SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I – Chemical Reaction Engineering-1 – SCHA1402

1.1 Basic Reaction Theory

A chemical reaction is a process that leads to the transformation of one set of chemical substances to another. The substance (or substances) initially involved in a chemical reaction are called reactants or reagents. Chemical reactions are usually characterized by a chemical change and they yield one or more products which usually have properties different from the reactants. Reactions often consist of a sequence of individual sub-steps, the so-called elementary reactions, and the information on the precise course of action is part of the reaction mechanism. Chemical reactions are described with chemical equations which symbolically present the starting materials, end products, and sometimes intermediate products and reaction conditions.

Chemical reactions happen at a characteristic reaction rate at a given temperature and chemical concentration. Typically, reaction rates increase with increasing temperature because there is more thermal energy available to reach the activation energy necessary for breaking bonds between atoms.

1.2 Classification Of Reactions

Reactions may be classified by (a) the number of phases involved, (b) the presence or absence of

a catalyst, and (c) the nature of the overall reaction.

If all the reactants and products, and catalysts, if any, are in a single phase, the reaction is said to be homogeneous. An example is provided by the thermal cracking of ethane to ethylene

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

On the other hand, if more than one phase is involved, the reaction is said to be heterogeneous. An example is provided by the chemical vapour deposition (CVD) of Si on a substrate

$$SiH_4(g) \rightarrow Si(s) + 2 H_2(g)$$
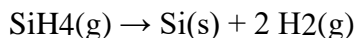
an enzyme called glucose isomerase catalyzes the isomerization of glucose to fructose in the liquid phase. It can be noted that this is the largest bioprocess in the chemical industry. As fructose is five times sweeter than glucose, the process is used to make high-fructose corn syrup for the soft drink industries. The overall reaction, as written, may represent either an elementary reaction or a non-elementary reaction. An example of the former is given by the gas-phase reaction
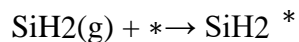
$NO2(g) + CO(g) \rightarrow NO(g) + CO2(g)$
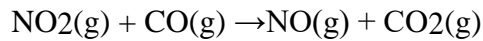
Here NO is formed by the collision between molecules of $NO2$ and CO, and the rate expression conforms to the stoichiometry shown. On the other hand,

$SiH4(g) \rightarrow Si(s) + 2 H2(g)$
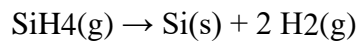
represents a non-elementary reaction, as it actually proceeds by the sequence of reactions shown

below

$SiH4(g) \rightarrow SiH2(g) + H2(g)$

$SiH2(g) + * \rightarrow SiH2 *$

$SiH2 * \rightarrow Si(s) + H2(g)$ where * represents an active site on the substrate.

Irreversible Reactions: Reactions that proceed unidirectionally under the conditions of interest

Reversible Reactions: Reactions that proceed in both forward and reverse directions under conditions of interest. Thermodynamics tells us that all reactions are reversible. However, in many cases the reactor is operated such that the rate of the reverse reaction can be considered negligible.

Homogeneous Reactions: reactions that occur in a single-phase (gas or liquid) NOx formation $NO (g) + 0.5 O2 (g) \leftrightarrow NO2 (g)$ Ethylene Production $C2H6 (g) \leftrightarrow C2H4 (g) + H2 (g)$ Heterogeneous Reactions: reactions that require the presence of two distinct phases Coal

combustion C (s) + O 2 (g) ↔ CO 2 (g) SO 3(for sulphuric acid production) SO 2 (g) + 1/2 O 2 (g) ↔ SO 3 (g) Vanadium catalyst (s)

Single and Multiple reactions:

Single reaction: When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, then it is said to be 'single reaction'. Multiple reactions: When more than one stoichiometric equation is chosen to represent the observed changes, then more than one kinetic expression is needed to follow the changing composition of all the reaction components, it is said to be 'multiple reactions'. Multiple reactions may be classified as; Series reactions, Parallel reactions, and SeriesParallel reactions.

Elementary and Non- Elementary reactions

The reactions in which the rate equation corresponds to a stoichiometric equation are called

elementary reaction. The reactions in which there is no correspondence between stoichiometry

and rate equation are known as Non-elementary reaction

1.3 Kinetic Models of Non- Elementary reactions

Free radicals, ions and polar substances, molecules, transition complexes are the various intermediates that can be formed in a non-elementary reaction.

In testing the kinetic models that involve a sequence of elementary reaction, we hypothesize the existence of two types of intermediates; Type-I: An unseen and unmeasured intermediate 'X' usually present at such small concentration that its rate of change in the mixture can be taken to be zero. Thus, we have [X] is small and $d[X]/dt = 0$. This is called the 'steady-state approximation'. Type-II: Where a homogeneous catalyst of initial concentration Co is present in two forms, either as free catalyst 'C' or combined in an appreciable extent to form the intermediate 'X', an accounting for the catalyst gives [Co] = [C] + [X]. We then also assume that either $(dX/dt) = 0$ or that the intermediate is in equilibrium with its reactants. Using the above

two types of approach, we can test the kinetic model or search a good mechanism; Trial and error procedure is involved in searching for a good mechanism.

1.4 Reaction rate and kinetics

Reaction rate

The rate expression provides information about the rate at which a reactant is consumed. Consider a single phase reaction $aA + b B \rightarrow rR + Ss$. Rate of reaction is defined as number of moles of reactant disappearing per unit volume per unit time

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = \frac{(\text{amount of A disappearing})}{(\text{volume})(\text{time})}, \quad \frac{mol}{m^3.s}$$

In addition, the rates of reaction of all materials are related by

$$-\frac{r_A}{a} = -\frac{r_B}{b} = \frac{r_R}{c} = \frac{r_S}{d}$$

<u>Rate constant k</u>

When the rate expression for a homogeneous chemical reaction is written in the form

$$- rA = kCA^aCB^b.....CD^d \quad , \; a+b+.......+d \; = n$$

The dimensions of the rate constant k for the nth order reaction are

$(time)^{-1}(concentration)^{1-n}$

Which for a first order reaction becomes

$(time)^{-1}$

1.5 Factors affecting rate of reaction

Many variables affect the rate of reaction of a chemical reaction. In homogeneous systems the temperature, pressure, and composition are obvious variables. In heterogeneous systems, material may have to move from phase to phase during reaction; hence, the rate of mass transfer can be important. In addition, the rate of heat transfer may also become a factor. In short, the variables affecting the rate of the reaction are (1) temperature (2) Pressure and (3) Composition of materials involved.

1.6 Various forms of rate equation

Based on unit volume of the reaction mixture

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid) (time)}}$$

Based on unit mass in fluid-solid system

$$r_i''' = \frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid})(\text{time})}$$

Based on unit surface of solid in fluid-solid system or unit interfacial area in two fluid systems

$$r_i''' = \frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor})(\text{time})}$$

Based on unit volume of solid in fluid-solid system

$$r_i' = \frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid})(\text{time})}$$

Based on unit volume of reactor when different from unit volume of the reaction mixture

$$r_i'' = \frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface})(\text{time})}$$

Rates defined on various basis are interchangeable and the following may be shown

$$\left(\begin{array}{c}\text{volume}\\\text{of fluid}\end{array}\right)r_i = \left(\begin{array}{c}\text{mass of}\\\text{solid}\end{array}\right)r_i' = \left(\begin{array}{c}\text{surface}\\\text{of solid}\end{array}\right)r_i'' = \left(\begin{array}{c}\text{volume}\\\text{of solid}\end{array}\right)r_i''' = \left(\begin{array}{c}\text{volume}\\\text{of reactor}\end{array}\right)r_i'''$$

