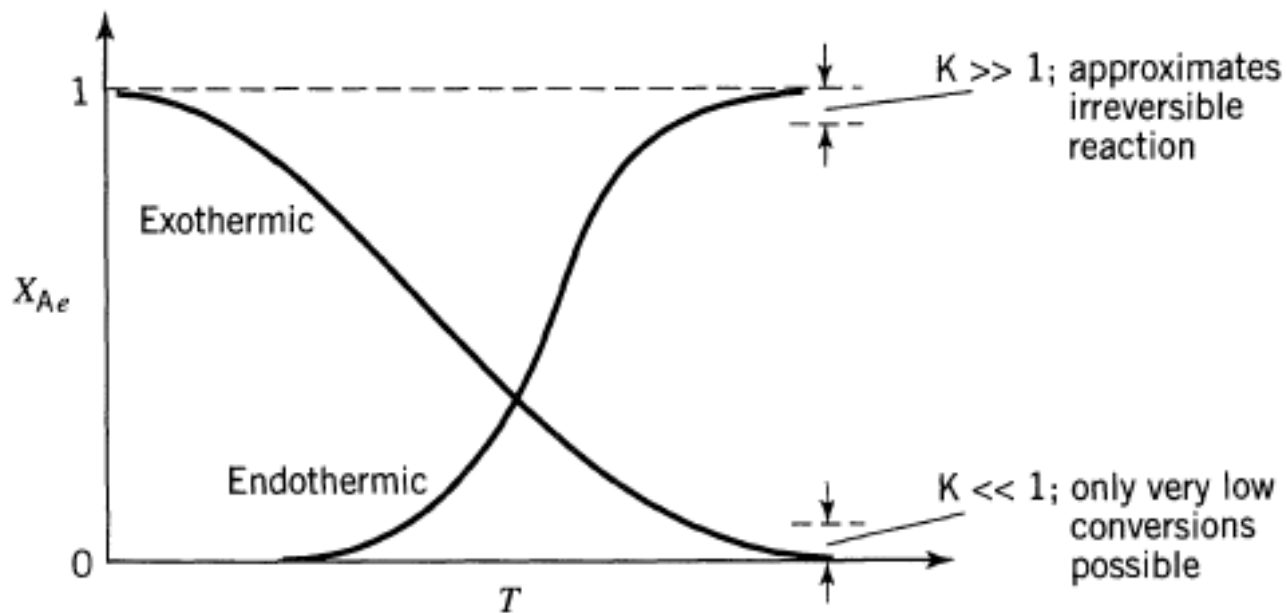When the variation of ∆H, must be accounted for in the integration we have

$$\ln \frac{K_2}{K_1} = \frac{1}{\mathbf{R}} \int_{T_1}^{T_2} \frac{\Delta H_r}{T^2} dT$$

where *∆Hr* is given by a special form of Eq in which subscript o refers to the base temperature

$$\Delta H_r = \Delta H_{r0} + \int_{T_0}^{T} \nabla C_p dT$$

Replacing Eqs and integrating, while using the temperature dependency for **Cp** , gives

$$\mathbf{R} \ln \frac{K_2}{K_1} = \nabla \alpha \ln \frac{T_2}{T_1} + \frac{\nabla \beta}{2} (T_2 - T_1) + \frac{\nabla \gamma}{6} (T_2^2 - T_1^2)$$

$$+ \left(-\Delta H_{r0} + \nabla \alpha T_0 + \frac{\nabla \beta}{2} T_0^2 + \frac{\nabla \gamma}{3} T_0^3 \right) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

1.   The thermodynamic equilibrium constant is unaffected

 by the pressure of the system,

 by the presence or absence of inerts,

 by the kinetics of the reaction,

but is affected by the temperature of the system.

2. Though the thermodynamic equilibrium constant is unaffected by pressure or inerts, the equilibrium concentration of materials and equilibrium conversion of reactants can be influenced by these variables.

Approximates irreversible reaction only very low conversions possible

Effect of temperature on equilibrium conversion as predicted by thermodynamics

3. $K \gg 1$ indicates that practically complete conversion may be possible and that the reaction can be considered to be irreversible. $K \ll 1$ indicates that reaction will not proceed to any appreciable extent.
4. For an increase in temperature, equilibrium conversion rises for endothermic reactions and drops for exothermic reactions.
5. For an increase in pressure in gas reactions, conversion rises when the number of moles decreases with reaction; conversion drops when the number of moles increases with reaction.
6. A decrease in inerts for all reactions acts in the way that an increase in pressure acts for gas reactions.

EQUILIBRIUM CONVERSION AT DIFFERENT TEMPERATURES
    (a) Between 0°C and 100°C determine the equilibrium conversion for the elementary aqueous reaction

$$A \rightleftarrows R \begin{cases} \Delta G^\circ_{298} = -14\,130 \text{ J/mol} \\ \Delta H^\circ_{298} = -75\,300 \text{ J/mol} \end{cases} \qquad C_{pA} = C_{pR} = \text{constant}$$
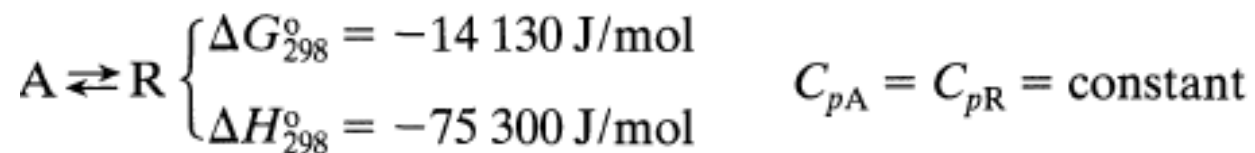
Present the results in the form of a plot of temperature versus conversion.

(b) What restrictions should be placed on the reactor operating isothermally if we are to obtain a conversion of 75% or higher?

(a) With all specific heats alike, $\Delta C_p = 0$. Then from the heat of reaction is independent of temperature and is given by

$$\Delta H_r = \Delta H_{r,298} = -75\,300\ \text{J/mol}$$

the equilibrium constant at 25°C is given by

$$K_{298} = \exp(-\Delta G^0_{298}/\mathbf{R}T)$$

$$= \exp\left(\frac{14\,130\ \text{J/mol}}{(8.314\ \text{J/mol} \cdot \text{K})\,(298\text{K})}\right) = 300$$

Since the heat of reaction does not change with temperature, the equilibrium constant K at any temperature T is now found from

$$\ln \frac{K}{K_{298}} = -\frac{\Delta H_r}{8.314}\left(\frac{1}{T} - \frac{1}{298}\right) \quad \longrightarrow \quad K = K_{298}\exp\left[\frac{-\Delta H_r}{\mathbf{R}}\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

$$K = \exp\left[\frac{75\,300}{\mathbf{R}T} - 24.7\right]$$

$$K = \frac{C_R}{C_A} = \frac{C_{A0}X_{Ae}}{C_{A0}(1 - X_{Ae})} = \frac{X_{Ae}}{1 - X_{Ae}} \quad \longrightarrow \quad X_{Ae} = \frac{K}{K+1}$$

Selected Temperature		$K = \exp\left[\dfrac{75\,300}{\mathbf{R}T} - 24.7\right]$	X_{Ae}
°C	K	from Eq. (iii)	from Eq.
5	278	2700	0.999+
15	288	860	0.999
25	298	300	0.993
35	308	110	0.991
45	318	44.2	0.978
55	328	18.4	0.949
65	338	8.17	0.892
75	348	3.79	0.791
85	358	1.84	0.648
95	368	0.923	0.480
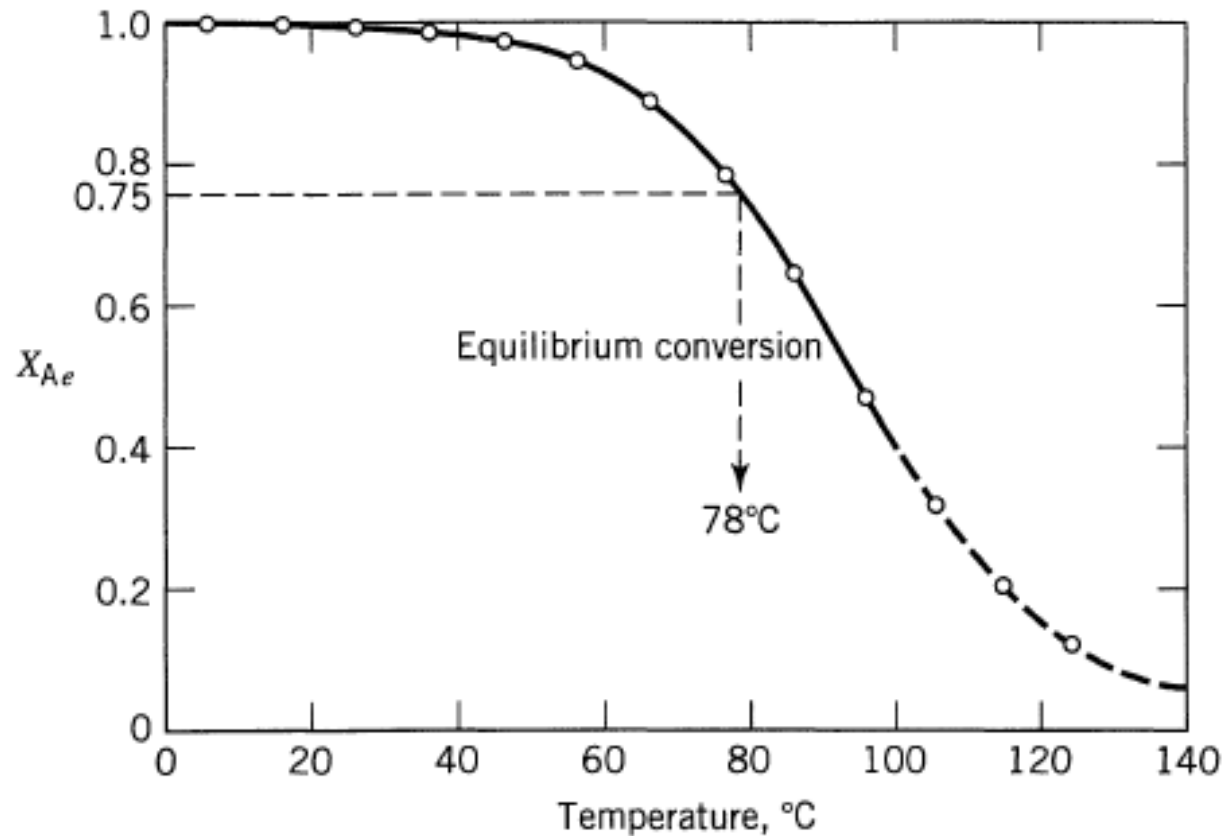
From the graph we see that the temperature must stay below 78°C if conversion of 75% or higher may be expected.

General Graphical Design Procedure

- Temperature, composition, and reaction rate are uniquely related for any single homogeneous reaction, and this may be represented graphically in one of three ways,
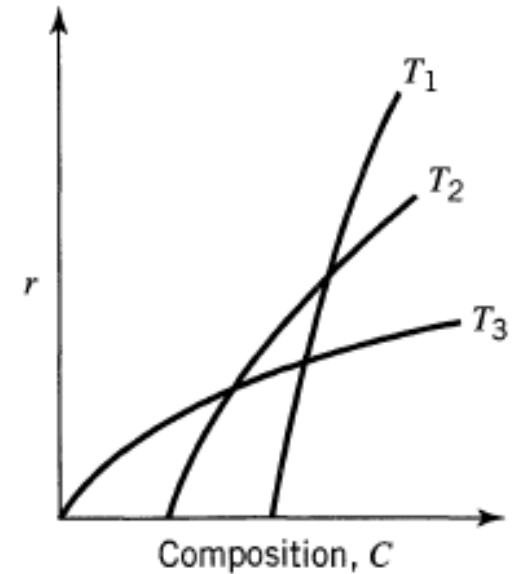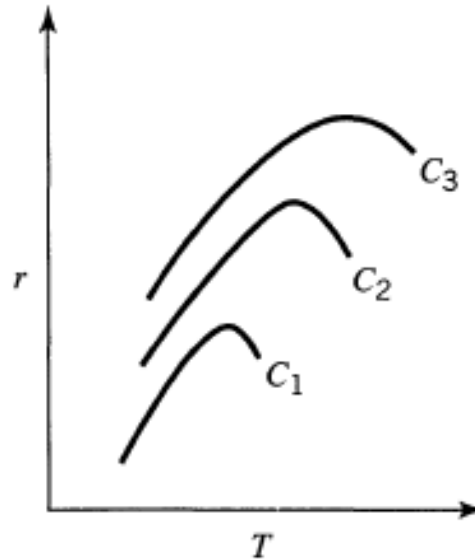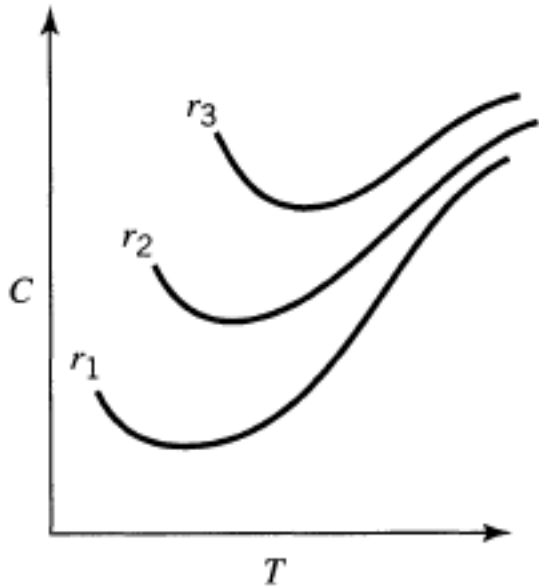
General shape of the temperature-conversion plot for different reaction types.

Irreversible

Reversible exothermic

Reversible endothermic
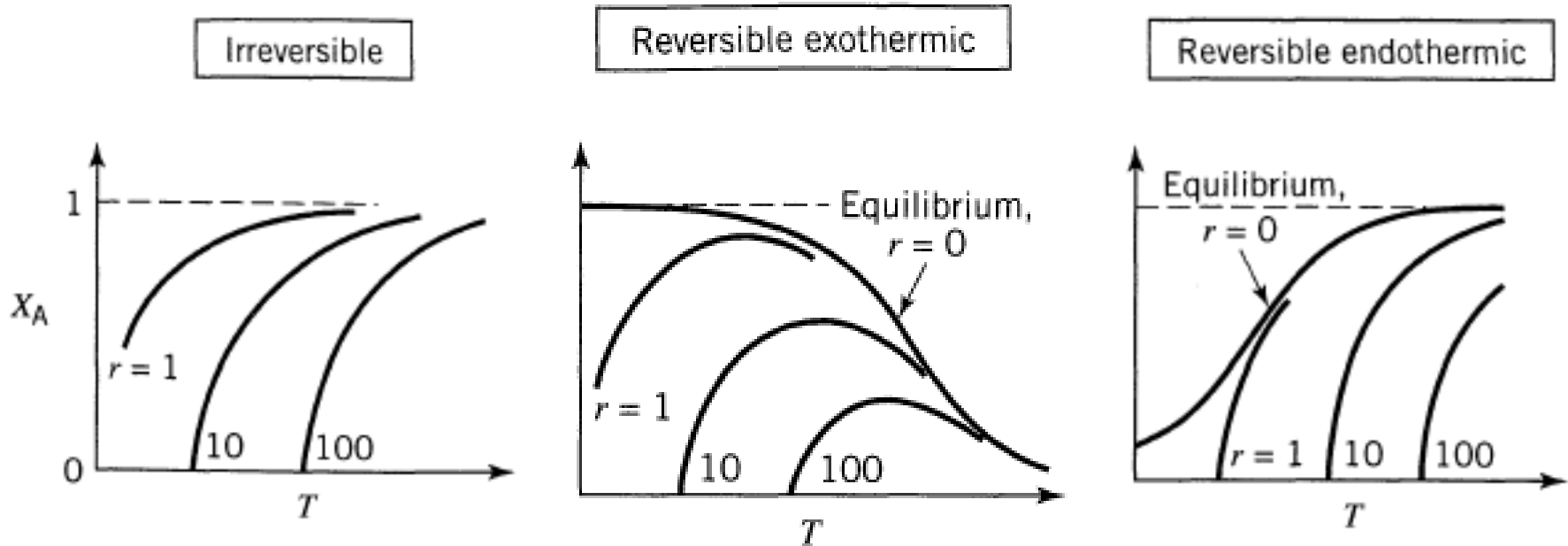
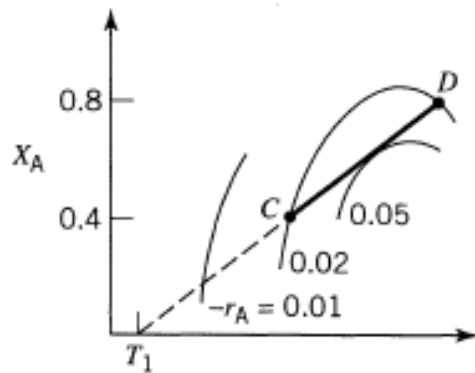The size of reactor required for a given duty and for a given temperature progression is found as follows:

1. Draw the reaction path on the X_A versus T plot.
2. This is the *operating line* for the operation. Find the rates at various X_A along this path.

3. Plot the $l/(-rA)$ versus X_A curve for this path.

4. Find the area under this curve. This gives V/F_{Ao}.

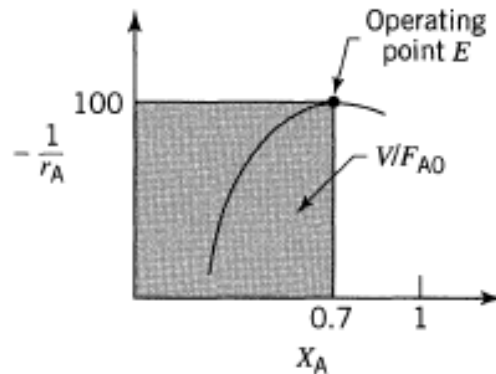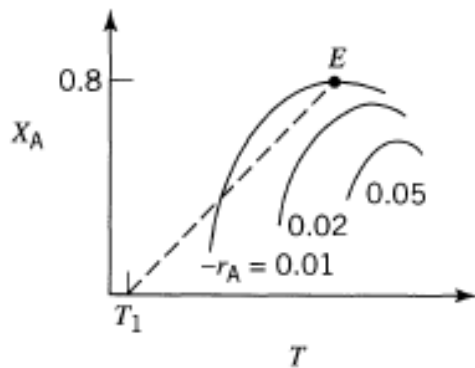# Finding the reactor size for different types of flow and for a feed temperature T_1
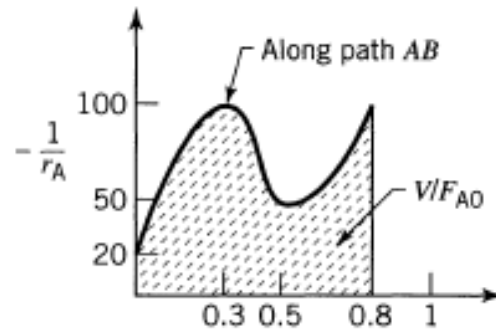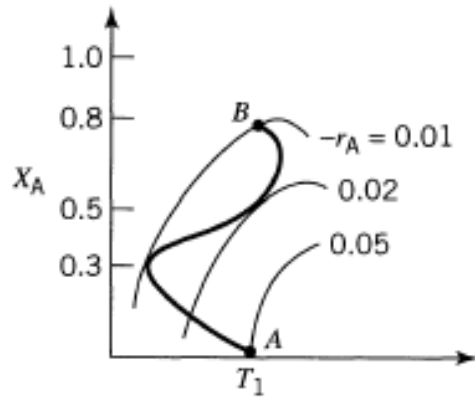
For exothermic reactions we illustrate this procedure in Fig.
For three paths:
1. Path AB for plug flow with an arbitrary temperature profile,
2. path CD for nonisothermal plug flow with 50% recycle,
3. point E for mixed flow. Note that for mixed flow the operating line reduces to a single point.
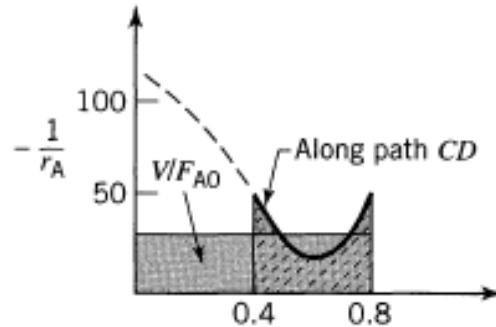
- This procedure is quite general, applicable for any kinetics, any temperature progression, and any reactor type or any series of reactors.

- So, once the operating line is known. the reactor size can be found.

Construction of the rate-conversion temperature chart from kinetic data

starting with an R-free solution, kinetic experiments in a batch reactor give 58.1% conversion in 1 min at 65^OC, 60% conversion in 10 min at 25^OC. Assuming reversible first-order kinetics, find the rate expression for this reaction and prepare the conversion-temperature chart with reaction rate as parameter.

Integrate the Performance Equation.

For a reversible first-order reaction, the performance equation for a batch reactor is

$$t = C_{A0} \int \frac{dX_A}{-r_A} = C_{A0} \int \frac{dX_A}{k_1 C_A - k_2 C_R} = \frac{1}{k_1} \int_0^{X_A} \frac{dX_A}{1 - X_A/X_{Ae}}$$

$$\frac{k_1 t}{X_{Ae}} = -\ln\left(1 - \frac{X_A}{X_{Ae}}\right)$$

Calculate the Forward Rate Constant. From the batch run at 65^oC, noting from Example that $X_{Ae} = 0.89$, we find with Eq.

$$\frac{k_1 (1 \text{ min})}{0.89} = -\ln\left(1 - \frac{0.581}{0.89}\right)$$

$$k_{1, 338} = 0.942 \text{ min}^{-1}$$

Similarly, for the batch run at 25°C we find $k_{1\ 298} = 0.0909$ min^{-1}
Assuming an Arrhenius temperature dependency, the ratio of forward rate constants at these two temperatures gives

$$\frac{k_{1,338}}{k_{1,298}} = \frac{0.942}{0.0909} = \frac{k_{10}e^{-E_1/R(338)}}{k_{10}e^{-E_1/R(298)}}$$

from which the activation energy of the forward reaction can be evaluated, giving

$$E_1 = 48\,900 \text{ J/mol} \qquad k_1 = 34 \times 10^6 \exp\left[\frac{-48\,900}{RT}\right] = \exp\left[17.34 - \frac{48\,900}{RT}\right]$$