Or

$$Vr_i = Wr_i' = Sr_i'' = V_sr_i''' = V_sr_i''''$$

Power law kinetics is simply put rate is proportional to concentration of species 1 to the power q 1 concentration of species 2 to the power q 2. So, products of all the, such C 1 raise to q 1 C 2 raise to q 2, up to C N raise to raise to q n. In a compact form, we can express this as rate equal to K, K is that proportionality constant, product of C j rise to q j, j going from 1 to N. So, q j is the order of the reaction with respect to species A j; and this is the simplest form of form of power law power law kinetics. Now, we call this q j as order with respect to A j and if you sum up all these q j s, we get q, what we call as overall overall order. reaction of hydrogen iodide getting decomposed to H 2 plus I 2. Now, it turns out for this particular reaction, the rate of reaction is proportional to concentration of hydrogen iodide raise to power 2. So, clearly in this case, q is 2 there is only one species in the reactant side, so our q j and q r q r are same. So, this is the this is the order of the reaction, so q can be integer. Let us take another example, decomposition of acetaldehyde to give us methane and carbon monoxide. Now, it turns out the rate of these reactions is proportional to concentration of acetaldehyde raise to power 3 by 2. So, q in this case is 3 by 2, or in other words, orders can be integers, they can be even fractions.

1.7 Molecularity

It is the number of molecules taking part in the reaction

e.g. A → C : Unimolecular reaction

A+ B → C : Bimolecular reaction

1.8 Order

It is defined as the sum of the powers to which the concentration terms are raised. The overall kinetic order of a reaction is defined by how many concentrations appear on the right side of the rate expression. The order of the reaction with respect to a particular species is defined by whether that species appears one or more times. For example, if the right side of the rate law is $[A]^m[B]^n$, then the overall order of the reaction is m+n and the reaction is m'th order with respect to [A] and n'th order with respect to [B]. Zeroth order means that the reaction rate does not change as the concentration of a species is changed. There are no biochemical reactions that are zeroth order overall.

e.g. A+ B → C

-- rA = kCACB

n (order) = 1+1=2

1.9 Concentration dependent term of rate equation

Rate of reaction is defined as number of moles of reactant disappearing per unit volume per unit time

$$- r_A = - \frac{1}{V} \frac{dN_A}{dt}$$

If constant volume systems are considered , the rate of reaction is modified to

$$- r_A = - \frac{dC_A}{dt}$$

The definition of rate of a chemical reaction describing change in molar concentration with respect to time, i.e., is not general and valid only when the volume of the mixture does not change during the course of the reaction. This may be only true for liquid phase reactions where volume changes are not significant. The volume of a gas also changes due to changes in operating conditions (temperature and pressure) in addition to changes in number of moles.

1.10 Rate equation in terms of partial pressure

For isothermal (elementary) gas reactions where the number of moles of material ' to The changes during reaction, the relation between the total pressure of the system ' changing concentration or partial pressure of any of the reaction component is r R + s S + …a A + b B + ...   o)] - n) (For the component 'A', pA = CA R T = pAo – [(a/ o)] - n) (For the component 'R', pR = CR R T = pRo + [(r/ And the rate of the reaction, for any component 'i', is given by ri = (1/RT) (dpi/dt)

1.12 Effect of temperature on reaction

Temperature dependency from Arrhenius law

For many reactions and particularly elementary reactions, the rate expression can be written as a
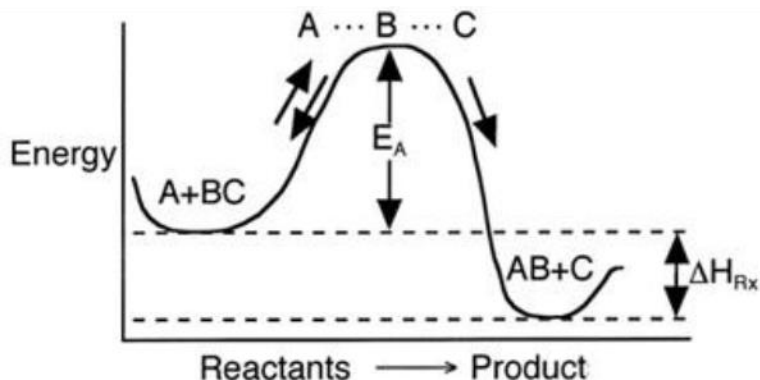
P

roduct of a temperature . The excess energy of the reactants required to dissociate into products is known as activation energy. The temperature dependency on the reaction rate constant is given by Arrhenius Law. That is, k = ko e-E/RT Where k = rate constant, k0 = frequency factor, E = Activation energy The temperature dependence of the rate constant k is usually fitted by the Arrhenius equation . Arrhenius equation is frequently applied to approximate the temperature dependency of reaction rate and the rate constant or velocity constant, k, is related to temperature, T, by the following expression:

$$k = k0e^{-E/RT}$$

Where, k0 = pre-exponential factor and has units similar to that of k. Ea = activation energy,

J·mol–1

where the pre-exponential factor k0 and the activation energy E are treated as constants and T is

the absolute temperature. If a plot of ln k versus 1/T shows a significant curvature, the rate constant k is a function of temperature

$$k = k_0 \, e^{-Ea/RT}$$

The higher the temperature the more molecules that have enough energy to make it over the barrier Arrhenius Plot $k = A \exp(-Ea/RT)$ $\ln k = \ln A - Ea/RT$ straight line plot $y = b + mx$ $y = \ln k$ $x = 1/T$ $b = \ln A$ $m = -Ea/R$ Plot $\ln k$ vs $1/T$, slope $= -Ea/R$ intercept $= \ln A$. A plot of $\ln k$ vs $1/T$ will be straight line, the slope of which is Ea/R. The units of the slope are K. A large slope of Arrhenius plot means large value of Ea and vice versa. Reactions having large value of Ea are more temperature sensitive while with low value of Ea are less temperature dependent.

Transition state theory

Transition state theory (TST) explains the reaction rates of elementary chemical reactions. The theory assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes. Describes the flow of systems from reactants-to-products over potential energy surfaces. Predicts the rate of an elementary equation in term of reactant concentration.

$$k = T \, A \, e^{-Ea/RT}$$

Collision theory This theory was proposed by Trautz (1916) and Lewis (1918) for gas phase reactions. It is based on the kinetic theory of dilute gases. Consider an elementary reaction of the form $A1 + A2 \rightarrow$ products The reaction rate, i.e the number of molecules of A1 consumed per unit volume per unit time is assumed to be equal to the number of collisions per unit volume per unit time between molecules of A1 and A2. The latter may be estimated as follows. Using the Maxwell-Boltzmann velocity distribution for each species, the activation energy can be found from