$$A \underset{2}{\overset{1}{\rightleftharpoons}} R; \qquad K = \frac{C_{Re}}{C_{Ae}}; \quad -r_A = r_R = k_1 C_A - k_2 C_R$$
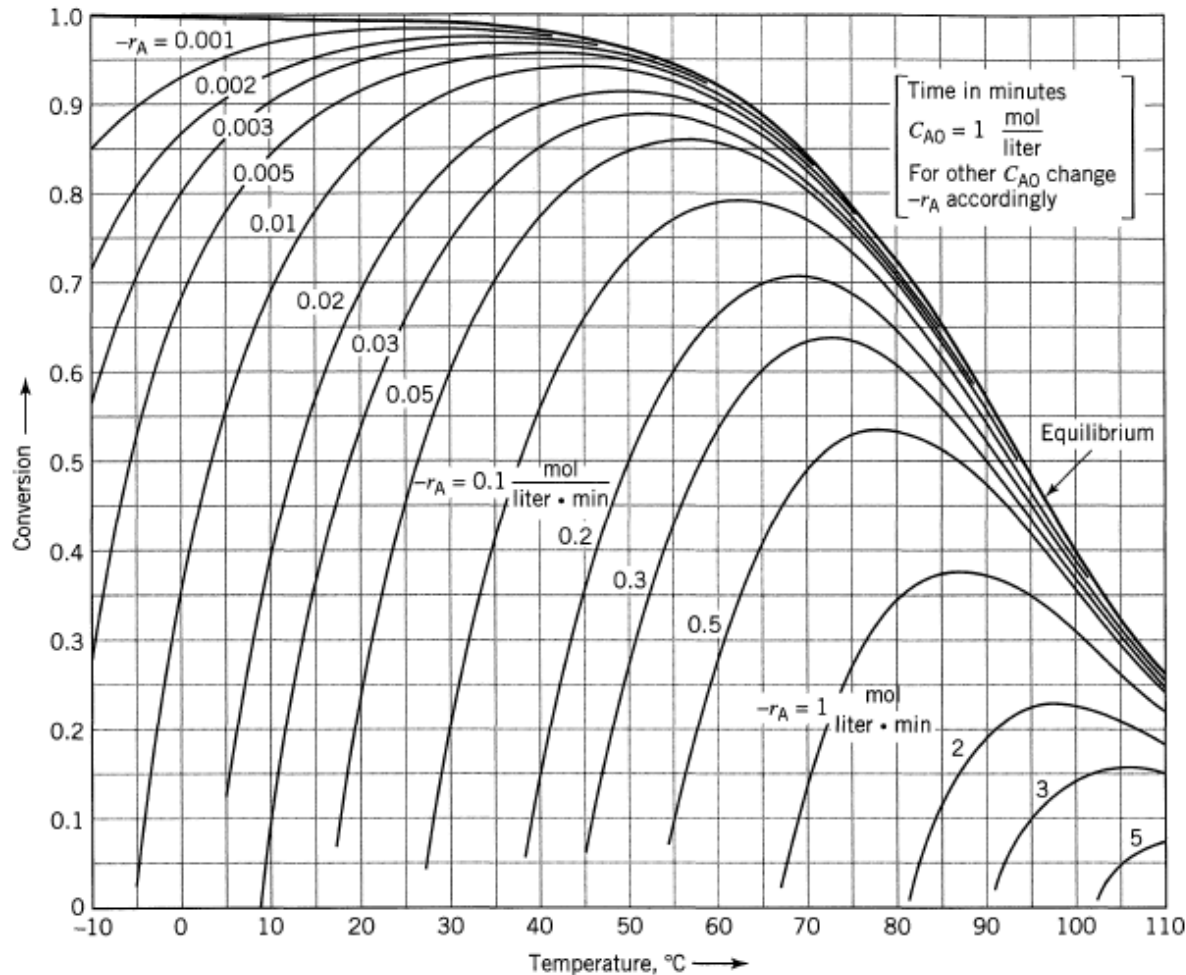
Equilibrium: $\qquad K = \exp\left[\frac{75\,300}{RT} - 24.7\right]$

Rate constants: $\quad k_1 = \exp\left[17.34 - \frac{48\,900}{RT}\right], \quad \text{min}^{-1}$

$$k_2 = \exp\left[42.04 - \frac{124\,200}{RT}\right], \quad \text{min}^{-1}$$

From these values the X_A versus T chart for any specific C_{A0} can be prepared

Figure is such a plot prepared for C_{A0} = 1 mol/liter and C_{Ro} = 0.
Since we are dealing with first-order reactions this plot can be used for any
C_{A0} value by properly relabeling the rate curves.


Thus, for C_{A0} = 10 mol/liter simply multiply all the rate values on this graph by a
factor of 10

Optimum Temperature Progression

- We define the optimum temperature progression to be that progression which minimizes V/F_{Ao} for a given conversion of reactant.

- This optimum may be an isothermal or it may be a changing temperature: in time for a batch reactor, along the length of a plug flow reactor, or from stage to stage for a series of mixed flow reactors.

- It is important to know this progression because it is the ideal which we try to approach with a real system.

- It also allows us to estimate how far any real system departs from this ideal.

- The optimum temperature progression in any type of reactor is as follows: At

- any composition, it will always be at the temperature where the rate is a maximum.

- The locus of maximum rates is found by examining the r(T, C) curves

Operating lines for minimum reactor size
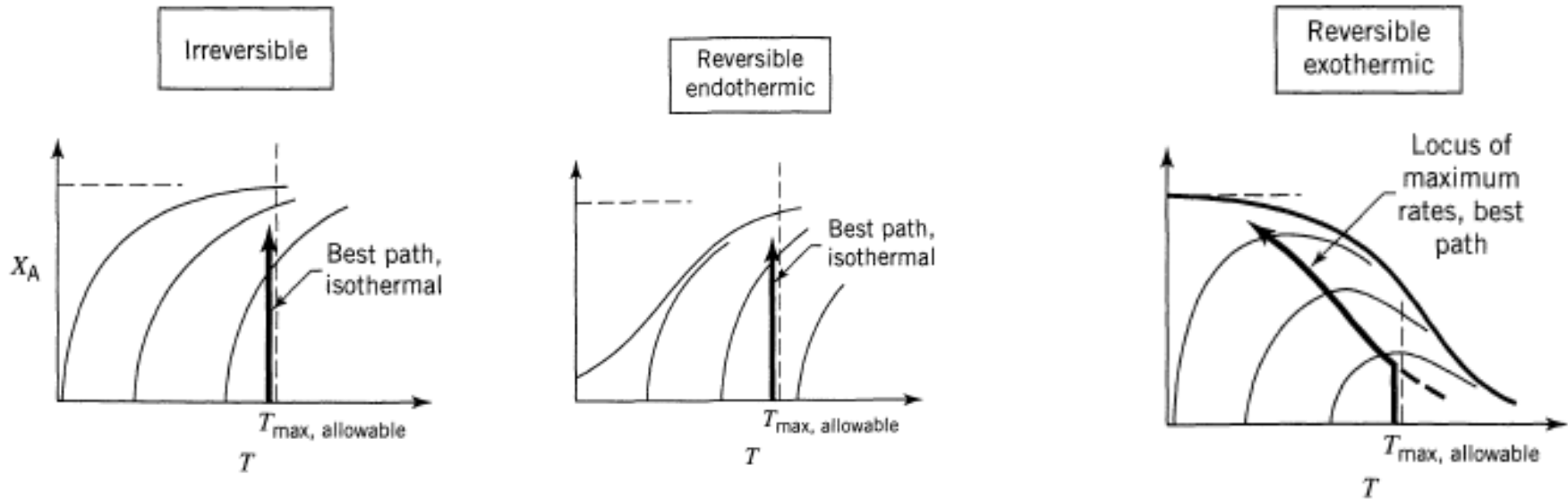
- Temperature is set by the materials of construction or by the possible increasing importance of side reactions.
- For endothermic reactions a rise in temperature increases both the equilibrium conversion and the rate of reaction.
- Thus, as with irreversible reactions, the highest allowable temperature should be used.
.

Reversible exothermic

Locus of maximum rates, best path

$T_{max, allowable}$

T
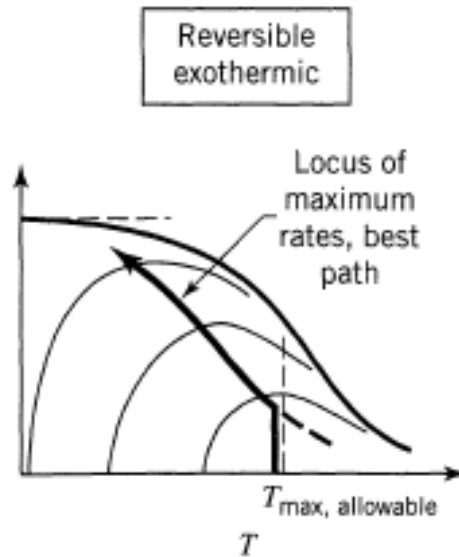
- For exothermic reversible reactions the situation is different, for here two opposing factors are at work when the temperature is raised-the rate of forward reaction speeds up but the maximum attainable conversion decreases.

- Thus, in general, a reversible exothermic reaction starts at a high temperature which decreases as conversion rises.

- Figure shows this progression, and its precise values are found by connecting the maxima of the different rate curves.

- We call this line the *locus of maximum rates.*

Heat Effects

- First of all, if the reaction is exothermic and if heat transfer is unable to remove all of the liberated heat, then the temperature of the reacting fluid will rise as conversion rises.

- By similar arguments, for endothermic reactions the fluid cools as conversion rises. Let us relate this temperature change with extent of conversion.

- We start with adiabatic operations, later extending the treatment to account for heat interchange with the surroundings.

- When the heat absorbed or released by reaction can markedly change the temperature of the reacting fluid, this factor must be accounted for in design.

- Thus we need to use both the material and energy balance expressions,

Adiabatic Operations

- Consider either a mixed flow reactor, a plug flow reactor, or a section of plug flow reactor, in which the conversion is X_A as shown in Fig.
- Usually the limiting reactant, was selected as the basis for all material balance calculations.
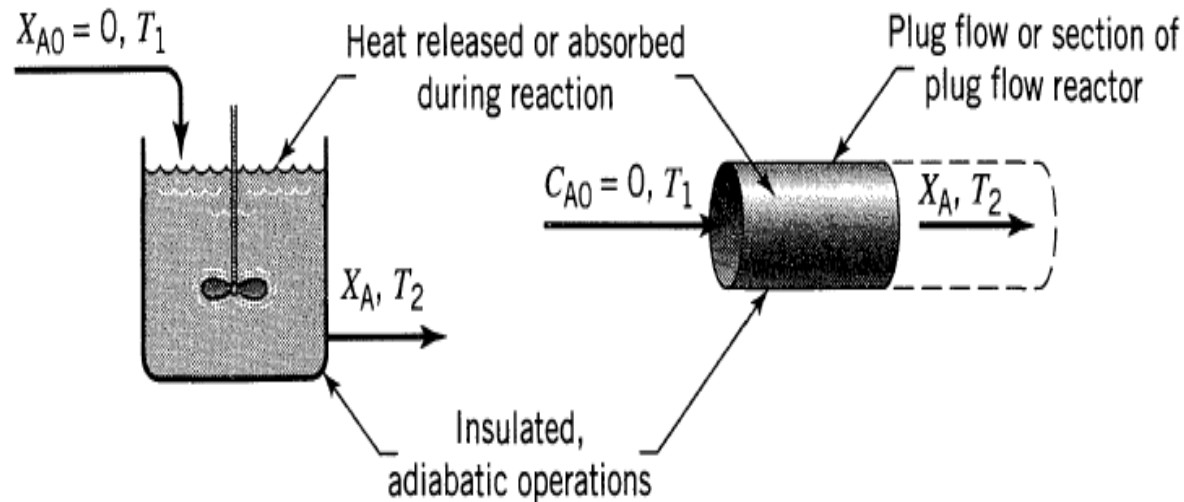
- The same procedure is used here, with limiting reactant A taken as the basis.
- Let Subscripts 1, 2 refer to temperatures of entering and leaving streams.

C'_p, C''_p = Mean specific heat of unreacted feed stream and of *completely* converted product stream per mole of entering reactant A.

H', H'' = enthalpy of unreacted feed stream and of *completely* converted product stream per mole of entering reactant A.

ΔH_{ri} = heat of reaction per mole of entering reacting A, and at temperature T_i.