$$k = T^{1/2} A \, e^{-Ea/RT}$$

**1.13 Constant volume reactions**

1. Integral method

2. Differential method

Method of analysis of data

1.13.1 Integral method

General Procedure

The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted C versus t curve with the experimental C versus t data. If the fit is unsatisfactory, another rate equation is guessed and tested. This procedure is shown in the figure. It should be noted that the integral method is especially useful for fitting simple reaction types corresponding to elementary reactions.
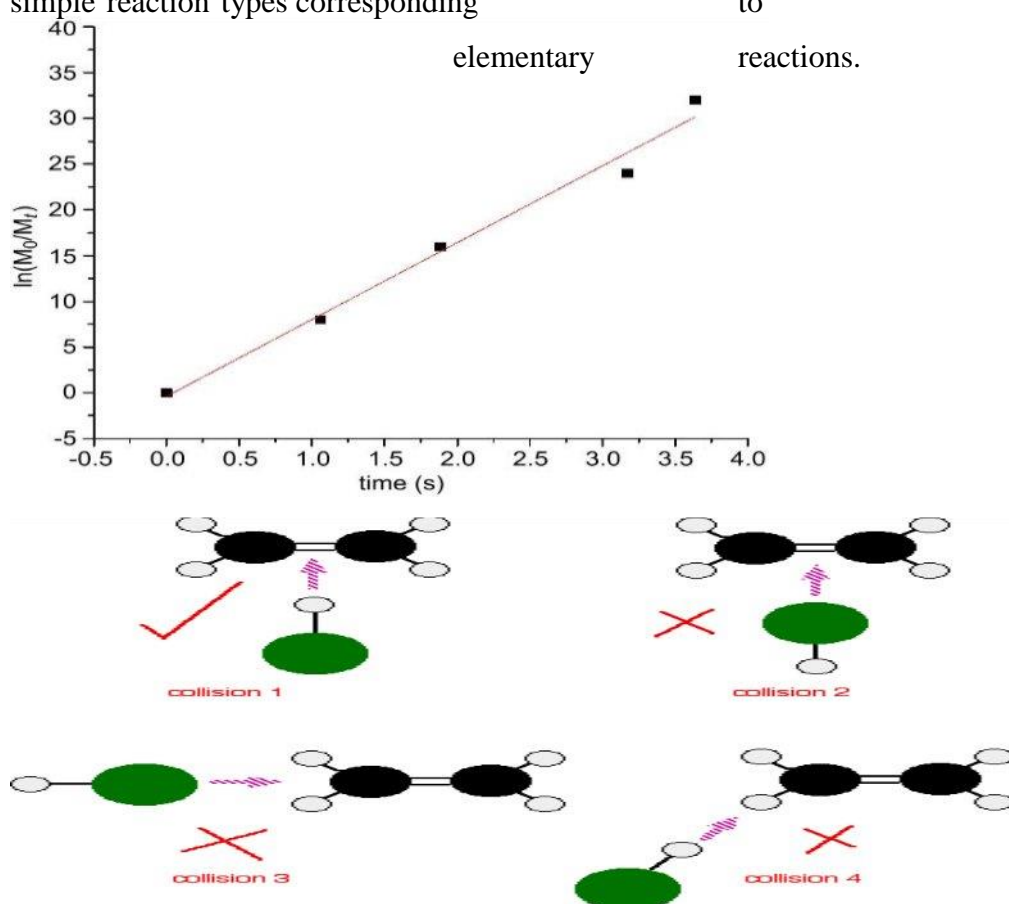
1.13.2 Differential method

Plot the concentration versus time data and then carefully draw a smooth curve to represent the

data. This curve will most likely not pass through all experimental points. Determine the slope of the curve at suitably selected concentration values. These slopes are rates of the reactant at particular concentration. Search for a rate expression to represent this rate versus concentration data either by fitting and testing a particular rate equation or by trail and error method or by testing the nth order equation.
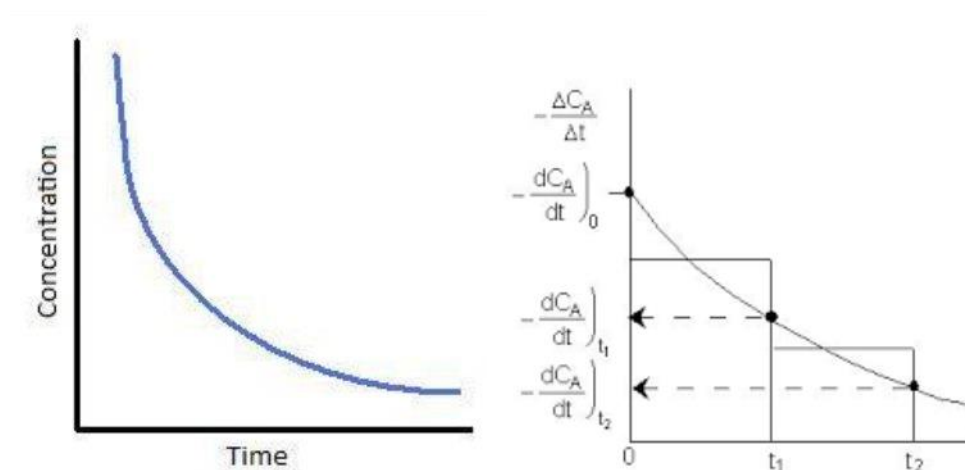
1.14 Irreversible Unimolecular-type first order reaction

First order (unimolecular) reaction:

Suppose we wish to test the first-order rate equation of the following type, for this reaction.

Reaction: $A \rightarrow B$

Rate Law: $-d[A]/dt = k[A]$

Integrated solution: $\int d[A]/[A] = -k \int dt \quad \ln [A] = -kt + \ln [Ao] \quad [A] = [Ao]\, e^{-kt}$

Separating and integrating we obtain a plot of In (1 - XA) or In (CA/CAo) vs. t, a straight line

through the origin for this form of rate of equation. If the experimental data seems to be better fitted by a curve than by a straight line, try another rate form because the first-order reaction does not satisfactorily fit the data.

Fractional conversion XA

Fractional conversion of a reactant A is defined as fractional reactant converted into product at

any time. It is given by the equation, $XA = (NAO – NA) / NAO$ Where 'NAO' is the initial no. of moles of reactant 'A' at t = 0. 'NA' is the remaining no. of moles of reactant at any time 't' in the reaction.

1.15 Irreversible Unimolecular-type second order reaction

Second-order reaction (dimerization) (like molecules)

Reaction: $2A \rightarrow Product$

Rate Law: $- d[A]/dt = k[A]^2$

Integrated solution: $\int d[A]/[A]^2 = -k \int dt$ $1/[A] = k (t) + 1/[A0]$ $[A] = A0/(A0kt + 1)$

The equation is a hyperbolic equation, and second-order, dimerization kinetics are often called hyperbolic kinetics.

Bimolecular reactions with different reactants: (unlike molecules)
Reaction: $A+B \rightarrow AB$

Rate Law: $-d[A]/dt = -d[B]/dt = k[A][B]$

Integrated solution:

-rA =CAO dXA/dt = k(CAO-CAOXA)(CBO-CBOXA)

Let M= CBO/CAO be the initial molar ratio of reactants , we obtain

-rA =CAO dXA/dt = kCAO ^{2}(1-XA)(M-XA)

after breakdown into partial fractions, integration and rearrangement , the final result in a number

of different forms is

ln (1-XB /1-XA) = ln (M-XA /M(1-XA) = ln CBCAO/CBOCA = ln CB/MCA = CAO (M-1)kt=(CBO-CAO)kt

$$M \neq 1$$

A linear plot will be obtained between the concentration function and time for this second order

rate law.

1.16 Half life

The half-life (t 1/2) for a reaction is the time required for half of the reactants to convert to

products.

 For a first-order reaction, t 1/2 is a constant and can be calculated from the rate constant as:

t 1/2 = -ln(0.5)/k = 0.693/k

1.17 Pseudo First order reaction

A second order rate equation which follows the first order rate equation is defined as pseudo First

order reaction. Example: Ester hydrolysis. CH $_3$COOH + C $_2$H $_5$OHCH3 COO C2 H5 + H 2O (A) (B) (C) (D) When C BO >>C Ao, Concentration of H $_2$O is very large, - rA = - dCA/dt =k 'CA

1.18 Zero order reaction

When the rate of the reaction is independent of the concentration of the reactants, it is called as Zero order reaction. Example: Decomposition of HI

1.19 Third-order reaction

An irreversible trimolecular-type third-order reaction may fall on two categories; Products with corresponding rate equation(1) The reaction A + B + D -rA = - (dCA/dt) = k CA CB CD. If CDo is much greater than both CAo and CBo, the reaction becomes second order. Products with corresponding rate equation(2) The reaction A + 2B -rA = - (dCA/dt) = k CA CB 2 .