With T_1 as the reference temperature on which enthalpies and heats of reaction are based we have Enthalpy of entering feed:

$$H'_1 = C'_p (T_1 - T_1) = 0 \text{ J/mol A}$$

Enthalpy of leaving stream: Energy absorbed

$$H''_2 X_A + H'_2(1 - X_A) = C''_p (T_2 - T_1)X_A + C'_p(T_2 - T_1)(1 - X_A) \text{ J/mol A}$$

Energy absorbed by reaction:

$$\Delta H_{r1} X_A \text{ J/mol A}$$

Replacing these quantities in the energy balance,
input = output + accumulation + disappearance by reaction

we obtain at steady state

$$0 = [C''_p (T_2 - T_1)X_A + C'_p (T_2 - T_1)(1 - X_A)] + \Delta H_{r1} X_A$$

$$X_A = \frac{C'_p (T_2 - T_1)}{-\Delta H_{r1} - (C''_p - C'_p) (T_2 - T_1)} = \frac{C'_p \Delta T}{-\Delta H_{r1} - (C''_p - C'_p)\Delta T}$$

$$X_A = \frac{C'_p \Delta T}{-\Delta H_{r2}} = \left(\frac{\text{heat needed to raise feed stream to } T_2}{\text{heat released by reaction at } T_2}\right) \qquad\qquad -\Delta H_{r2} = C'_p \Delta T, \qquad \text{for } X_A = 1$$

The latter form of the equation simply states that the heat released by reaction just balances the heat necessary to raise the reactants from T_l to T_2.
The relation between temperature and conversion, as given by the energy balances of Eq. is shown in Fig.
The resulting lines are straight for all practical purposes since the variation of the denominator term of these equations is relatively small.
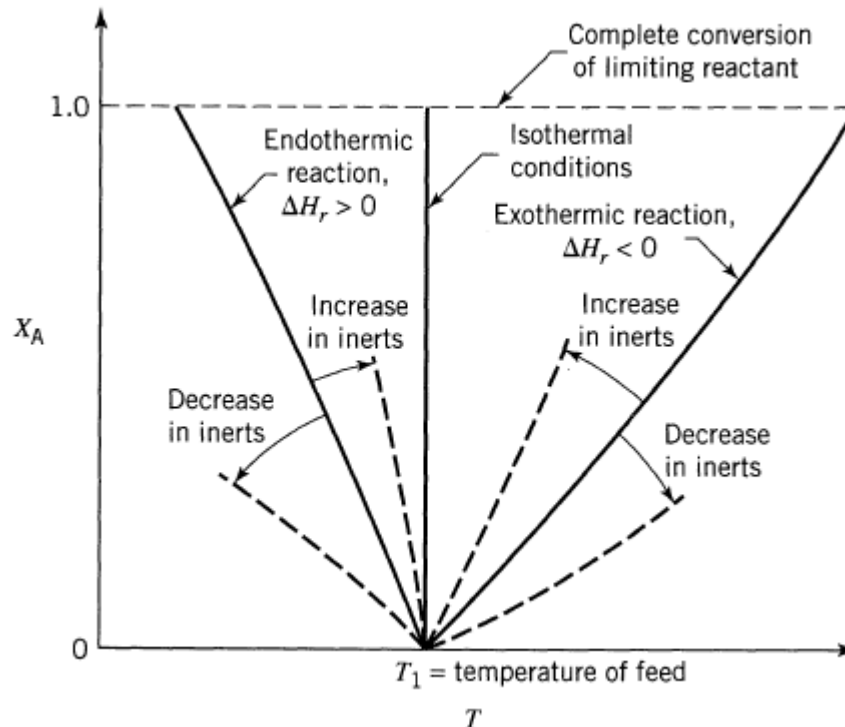
When $C_p'' - C_p' = 0,$ the heat of reaction is independent of temperature and Eqs. reduce to

$$X_A = \frac{C_p \Delta T}{-\Delta H_r}$$

- This figure illustrates the shape of the energy balance curve for both endothermic and exothermic reactions for both mixed flow and plug flow reactors.

- This representation shows that whatever is the conversion at any point in the reactor, the temperature is at its corresponding value on the curve.

- For plug flow the fluid in the reactor moves progressively along the curve,

- For mixed flow the fluid immediately jumps to its final value on the curve.

- These are the adiabatic operating lines for the reactor.

- With increased inerts C_p rises, and these curves become more closely vertical.

- A vertical line indicates that temperature is unchanged as reaction proceeds.

Reactor size for Adiabatic operations

- For plug flow tabulate the rate for various X_A along this adiabatic operating line,

- Prepare the $1/(-r_A)$ versus X_A plot and integrate.

- The best adiabatic operations of a single plug flow reactor are found by shifting the operating line (changing the inlet temperature) to where the rates have the highest mean value.

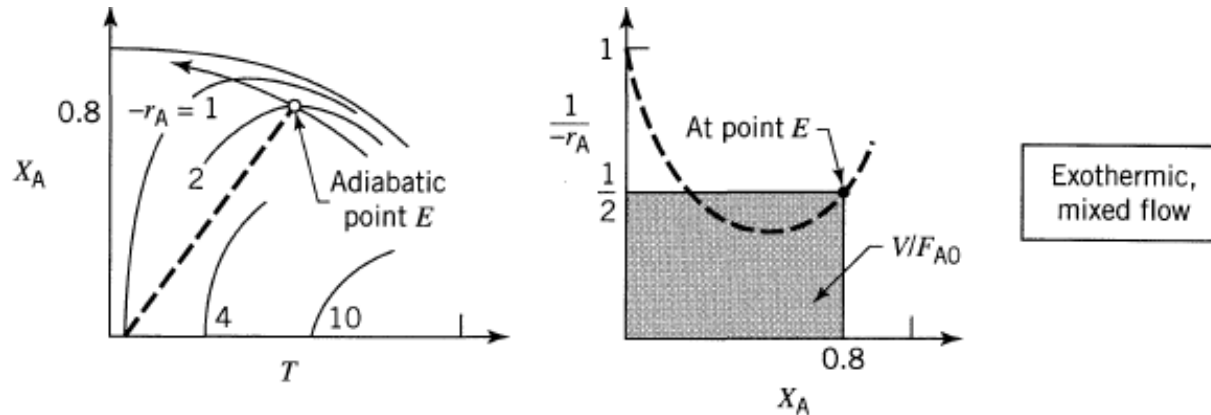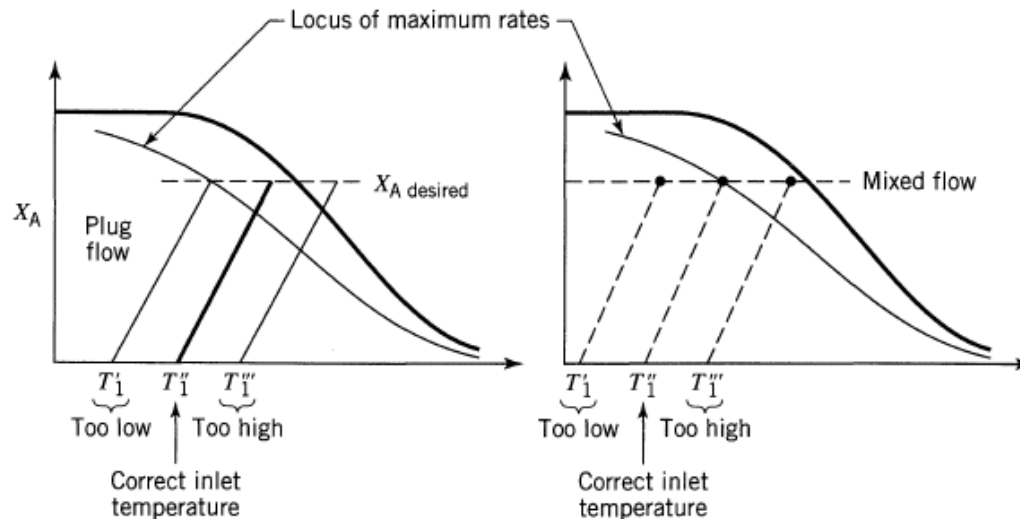- For endothermic operations this means starting at the highest allowable temperature.
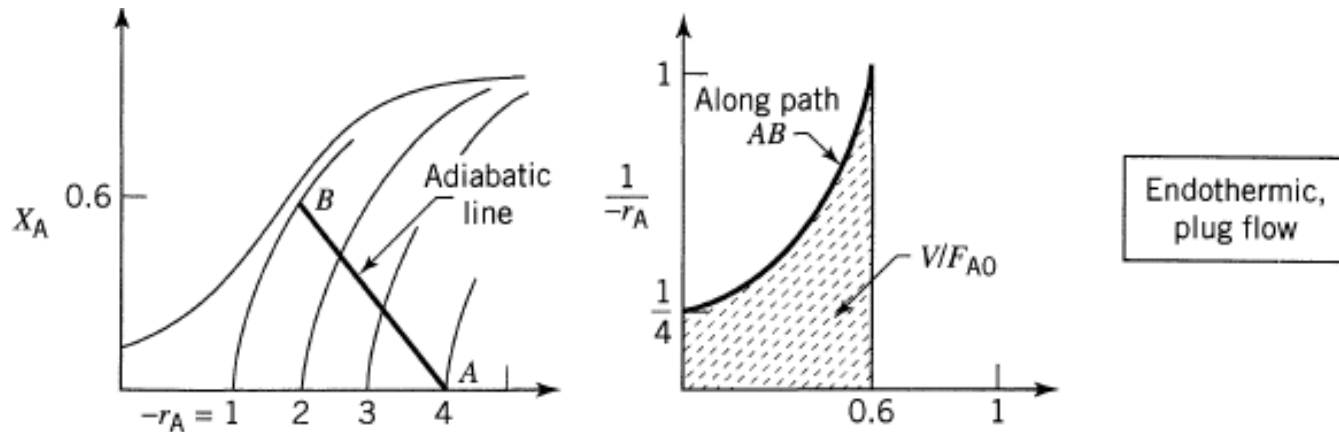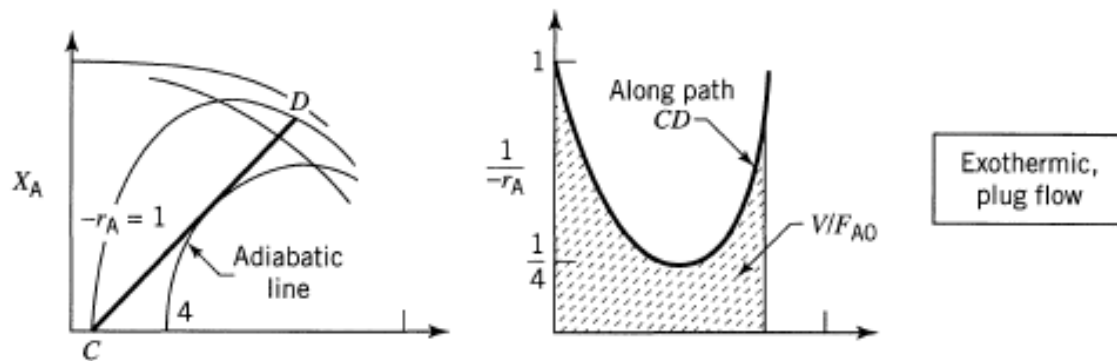
- The best reactor type, that which minimizes V/F_{Ao} is found directly from this X_A versus T graph.
- If the rate progressively decreases with conversion, then use plug flow.
- This is the case for endothermic reactions and close to isothermal exothermic reactions.
- For exothermic reactions that have a large temperature rise during reaction, the rate rises from a very low value to a maximum at some intermediate X_A, then falls.
- This behavior is characteristic of autocatalytic reactions, thus recycle operations are best.

Mixed flow Reactor

- For mixed flow simply use the rate at the conditions within the reactor.

For endothermic operations this means starting at the highest allowable temperature.

Best location for the adiabatic operating line

For plug flow, a trial and error search is needed to find this line;

for mixed flow, no search is needed

For exothermic reactions this means straddling the locus of maximum rates as shown

A few trials will locate the best inlet temperature, that which minimizes V/F_{Ao}

For mixed flow the reactor should operate on the locus of maximum rates.

For exothermic reactions mixed flow is best where the temperature rise is large;

Plug flow is best for close to isothermal systems.
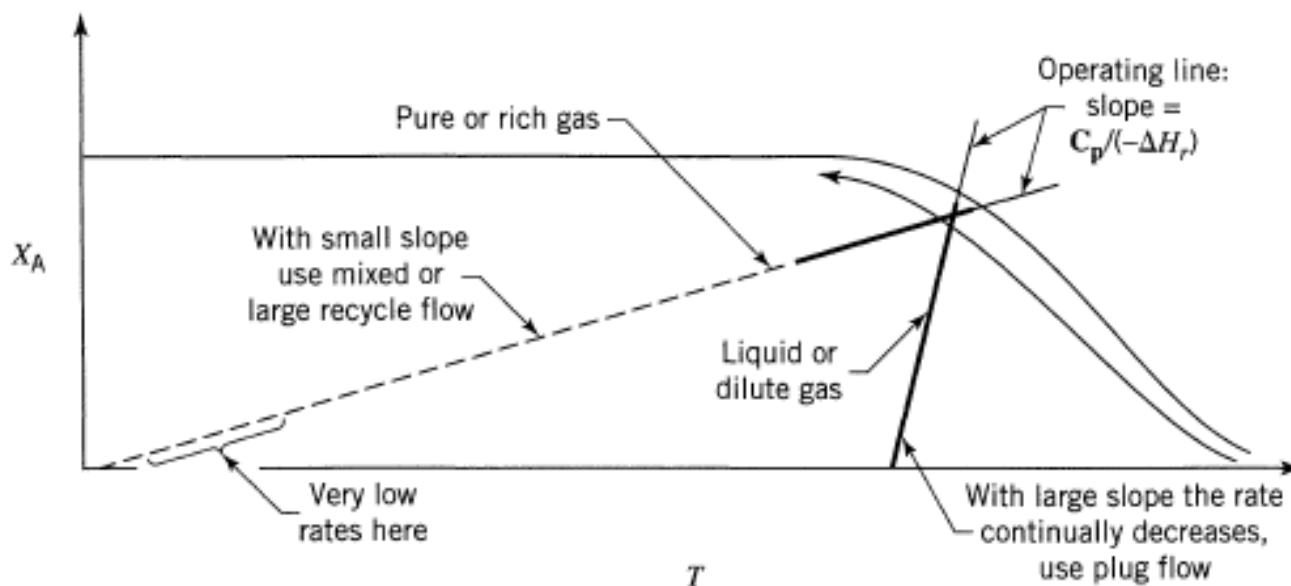
Illustrates two situations, one where plug flow is best, the other where large recycle or mixed flow is best.
The slope of the operating line, Cp/-ΔHr will determine which case one has at hand.
Thus

1. for small $C_p/-\Delta H_r$ (pure gaseous reactants) mixed flow is best.
2. for large $C_p/-\Delta H_r$ (gas with much inerts, or liquid systems) plug flow is best.