1.20 nth order

The empirical rate equation of nth order, -rA = - dCA/dt = k CA ^{n} (constant volume). Separating the variables and integrating, we get CA 1-n - CAo 1-n = (n - 1) k t. Case i) n>1, CAo 1-n = (1 -n) k t. The slope is (1 - n) k is negative Or the time decreases. Case ii) n

1.21 Steady-State approximation

The kinetics of reactions of this type can also be also analyzed by writing the overall expression for the rate of change of B and setting this equal to 0. By doing this, we are making the assumption that the concentration of B rapidly reaches a constant, steady-state value that does not change appreciably during the reaction. d[B]/dt = k1[A] - k-1[B] - k2[B] = k1[A] - (k-1+k2) [B] = 0 (k-1+k2)[B] = k1[A] [B] = (k1)/(k-1 + k2) [A] substituting

into $d[C]/dt = k_2[B]$ gives: $d[C]/dt = (k_1k_2)/(k_{-1} + k_2) [A]$ now if $k_{-1} \gg k_2$ $d[C]/dt \approx (k_1 k_2)/(k_{-1}) [A]$, if $k_2 \gg k_{-1}$ $d[C]/dt \approx (k_1k_2)/(k_2) [A] = k_1[A]$

Limiting reactant

Usually in a reaction, one of the reactants is present in excess to that required stoichiometrically. If the reactants are added in stoichiometric amounts, there is no point using the concept of limiting reactant. The limiting reactant is the one which is consumed first and may be indicated by dividing the number of moles of each reactant in feed to the corresponding stoichiometric amount (form a balanced chemical equation) of the reactant. The reactant with the lowest ratio is the limiting reactant and will be the first to fully consumed in the reaction, if the reaction goes to completion.

Constant volume method: It refers to the volume of reaction mixture, and not the volume of reactor. It actually means a constant density reaction system, that is, the composition of reaction mixture is constant. Most of the liquid phase as well as gas phase reactions occurring in a constant volume bomb fall in this class. In a constant volume system, the measure of reaction rate of component 'i' (reactant 4 or product) becomes $r_i = (1 / V)$ $(dN_i / dt) = dC_i / dt$. Conversion of reactant 'A' in this method is given by $X_A = 1 - (C_A/C_{Ao})$. Variable volume method: It actually means the composition of reaction mixture varies with time by the presence of inerts. Gas phase reactions involving the presence of inerts or of impure reactants occurring in a reactor fall in this class. The measure of reaction rate of component 'i' (reactant or product), in this method, i) $[d (\ln V) / dt]$. becomes $r_i = (C_{io} /$ In variable volume system, the fractional change in volume of the system between the initial and final stage of the reaction will be accounted. Thus, conversion of reactant A (C_A/C_{Ao})]. 'A' becomes $X_A = [1 - (C_A/C_{Ao})] / [1 + 'A(C_A/C_{Ao})]$

UNIT – II – Chemical Reaction Engineering-1 – SCHA1402

Reactor Design for Single Reactions
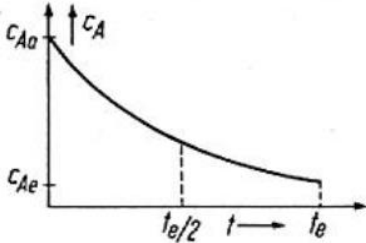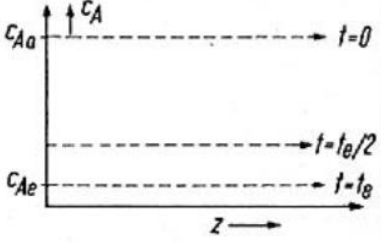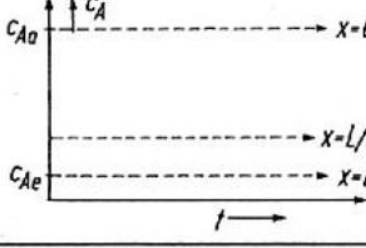
2.1 CLASSIFICATION OF REACTORS

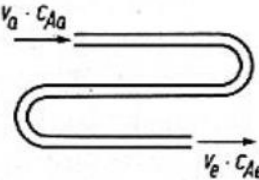Reactors are classified based on

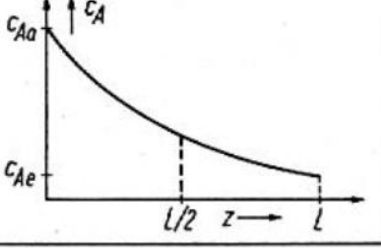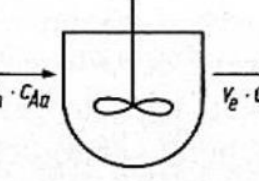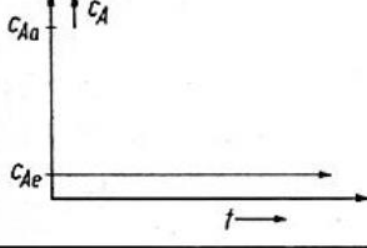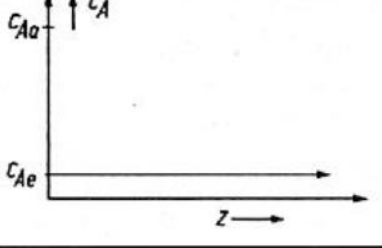1. Method of operation: Batch or Continuous reactor

2. Phases: Homogeneous or Heterogeneous reactor

2. 2 REACTOR TYPES

Equipment in which homogeneous reactions are effected can be one of three general types : the batch , the steady –state flow and the un-steady-state flow or semibatch reactor. The batch reactor is simple, needs little supporting equipment and is therefore ideal for small scale

experimental studies on reaction kinetics. Industrially it is used when relatively small amounts of material are to be treated. The steady state flow reactor is ideal for industrial purposes when large quantities of material are to be processed and when the rate of the reaction is fairly high to extremely high. Extremely good product quality control can be obtained. This is a reactor which is widely used in the oil industry. The semibatch reactor is a flexible system but is more difficult to analyze than the other reactor types. It offers good control of reaction speed because the reaction proceeds as reactants are added. Such reactors are used in a variety of applications from the calorimetric titrations in the laboratory to the large open hearth furnaces for steel production.

Type	Concentration course	
	time	space

2.3 Reactor Design

The starting point for all design is the material balance expressed for any reactant

2.3.1 Material balance

Rate of reactant flow into element of volume =rate of reactant flow out of element of volume + rate of reactant loss due to chemical reaction within the element of volume + rate of accumulation of reactant in element of volume.

In non isothermal operations energy balance must be used in conjunction with material balances

2.3.2 Energy balance

Rate of heat flow into element of volume =rate of heat flow out of element of volume + rate of disappearance of heat by reaction within the element of volume + rate of accumulation of heat in element of volume.

## 2.3.3. Factors to be considered for design of reactor

The different factors required for reactor design are (i) Size of reactor (ii) Type of reactor (iii)

Time or duration of reaction (iv) Temperature & Composition of reacting material in the reactor (v) Heat removal or added and (vi) Flow pattern of fluid in the reactor.

2.4 Ideal Reactors

Ideal reactors (BR, PFR, and MFR) are relatively easy to treat. In addition, one or other usually represents the best way of contacting the reactants – no matter what the operation. For these reason, we often try to design real reactors so that their flows approach these ideals.