Let us see how these forms of heat interchange modify the shape of the adiabatic operating line.
Let Q be the total heat *added* to a reactor *per mole* of entering reactant A, and let this heat also include the losses to the surroundings.

Then previous Eq. (input=0), The energy balance about the system, is modified to

$$Q = C_p''(T_2 - T_1) X_A + C_p'(T_2 - T_1)(1 - X_A) + \Delta H_{r1} X_A$$

$$X_A = \frac{C_p' \Delta T - Q}{-\Delta H_{r2}} = \left(\frac{\begin{array}{c}\text{net heat still needed after heat} \\ \text{transfer to raise feed to } T_2\end{array}}{\text{heat released by reaction at } T_2} \right)$$

and for $C_p'' = C_p'$, which often is a reasonable approximation

$$X_A = \frac{C_p \Delta T - Q}{-\Delta H_r}$$

With heat input proportional to $\Delta T = T_2 - T_1$ the energy balance line rotates about T_1. This change is shown in Fig. 9.11. Other modes of heat addition or removal yield corresponding shifts in the energy balance line.

Using this modified operating line, the procedure for finding the reactor size and optimum operations follows directly from the discussion on adiabatic operations.

Adiabatic operations of an exothermic reaction give a rising temperature with conversion.
However, the desired progression is one of falling temperature.
Very drastic heat removal may be needed to make the operating line approach the ideal, and many schemes may be proposed to do this.

Sketch of the energy balance equation showing the shift in adiabatic line caused by heat exchange with surroundings.
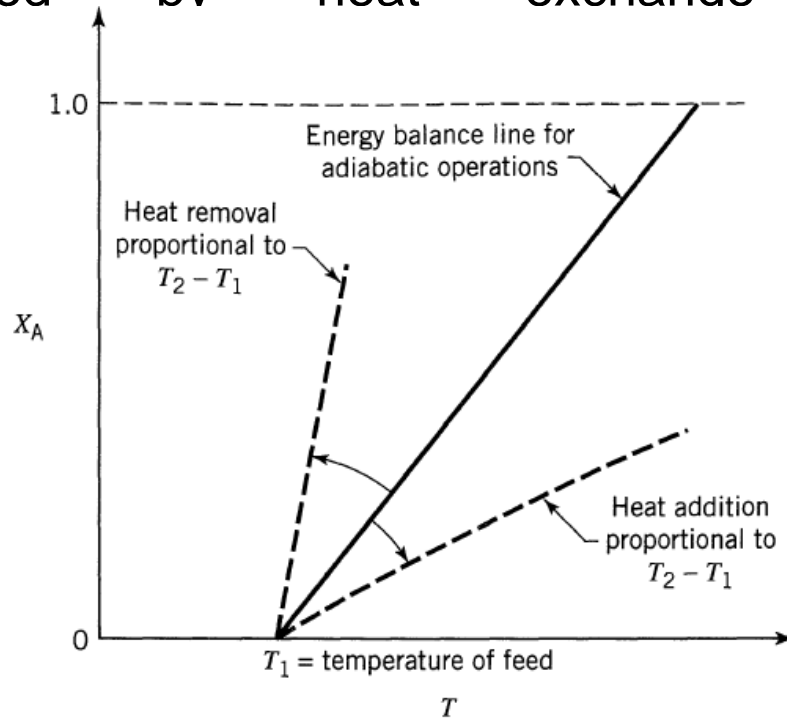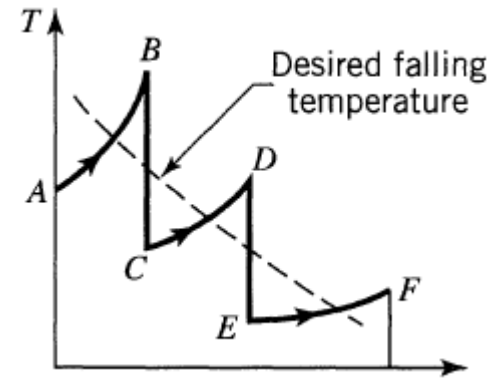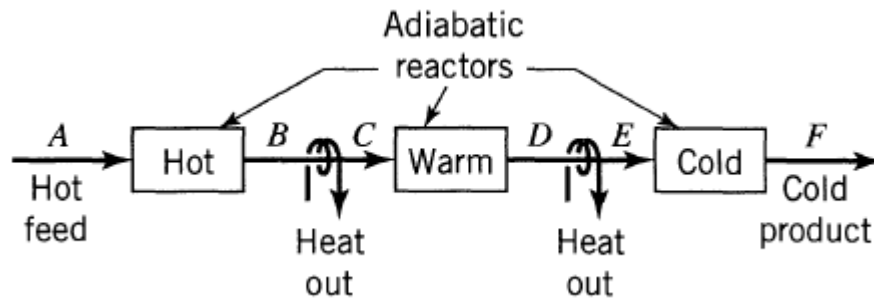

As an example, we may have heat exchange with the incoming fluid.
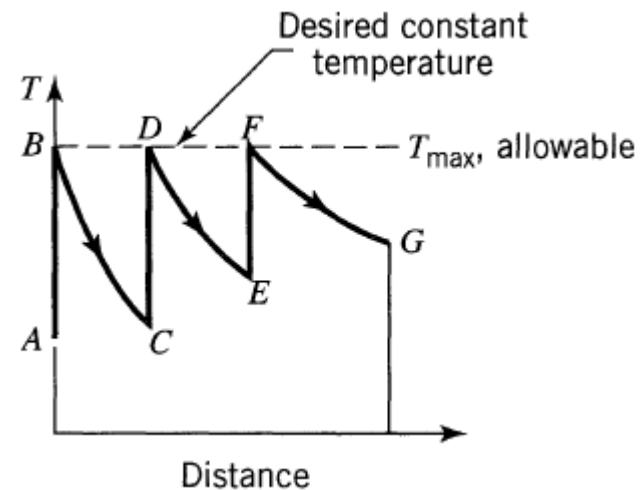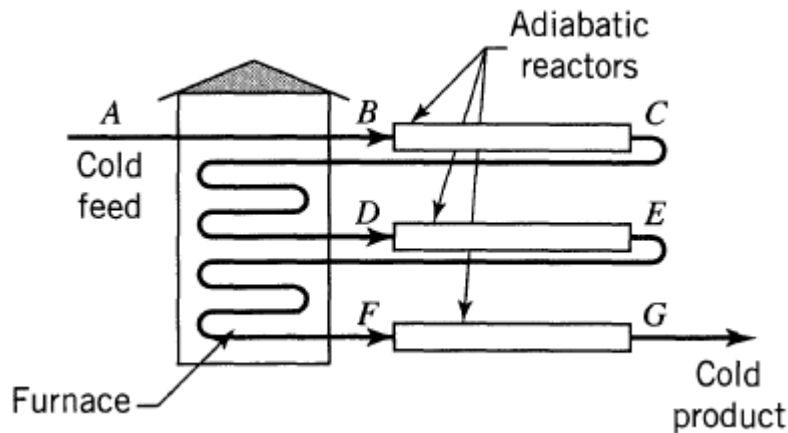Exothermic reaction
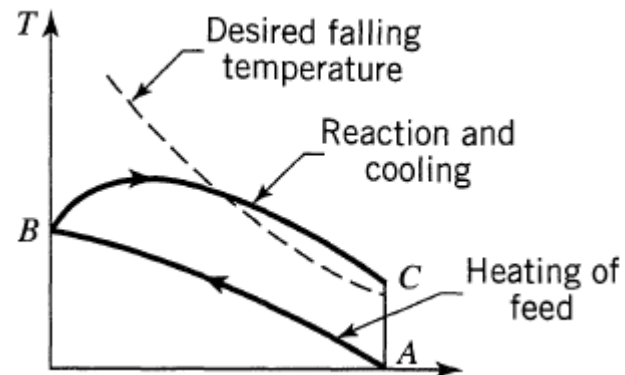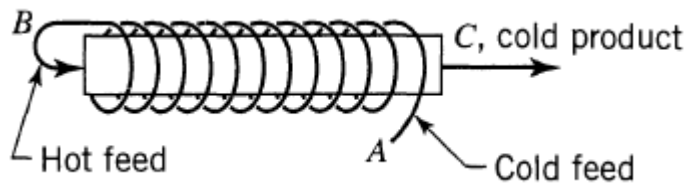
- Another alternative is to have multistage operations with interstage cooling between adiabatic sections.

Exothermic reaction

In general multistaging is used when it is impractical to effect the necessary heat exchange within the reactor itself.
This is usually the case with gas-phase reactions with their relatively poor heat transfer characteristics.

For endothermic reactions, multi-staging with reheat between stages is commonly used to keep the temperature from dropping too low.

# Exothermic Reactions in Mixed Flow Reactors-A Special Problem

- For exothermic reactions in mixed flow (or close to mixed flow) an interesting situation may develop in that more than one reactor composition may satisfy the governing material and energy balance equations.

- This means that we may not know which conversion level to expect.

- Let us examine it.

- First, consider reactant fluid fed at a given rate (fixed r or V/F_{Ao}) to a mixed flow reactor.

- At each reactor temperature there will be some particular conversion which satisfies the material balance equation,

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{\Delta X_A}{-r_A} = \frac{X_A}{-r_A}$$

$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A}$$

any ε_A

- At low temperature the rate is low so this conversion is low.

- At higher temperature the conversion rises and approaches the equilibrium.

- At a still higher temperature we enter the region of falling equilibrium so the conversion for given T will likewise fall.
- Figure illustrates this behavior for different T values.
- Note that these lines do not represent an operating line or a reaction path.
- Actually any point on these curves represents a particular solution of the material balance equations; thus,
-
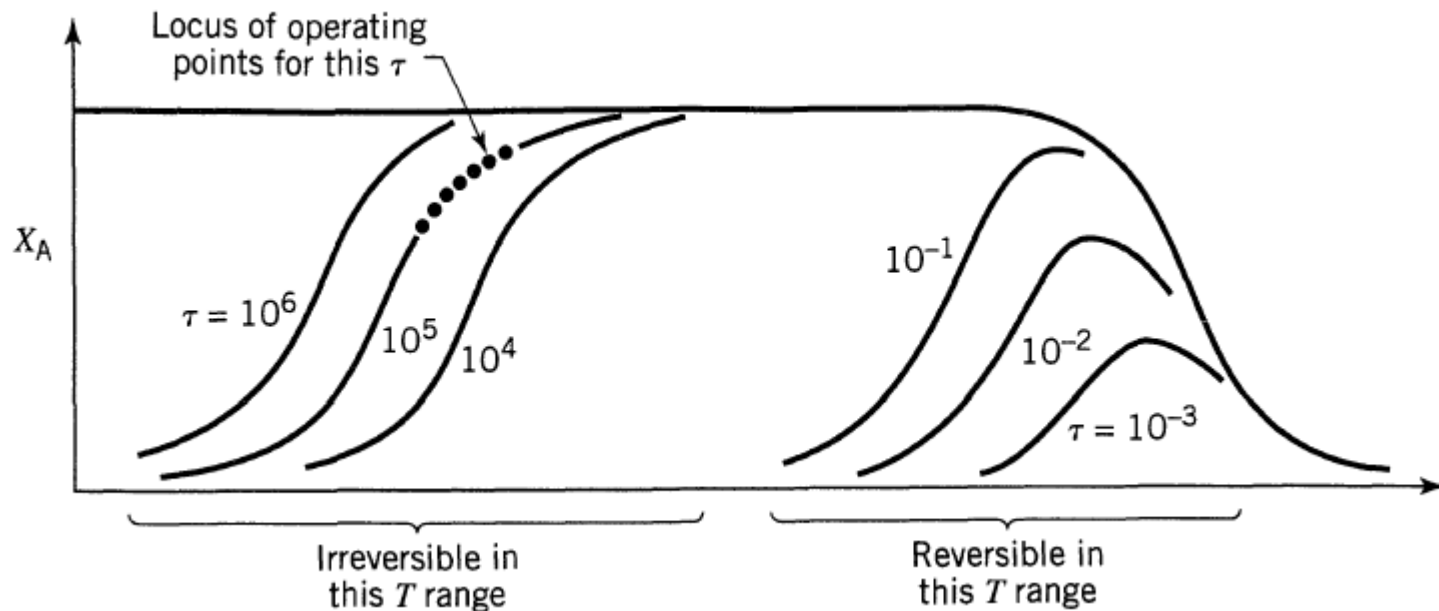
Conversion in a mixed flow reactor as a function of T and τ, from the material balance equation,

Now, for a given feed temperature T, the intersection of the energy balance line with the S-shaped material balance line for the operating T gives the conditions within the reactor.

Here three cases may be distinguished. These are shown in Fig. for *irreversible reactions* Three types of solutions to the energy and material balances for exothermic irreversible reactions.
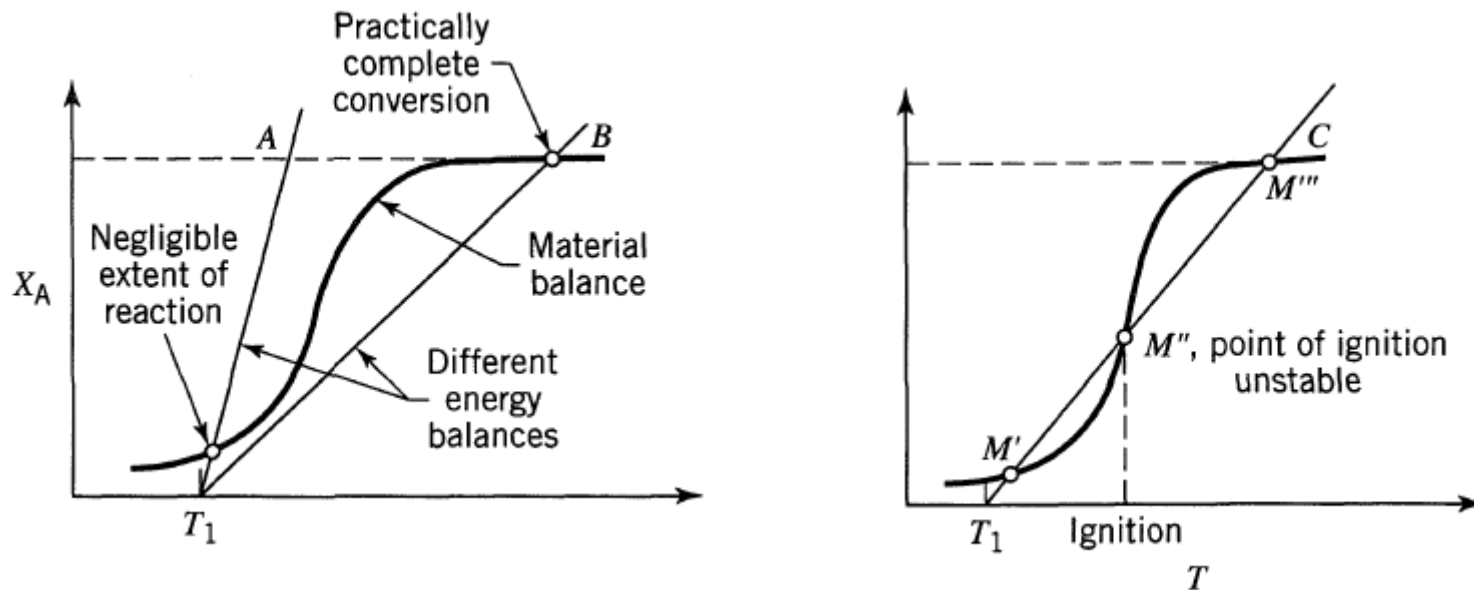
First, the energy balance line T_1A represents the situation where insufficient heat is liberated by reaction to raise the temperature to a high enough level for the reaction to be self-sustaining.
Hence, conversion is negligible.

- At the other extreme, if we have more than enough heat liberated, the fluid will be hot and conversion essentially complete.

- This is shown as line T_lB. Finally, line T_lC indicates an intermediate situation which has three solutions to the material and energy balance equations, points *M', M", and M"'.*

- However, point *M"* is an unstable state because with a small rise in temperature the heat produced (with the rapidly rising material balance curve) is greater than the heat consumed by the reacting mixture (energy balance curve).

- The excess heat produced will make the temperature rise until *M"'* is reached.

- By similar reasoning, if the temperature drops slightly below *M"* it will continue to drop until *M'* is reached.

- Thus, we look upon *M"* as the ignition point.

- If the mixture can be raised above this temperature, then the reaction will be self-sustaining.

- For reversible exothermic reactions the same three cases occur, as shown in Fig. below.
- However, it can be seen that here there is an optimum operating
- temperature for the given T value where conversion is maximized.
- Above or below this temperature the conversion drops; thus, proper control of heat removal is essential.
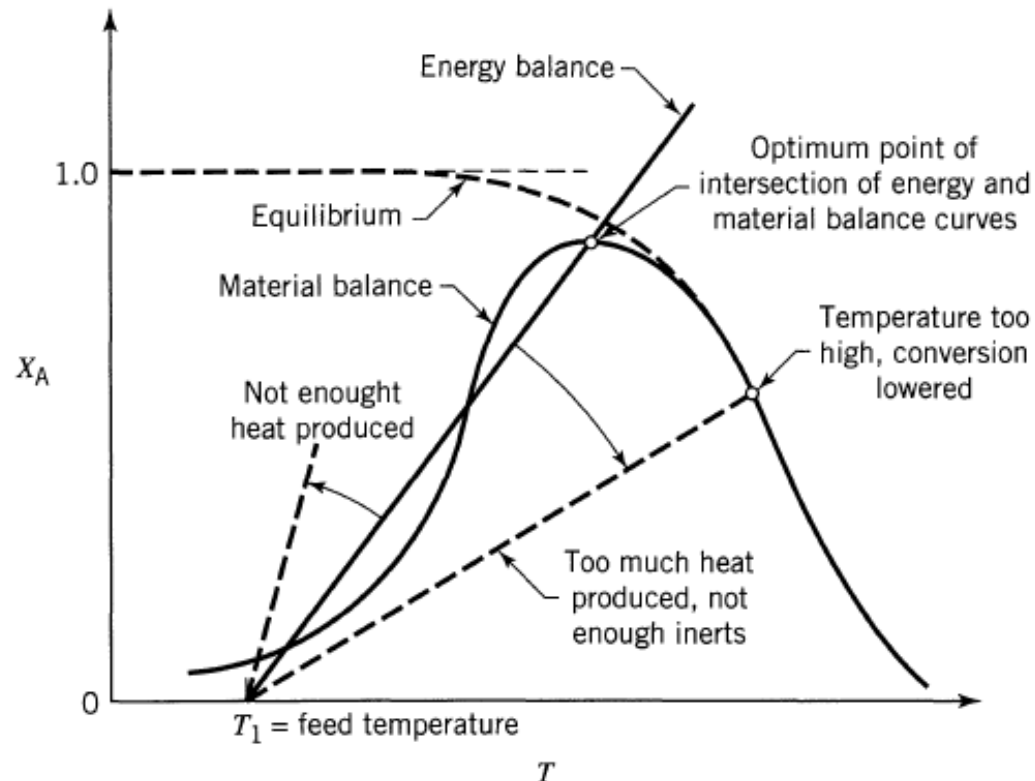
Solution of energy and material balances for reversible exothermic reaction.

- The type of behavior described here occurs in systems where the slope of the energy balance line,

- $C_P/-\Delta H_r$ is small; thus, large liberation of heat and pure reactants which leads to far from isothermal operations.

- In addition, though it is a much more complex situation, a gas flame illustrates well multiple solutions discussed here: the unreacted state, the reacted state, and the ignition point.

- Reactor dynamics, stability, and start-up procedures are particularly important for auto-induced reactions such as these.

- For example, a small change in feed rate (τ value), feed composition or temperature, or heat transfer rate may cause the reactor output to jump from one operating point to the other.

PERFORMANCE FOR THE OPTIMAL TEMPERATURE ROGRESSION

(a) calculate the space time and volume needed for 80% conversion of a feed of $F_{A0} = 1000$ mol/min where $C_{A0} = 4$ mol/liter.

(b) plot the temperature and conversion profile along the length of the reactor.

Let the maximum allowable operating temperature be 95°C.

Note that Fig. E9.3 was prepared for $C_{A0} = 1$ mol/liter, not 4 mol/liter.

(a) *Minimum Space-Time.* On the conversion-temperature graph draw the locus of maximum rates. Then, remembering the temperature restriction, draw the optimum path for this system (line *ABCDE* in Fig)
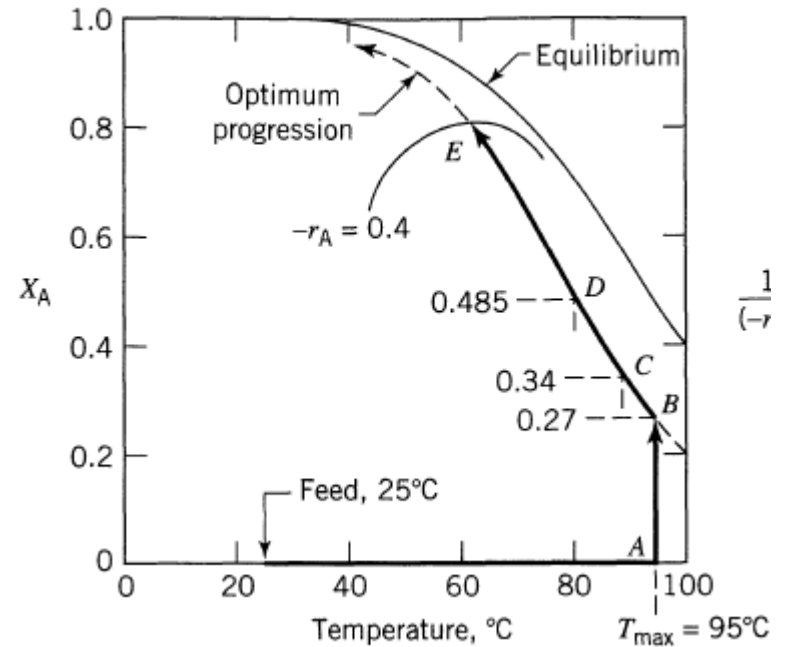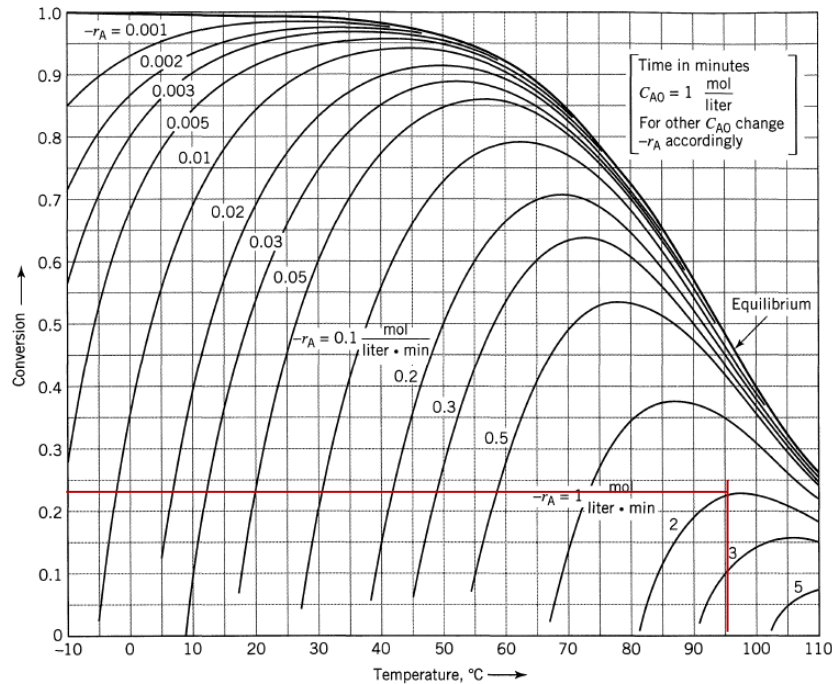
integrate graphically along this path to obtain

$$= \quad \frac{\tau}{C_{A0}} = \frac{V}{F_{A0}} = \int_0^{0.8} \frac{dX_A}{(-r_A)_{\text{optimum path ABCDE}}}$$

$$\left(\frac{\text{shaded area}}{} \right) = 0.405 \text{ liter/mol} \cdot \text{min}$$