2.4.1 Ideal Batch Reactor
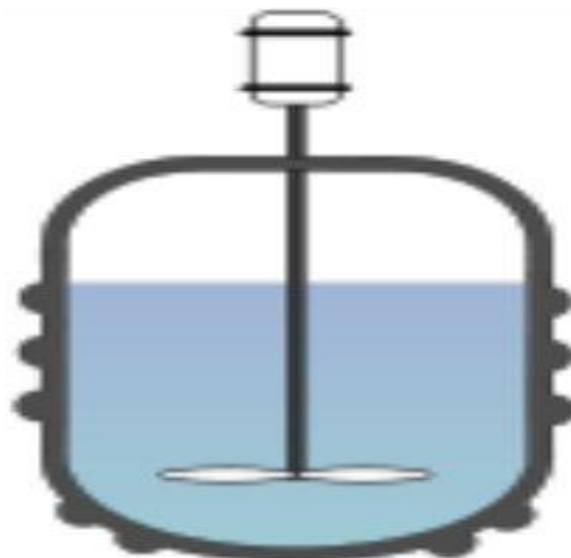
A batch reactor (BR) is one in which reactants are initially charged into a container, are well mixed, and are left to react for a certain period. The resultant mixture is then discharged. This is an unsteady state operation where composition changes with time; however at any instant the composition throughout the reactor is uniform. The advantages of a batch reactor are (i) small instrumentation cost and (ii) flexibility of operation. A batch reactor has the disadvantages of (i) high labour (ii) poor quality control of the product and (iii) considerable shutdown time has taken to empty, clean out and refill.

Making a material balance for component A. Noting that no fluid enters or leaves the reaction

mixture

Input = output + disappearance +accumulation   (1)

Input = 0

Output = 0

Disappearance of A by reaction moles/time $= (-r_A)V$

Accumulation of A by reaction moles/time $= dN_A/dt$

By replacing these two terms

$(-r_A)V = N_{AO} \, dX_A/dt$

Rearranging and integrating gives

$t = N_{AO} \int dX_A/ (-r_A)V$

$t = C_{AO} \int dX_A/ (-r_A) = - \int dC_A/ (-r_A)$ FOR $\epsilon_A = 0$

2.4.2 Space time and space velocity

Space velocity: It is the reciprocal of space time and applied in the analysis of continuous flow reactors such as plug flow reactor and CSTR. It is defined as the number of rector volumes of a feed at specified conditions which can be treated in unit time. A space velocity of 10 h −1 means that ten reactor volumes of the feed at specified conditions are treated in a reactor per hour.

Space time and space velocity are the proper performance measures of flow reactors.

Space time

$\tau = 1/s$ = time required to process one reactor volume of feed measured at specified conditions (time)

Space velocity

$s = 1/\tau$ = number of reactor volumes of feed at specified conditions which can be treated in unit time (time^{-1})

$\tau = VC_{AO}/F_{AO} = 1/s$

Holding time: It is the mean residence time of flowing material in the reactor. It is given by the expression $t = C_{Ao} + d X_A)/] / [(-rA) (1+ _AX_A)$

For constant density systems (all liquids and constant density gases) $t = \tau$ Where 'V' is the volume of the reactor and 'v' is the volumetric flow rate of reacting fluid

For constant density systems, the performance equation for Batch reactor and Plug flow reactor are identical.

2.5 Steady state mixed flow reactor or Continuous stirred tank reactor (CSTR)
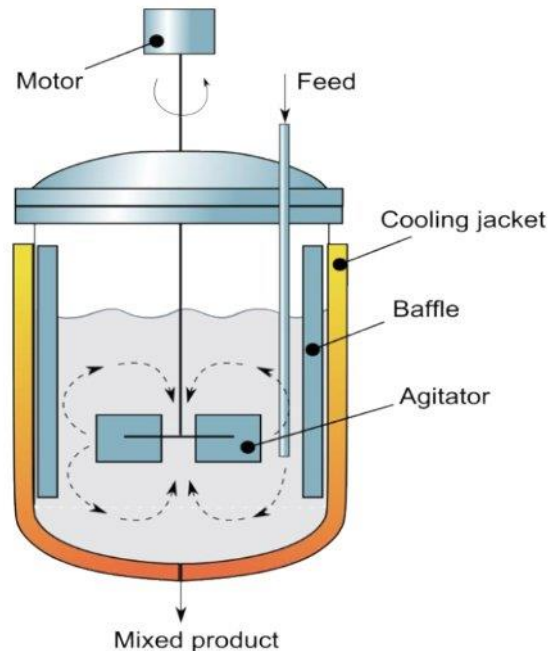
Mixed flow reactor (MFR) is also called as back mix reactor or continuous stirred rank reactor (CSTR) or constant flow stirred tank reactor (CFSTR). In this reactor, the contents are well stirred and uniform throughout. The exit stream from the reactor has the same composition as the fluid within the reactor.

Since the composition is uniform throughout , the accounting can be made about the reactor as a

whole.

Input = output + disappearance +accumulation   (2)

Accumulation = 0

Input of A.moles /time = F_{AO}

Output of A.moles /time = $F_A = F_{AO} (1-X_A)$

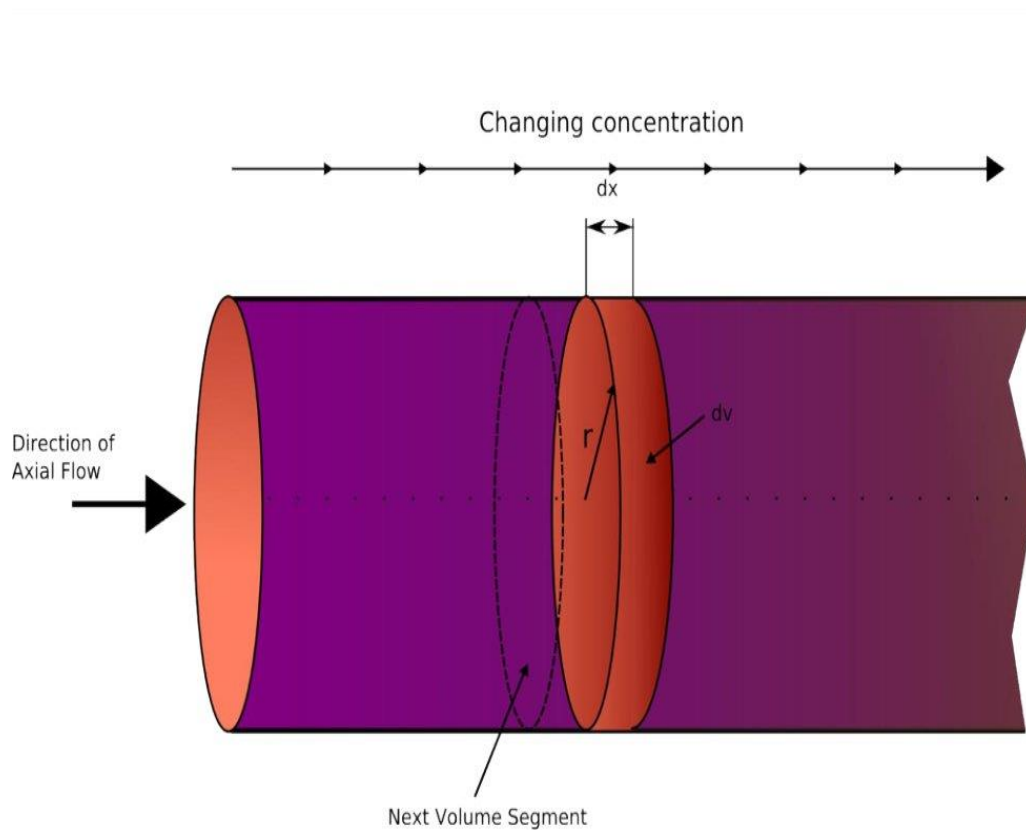Disappearance of A by reaction moles/time = $(-r_A)V$