In addition we note that the temperature starts at 95°C, and at $X_A = 0.27$ (point B) it drops. Measuring areas in Fig. we see that this happens after the fluid has passed 7% of the distance through the reactor.

$$\underline{\underline{\tau}} = C_{A0}\,(\text{area}) = (4\;\text{mol/liter})\,(0.405\;\text{liter}\cdot\text{min/mol}) = \underline{1.62\;\text{min}}$$

$$\underline{\underline{V}} = F_{A0}\,(\text{area}) = (1000\;\text{mol/min})\,(0.405\;\text{liter}\cdot\text{min/mol}) = \underline{405\;\text{liters}}$$

In this manner the temperature and conversion profiles are found. The result is shown in Fig.
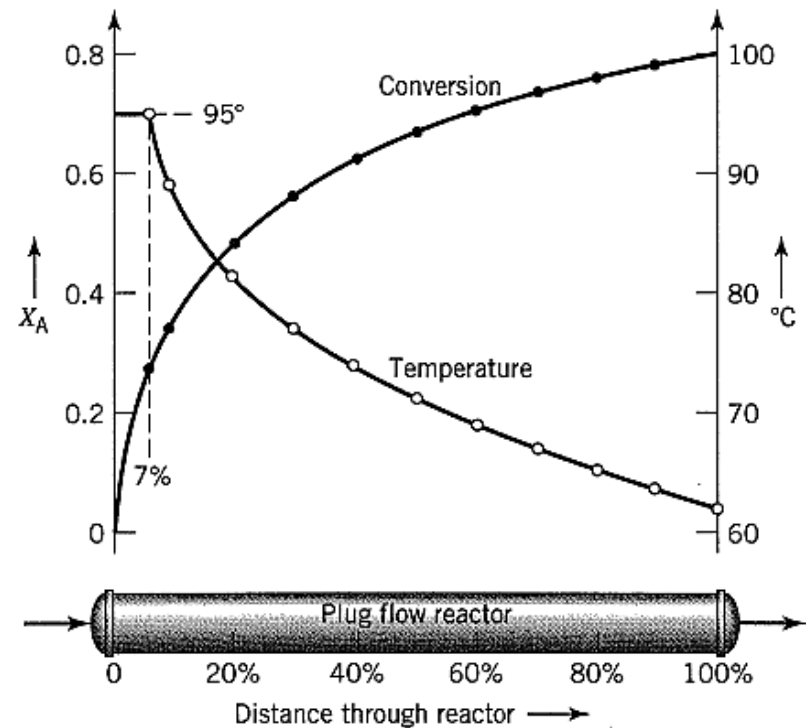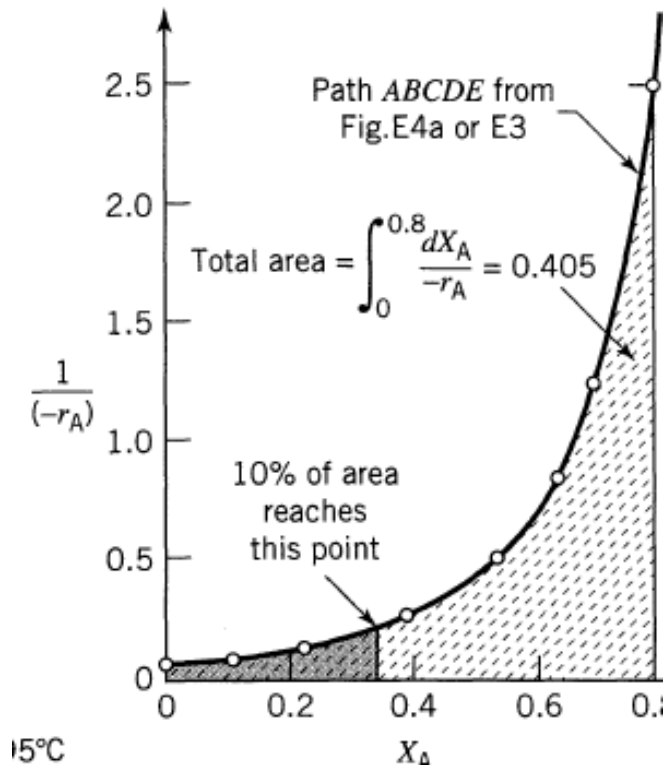
(b) T and X_A Profiles Through the Reactor. Let us take 10% increments through the reactor by taking 10% increments in area under the curve of Fig. E9.4b. This procedure gives $X_A = 0.34$ at the 10% point, $X_A = 0.485$ at the 20% point, etc. The corresponding temperatures are then 362 K at $X_A = 0.34$ (point C), 354 K at $X_A = 0.485$ (point D), etc.

OPTIMUM MIXED FLOW REACTOR PERFORMANCE

A concentrated aqueous A-solution of the previous examples (C_{Ao}= 4 mol/liter, F_{Ao} = 1000 mol/min) is to be 80% converted in a mixed flow reactor.

(a) What size of reactor is needed?

(b) What is the heat duty if feed enters at 25°C and product is to be withdrawn at this temperature?

$$C_{pA} = \frac{1000 \text{ cal}}{\text{kg} \cdot \text{K}} \cdot \frac{1 \text{ kg}}{1 \text{ liter}} \cdot \frac{1 \text{ liter}}{4 \text{ mol A}} = 250 \frac{\text{cal}}{\text{mol A} \cdot \text{K}}$$

(a) Reactor Volume. For C_{Ao} = 4 mol/liter we may use the X_A versus T chart of Fig. as long as we multiply all rate values on this chart by 4.
Following Fig. 9.9 the mixed flow operating point should be located where the locus of optima intersects the 80% conversion line (point C on Fig. E9.5~).
Here the reaction rate has the value
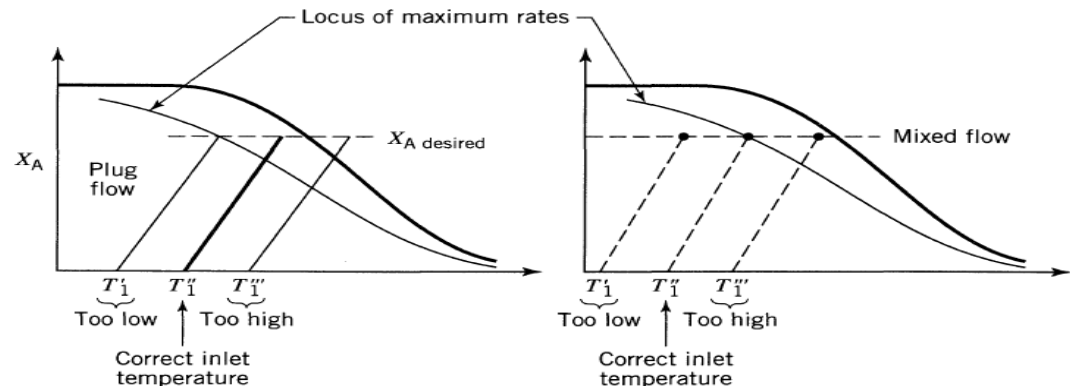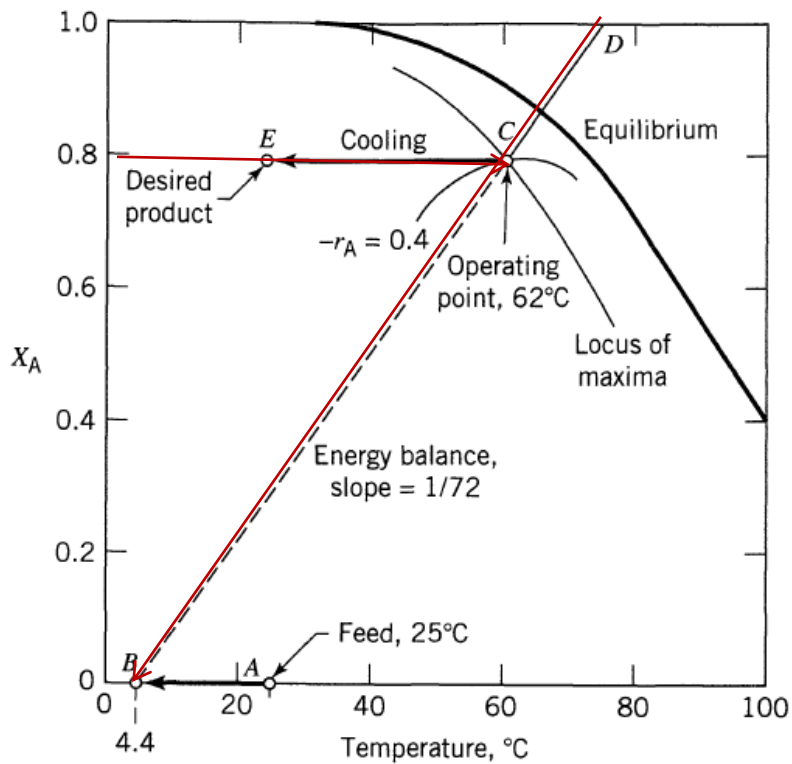
Following Fig. 9.9 the mixed flow operating point should be located where the locus of optima intersects the 80% conversion line (point C). Here the reaction rate has the value

$$-r_A = 0.4 \text{ mol A converted/min} \cdot \text{liter}$$

$$\underline{\underline{V}} = \frac{F_{A0}X_A}{(-r_A)} = \frac{(1000 \text{ mol/min})\,(0.80)}{0.4 \text{ mol/min} \cdot \text{liter}} = \underline{\underline{2000 \text{ liters}}}$$

(b) *Heat Duty.* Of course we can use joules in our calculations; however, since we are dealing with aqueous solutions it is simpler to use calories.
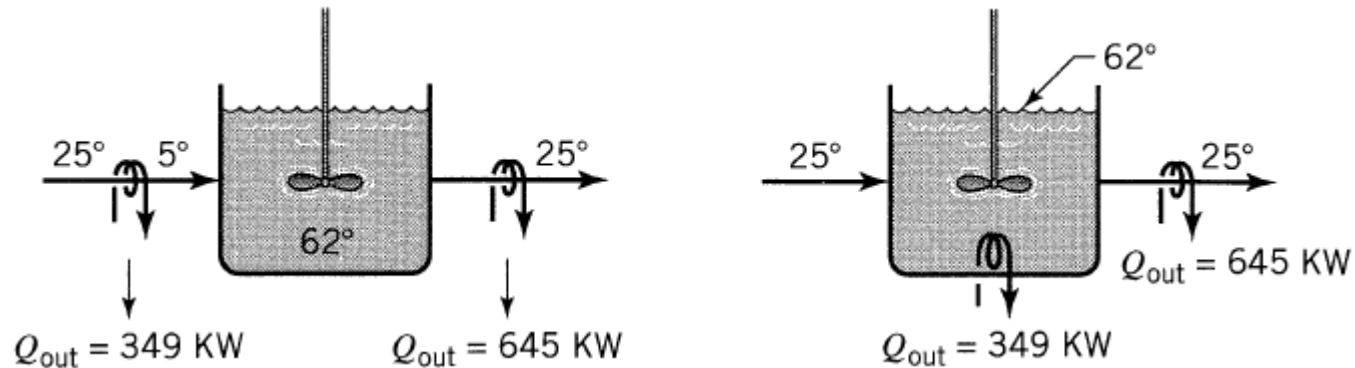
Let us use calories. Then the slope of the energy balance line is