Introducing all these terms in eqn 2

$F_{AO} X_A = (-r_A)V$

Which on rearrangement becomes

$V/ F_{AO} = \tau / C_{AO} = X_A / (-r_A)$

2.6 Steady state Plug flow reactor or Tubular reactor

Plug flow reactor (PFR) is also referred as slug flow, piston flow, ideal tubular, and unmixed flow reactor. It specifically refers to the pattern of flow as plug flow. It is characterized by the fact that the flow of fluid through the reactor is orderly no element of fluid overtaking or mixing with any other element ahead or behind. Actually, there may be lateral mixing of fluid in a PFR; however, there must be no mixing or diffusion along the flow path. The necessary and sufficient condition for plug flow is the residence time in the reactor to be the same for all elements of fluid

Input = output + disappearance +accumulation   (3)

Accumulation = 0

Input of A.moles /time = F_{AO}

Output of A.moles /time = F_A + d F_A

 Disappearance of A by reaction moles/time = ($-r_A$)dV

Introducing all these terms in eqn 3

$F_A = F_A + d F_A + (-r_A)dV$

Noting that

$d F_A = d [F_A (1-X_A)] = - F_{AO} dX_A$

we obtain on replacement

$F_{AO} dX_A = (-r_A)dV$

Grouping the terms accordingly and integrating

$V/ F_{AO} = \tau / C_{AO} = \int dX_A /(-r_A)$

ideal reactors are based on simple models of flow patterns and mixing in the reaction vessel. In

an ideal batch reactor, the concentration and temperature fields are assumed to be spatially uniform. In practice, the condition can be approximately realized by vigorous agitation or stirring. In the absence of stirring, beautiful spatial patterns, caused by an interaction between diffusion and reactions, may develop in some systems . All the elements of the fluid spend the same amount of time in the reactor, and hence have the same residence time. From the viewpoint of thermodynamics, a batch reactor represents a closed system. The steady states of the batch reactor correspond to states of reaction equilibria. Batch reactors are often used in the pharmaceutical industry, where small volumes of high-value products are made.

The ideal continuous stirred tank reactor (CSTR) like in an ideal batch reactor, the concentration and temperature fields in an ideal CSTR are spatially uniform. As there are no spatial gradients, the species concentrations in the exit stream are identical to the corresponding values in the reactor. On the other hand, the species concentrations in the inlet stream are in general different from those in the reactor. Unlike the batch reactor, the CSTR is an open system as it can exchange heat and mass with the surroundings. Hence it operates away from equilibrium, and steady states are usually not states of reaction equilibria. On account of the assumption of perfect mixing, the sequence in which fluid elements leave the reactor is uncorrelated with the sequence in which they enter. As shown later, this leads to a distribution of residence times for the fluid leaving the reactor. These reactors are widely used for polymerization reactions such as the polymerization of styrene, production of explosives, synthetic rubber, etc. Compared to tubular reactors, CSTRs are easier to clean and permit better control of the temperature. (c) The plug flow reactor (PFR) The PFR is an idealization of a tubular reactor. The velocity, temperature, and concentration fields are assumed to be uniform across the cross section of the reactor. In practice, this situation can be approximately realized for the case of turbulent flow through a tube with a large ratio of the length to the diameter. The latter condition ensures that axial mixing has a negligible effect on the conversion. In a PFR, there is perfect mixing in the radial or transverse direction. Further, there is no mixing or diffusion in the axial direction. Like a CSTR, the PFR also represents an open system, and hence steady states are not states of reaction equilibrium. Owing to the assumption of plug flow, all the fluid elements have the same residence time. The velocity of the fluid is often treated as a constant, but this assumption must be relaxed when the density of the fluid changes significantly along the length of the tube. The steady state equations for a PFR are similar in form to the dynamic equations for an ideal batch

reactor. In many cases, the results for the latter can be translated into results for a PFR operating at a steady state. Tubular reactors are used for many gas phase and liquid phase reactions, such as the oxidation of NO and the synthesis of NH3. These reactors are often modelled as PFRs, but more detailed models involving complications such as radial gradients, may be required in some cases.
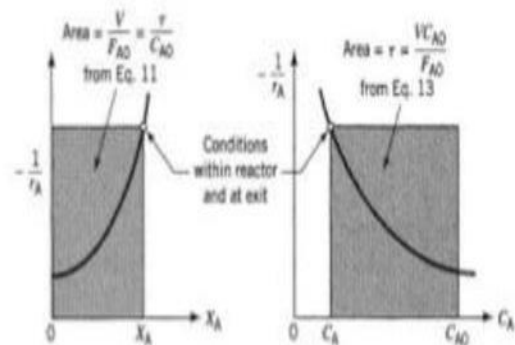
Plug flow and mixed flow reactor design

Mixed flow reactor design

Applying mass balance performance equation for mixed flow reactor

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

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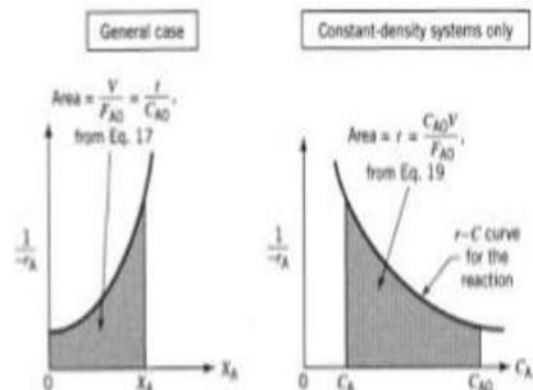
Plug flow reactor design

Performance equation for plug flow reactor

$$\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

$$\tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-r_A}$$
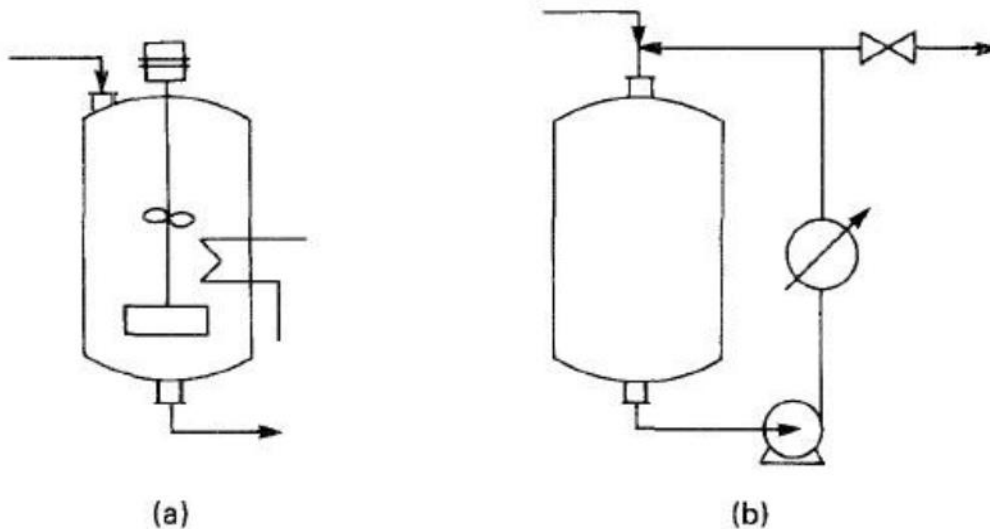
2.7 Steady state reactor

Reactors those in which the properties of the system do not change with time is said to be a steady state reactor. Example: Continuous stirred Tank reactor, plug flow reactor. Total mass inflow = Total mass outflow

2.8 Unsteady state reactor

Reactors are those in which the properties of the system changes with time and rate of reaction decreases with time expect for zero order reaction are said to be unsteady state reactor. Example: Batch reactor, Semi-batch reactor. There is accumulation in these reactors. Accumulation = input - output + generation - consumption.

2.9 Semi batch reactor

(a)   (b)

It is an unsteady state reactor. Reactors which are partially batch and partially continuous are referred to as semi-batch reactor. The semi batch reactors offers good control of reaction speed, because the reaction proceeds as reactants are added. Types: (i) volume changes but composition is unchanged (ii) composition changes but volume is constant.

2.10 Recycle reactor
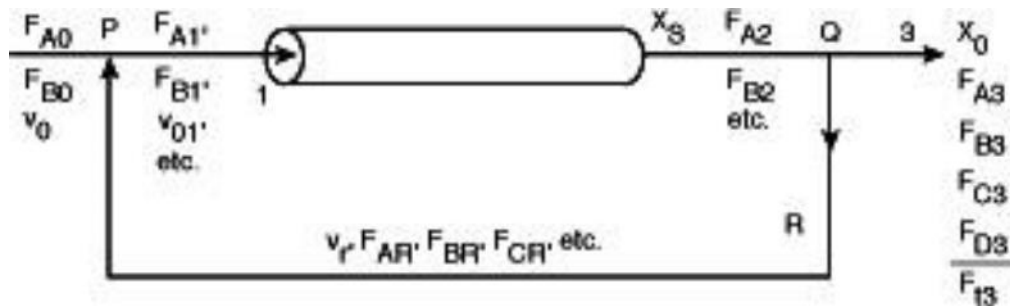
In some reaction system, it is advantageous to divide the product stream and a part returned to reactor as recycle to increase the conversion rate. These reactors are called recycle reactors. The recycling provides a means for obtaining various degree of backmixing. Recycle ratio 'R' can be defined as the ratio of the volume fluid returned to the reactor entrance to the volume of fluid leaving the system or reactor. Significance: Recycle ratio can be made to vary from zero to infinity. Reflection suggests that as the recycle ratio is raised, the behavior shifts from plug flow (R = 0) to). mixed flow (R =).), the recycle reactor. When the recycle ratio 'R' becomes or tends to infinity (R= behaves like a CSTR. When material is to be processed to some fixed final conversion in a recycle reactor, there must be a particular recycle ratio 'R' that minimizes the reactor volume or space time. That recycle ratio is said to be optimum and the operation is said

The actual conversion at inlet is given by:
$$X_{A1} = \frac{1 - C_{A1}/C_{A0}}{1 + \varepsilon_A C_{A1}/C_{A0}}$$

The concentration at inlet to the reactor is given by

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0} + F_{A3}}{v_0 + Rv_f} = \frac{F_{A0} + RF_{A0}(1 - X_{Af})}{v_0 + Rv_0(1 + \varepsilon_A X_{Af})} = C_{A0}\left(\frac{1 + R - RX_{Af}}{1 + R + R\varepsilon_A X_{Af}}\right)$$

So finally we get the following results:
$$X_{A1} = \left(\frac{R}{R+1}\right)X_{Af}$$

The final equation for any expansion factor value is:

$$\frac{V}{F_{A0}} = (R+1)\int_{\left(\frac{R}{R+1}\right)X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A} \quad \ldots \text{any } \varepsilon_A$$

Also in terms of concentration,

$$\tau = \frac{C_{A0}V}{F_{A0}} = -(R+1)\int_{\frac{C_{A0} + RC_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{-r_A} \quad \ldots \varepsilon_A = 0$$

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – III - Chemical Reaction Engineering-1 – SCHA1402

DESIGN OF MULTIPLE REACTORS FOR SINGLE REACTIONS

There are many ways of processing a fluid: in a single batch or flow reactor, in a chain of reactors possibly with interstage feed injection or heating and in a reactor with recycle of the product stream using various feed ratios and conditions. The reactor system selected will influence the economics of the process by dictating the size of the units needed and by fixing the ratio of products formed. The first factor, reactor size, may well vary a hundredfold among competing designs while the second factor, product distribution, is usually of prime consideration where it can be varied and controlled. For single reactions product distribution is fixed; hence, the important factor in comparing designs is the reactor size. The size comparison of various single and multiple ideal reactor systems is considered.

3.1 SIZE COMPARISON OF SINGLE REACTORS

3.1.1 Batch Reactor

The batch reactor has the advantage of small instrumentation cost and flexibility of operation (may be shut down easily and quickly). It has the disadvantage of high labor and handling cost, often considerable shutdown time to empty, clean out, and refill, and poorer quality control of the product. Hence it may be generalized to state that the batch reactor is well suited to produce small amounts of material and to produce many different products from one piece of equipment. On the other hand, for the chemical treatment of materials in large amounts the continuous process is nearly always found to be more economical.

3.1.2 Mixed Versus Plug Flow Reactors, First- and Second-Order Reactions

For a given duty the ratio of sizes of mixed and plug flow reactors will depend on the extent of reaction, the stoichiometry, and the form of the rate equation.
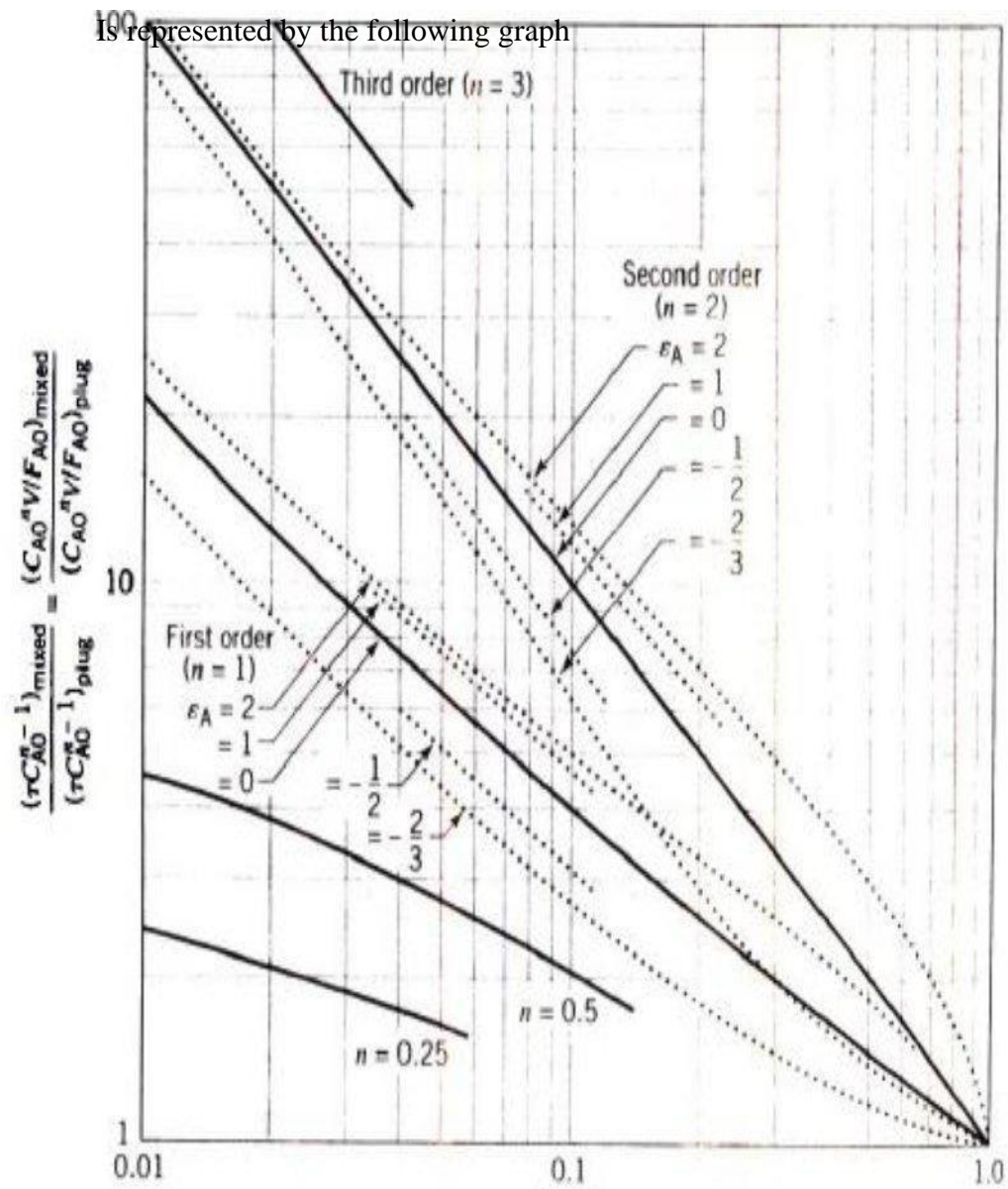
- $r_A = - 1 \, dN_A$