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{(250\,\text{cal/mol A} \cdot \text{K})}{18\,000\,\text{cal/mol A})} = \frac{1}{72}\,\text{K}^{-1}$$

Drawing this line through point C (line BCD) we see that the feed must be cooled 20° (from point A to point B) before it enters and reacts adiabatically. Also, the product must be cooled 37°C (from point C to point E). Thus the heat duty is   (62-25)

$$\underline{\underline{\text{Precooler:}}}\ Q_{AB} = (250\,\text{cal/mol A} \cdot \text{K})(20\,\text{K}) = 5000\,\text{cal/mol A fed}$$

$$= (5000\,\text{cal/mol A})(1000\,\text{molA/min}) = 5000\,000\,\text{cal/min}$$

$$= \underline{\underline{348.7\,\text{kW}}}$$

$$\underline{\underline{\text{Postcooler:}}}\ Q_{CE} = (250)(37) = 9250\,\text{cal/mol A fed}$$

$$= (9250)(1000) = 9250\,000\,\text{cal/min}$$

$$= \underline{\underline{645.0\,\text{kW}}}$$

$25°$ $5°$ $25°$ $62°$
$62°$ $25°$ $25°$
$Q_{out} = 349$ KW $Q_{out} = 645$ KW $Q_{out} = 645$ KW
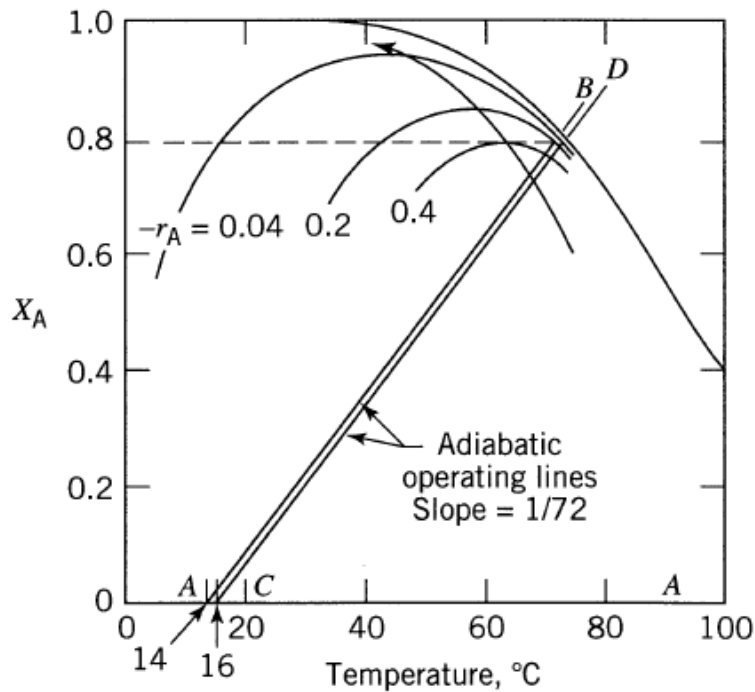 $Q_{out} = 349$ KW
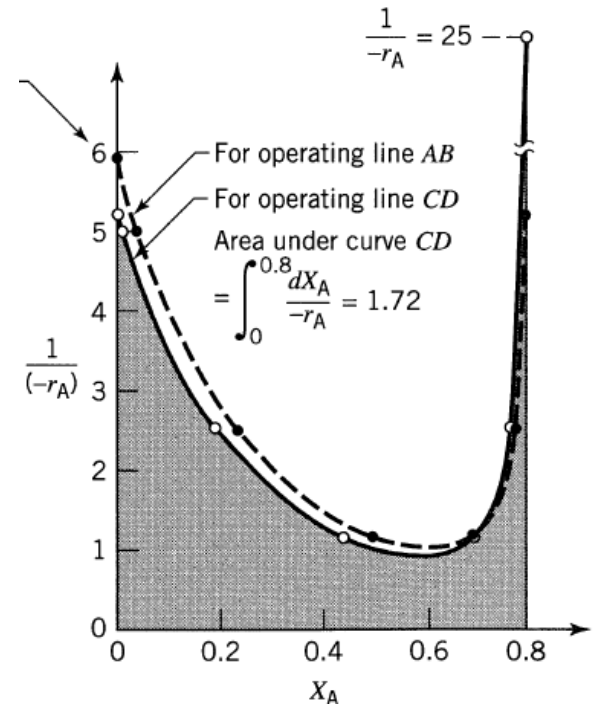
ADIABATIC PLUG FLOW REACTOR PERFORMANCE

Size of adiabatic plug flow reactor to react the feed of above Example (F_{Ao} = 1000 mol/min and C_{Ao} = 4 mol/liter) to 80% conversion.

Following the procedure of Fig. 9.9 draw trial operating lines (see Fig. E9.6~)
with a slope of (from Example 9.5), and for each evaluate the integral

- Draw trial operating lines Fig. with a slope of $\frac{1}{72}$ from Example and for each evaluate the integral

$$\int_0^{0.8} \frac{dX_A}{-r_A}$$

$\frac{1}{-r_A} = 25 \; -\!-\!\!\circ$

For operating line AB
For operating line CD
Area under curve CD

$$= \int_0^{0.8} \frac{dX_A}{-r_A} = 1.72$$

$$\underline{V} = F_{A0} \int_0^{0.8} \frac{dX_A}{-r_A} = F_{A0} \, (\text{area under curve } CD)$$

$$= (1000 \, \text{mol/min})(1.72 \, \text{liter} \cdot \text{min/mol})$$

$$= 1720 \, \text{liters}$$

therefore the desired adiabatic operating line.

- This volume is some what smaller than the volume of mixed flow reactor but it is still four times as large as the minimum possible (405 Liters).
- Regarding temperatures: Figure shows that the feed must first be cooled to 16.0°C, it then passes through the adiabatic reactor and leaves at 73.6^{O}C and 80% conversion.

ADIABATIC PLUG FLOW REACTOR WITH RECYCLE

- For operating line CD of above Example, we find an optimum recycle area, shown in Fig. as rectangle EFGH.
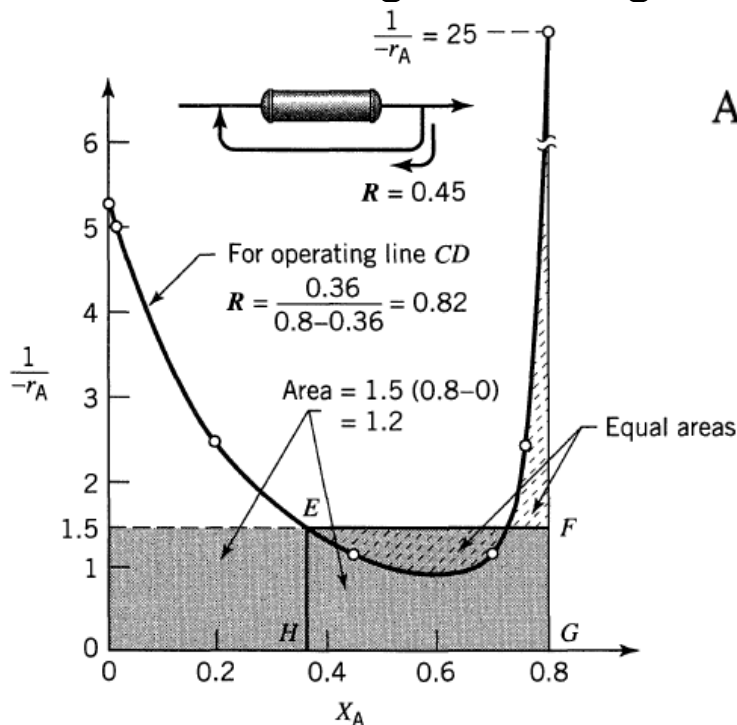
$$Area = (0.8 - 0)(15 \text{ liter} \cdot \text{min/mol}) = 1.2 \text{ liter} \cdot \text{min/mol}$$

$$\underline{V} = F_{A0} (\text{area}) = (1000 \text{ mol/min})(1.2 \text{ liter/mol} \cdot \text{min}) = \underline{\underline{1200 \text{ liter}}}$$

summarize the results of these four examples, all are performing the same duty with the same feed

for the plug flow with optimal T progression	$V = $ 405 liter (Example 4)
for the mixed flow reactor	$V = 2000$ liter (Example 5)
for the adiabatic plug flow reactor	$V = 1720$ liter (Example 6)
for the adiabatic recycle reactor	$V = 1200$ liter (Example 7)

- **Product Distribution and Temperature**
- If two competing steps in multiple reactions have rate constants k_1, and k_2, then the relative rates of these steps are given by

$$\frac{k_1}{k_2} = \frac{k_{10}e^{-E_1/RT}}{k_{20}e^{-E_2/RT}} = \frac{k_{10}}{k_{20}} e^{(E_2 - E_1)/RT} \propto e^{(E_2 - E_1)/RT}$$

This ratio changes with temperature depending on whether E_1 is greater or smaller than $\mathbf{E_2}$ so

$$\text{when } T \text{ rises} \begin{cases} k_1/k_2 \text{ increases if } \mathbf{E}_1 > \mathbf{E}_2 \\ k_1/k_2 \text{ decreases if } \mathbf{E}_1 < \mathbf{E}_2 \end{cases}$$

Thus the reaction with larger activation energy is the more temperature-sensitive of the two reactions.

This finding leads to the following general rule on the influence of temperature on the relative rates of competing reactions:

A high temperature favors the reaction of higher activation energy, a low temperature favors the reaction of lower activation energy.

Let us apply this rule to find the proper temperature of operations for various types of multiple reactions.

- For parallel reactions

$$A \begin{array}{c} \nearrow^{1} R_{desired} \\ \searrow^{2} S_{unwanted} \end{array}$$
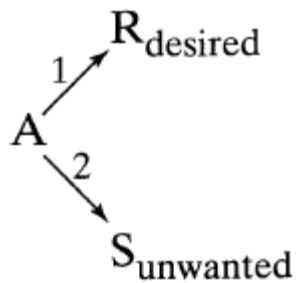
Step 1 is to be promoted, step 2 depressed, so k_1/k_2 is to be made as large as possible.
Thus, from the above rule

$$\left. \begin{array}{l} \text{if } E_1 > E_2 \text{ use high } T \\ \text{if } E_1 < E_2 \text{ use low } T \end{array} \right\}$$
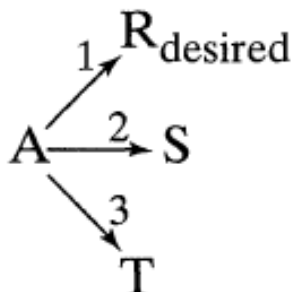
- For *reactions in series*

$$A \xrightarrow{1} R_{desired} \xrightarrow{2} S$$

production of R is favored if k_1/k_2 is increased. Thus

$$\left. \begin{array}{l} \text{if } E_1 > E_2 \text{ use high } T \\ \text{if } E_1 < E_2 \text{ use low } T \end{array} \right\}$$

-
$$A \begin{array}{c} \nearrow^{1} R_{desired} \\ \xrightarrow{2} S \\ \searrow^{3} T \end{array}$$

where $E_1 > E_2, E_1 < E_3$

For the general series-parallel reaction we introduce two additional considerations.

- First of all for *parallel steps* if one requirement is for a high temperature and another is for a low temperature, then a particular intermediate temperature is best in that it gives the most favorable product distribution.

Now, $E_1 > E_2$ requires a high T, $E_1 < E_3$ requires a low T, and it can be shown that the most favorable product distribution is obtained when the temperature satisfies the following condition

$$\frac{1}{T_{\text{opt}}} = \frac{R}{E_3 - E_2} \ln \left[\frac{E_3 - E_1}{E_1 - E_2} \frac{k_{30}}{k_{20}} \right]$$

- Second, for *steps* in *series* if an early step needs a high temperature and a later step needs a low temperature, then a falling progression of temperatures should be used.
- Analogous arguments hold for other progressions.
- The problems at the end of this chapter verify some of the qualitative findings on *To,,* and also show some possible extension.