  ----------- $= kC_A^n$

  V dt

$(\tau\, C_{AO}^{\,n-1})\, m \,/\, (\tau\, C_{AO}^{\,n-1})\, m$

is represented by the following graph

Third order ($n = 3$)

Second order
($n = 2$)

$\varepsilon_A = 2$
$= 1$
$= 0$
$= -\dfrac{1}{2}$
$= -\dfrac{2}{3}$

First order
($n = 1$)

$\varepsilon_A = 2$
$= 1$
$= 0$
$= -\dfrac{1}{2}$
$= -\dfrac{2}{3}$

$n = 0.5$

$n = 0.25$

y-axis: $\dfrac{(\tau C_{AO}^{\,n-1})_{mixed}}{(\tau C_{AO}^{\,n-1})_{plug}} = \dfrac{(C_{AO}^{\,n}V/F_{AO})_{mixed}}{(C_{AO}^{\,n}V/F_{AO})_{plug}}$

100

10

1

0.01   0.1   1.0

To provide a quick comparison of the performance of plug flow with mixed flow reactors, the performance graph is used. For identical feed composition CAo and flow rate FA, the ordinate of this figure gives directly the volume ratio required for any specified conversion.

1. For any particular duty and for all positive reaction orders the mixed reactor is always larger than the plug flow reactor. The ratio of volumes increases with reaction order.

2. When conversion is small, the reactor performance is only slightly affected by flow type. The performance ratio increases very rapidly at high conversion; consequently, a proper representation of the flow becomes very important in this range of conversion.

3. Density variation during reaction affects design; however, it is normally of secondary importance compared to the difference in flow type. Dashed lines represent fixed values of the dimensionless reaction rate group, defined as
$k\tau$ for first-order reaction

$kC_{A0}\tau$ for second-order reaction

With these lines we can compare different reactor types, reactor sizes, and conversion levels. Second-order reactions of two components and of the type behave as second-order reactions of one component when the reactant ratio is unity. Thus

$-rA = kCACB = kc;$ when $M = 1$

On the other hand, when a large excess of reactant B is used then its concentration does not change appreciably $(CB= CBO)$ and the reaction approaches first-order behavior with respect to the limiting component **A,** or

$-rA = kCACB = (kCBO)C=A\ krCA$ when $M + 1$

Thus terms of the limiting component A, the size ratio of mixed to plug flow reactors is represented by the region between the first-order and the second-order curves.

Any rate curve

$$\text{Area} = \tau_m/C_{A0}$$

$$\text{Area} = \tau_p/C_{A0}$$

$-\dfrac{1}{r_A}$

X_{Ai} X_{Af}

X_A
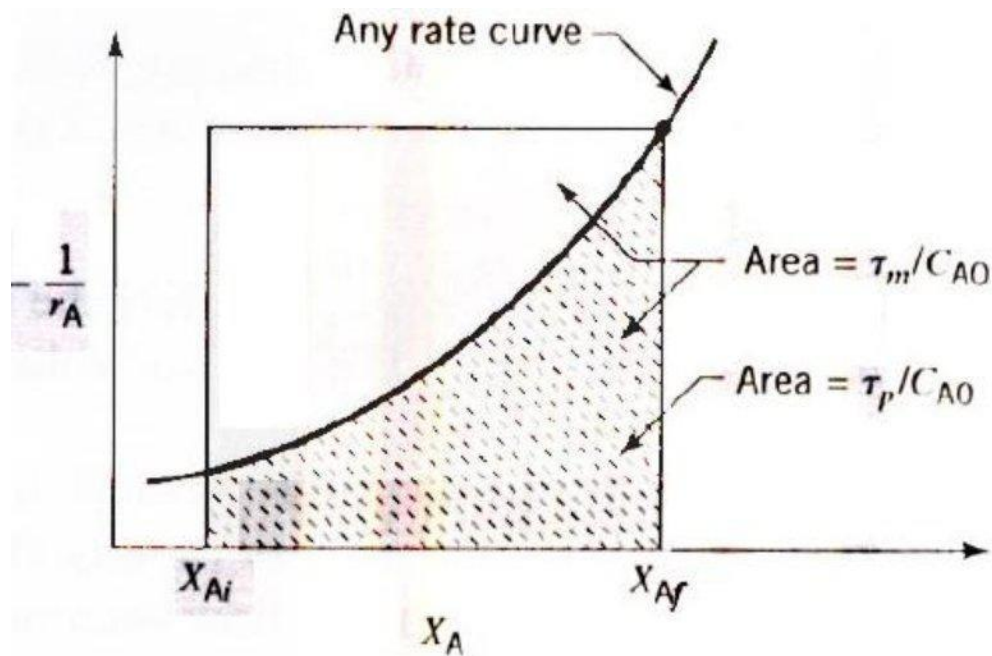
For reactions with arbitrary but known rate the performance capabilities of mixed and plug flow reactors are best illustrated in above figure. The ratio of shaded and of hatched areas gives the ratio of space-times needed in these two reactors. The rate curve drawn in above figure is typical of the large class of reactions whose rate decreases continually on approach to equilibrium (this includes all nth-order reactions, $n > 0$). For such reactions it can be seen that mixed flow always needs a larger volume than does plug flow for any given duty.

3.2 Plug Flow Reactors in Series and / or in Parallel

Consider N plug flow reactors connected in series, and let $X_1, X_2, \ldots, X_N$, be the fractional

conversion of component A leaving reactor 1, 2, . . . , N. Basing the material balance on the feed

rate of A to the first reactor, we find for the

ith reactor

$V_i / F_O = \tau_i / C_{AO} = \int dX /(-r)$

or for the N reactors in series

$V / F_O = \Sigma \, V_i / F_{O =} \int dX /(-r_)$

Hence, N plug flow reactors in series with a total volume V gives the same conversion as a single plug flow reactor of volume V.

3.2.1 Operating A Number Of Plug Flow Reactors

The reactor setup shown in Figure consists of three plug flow reactors in two parallel branches. Branch D has a reactor of volume 50 liters followed by a reactor of volume 30 liters. Branch E has a reactor of volume 40 liters. What fraction of the feed should go to branch D?
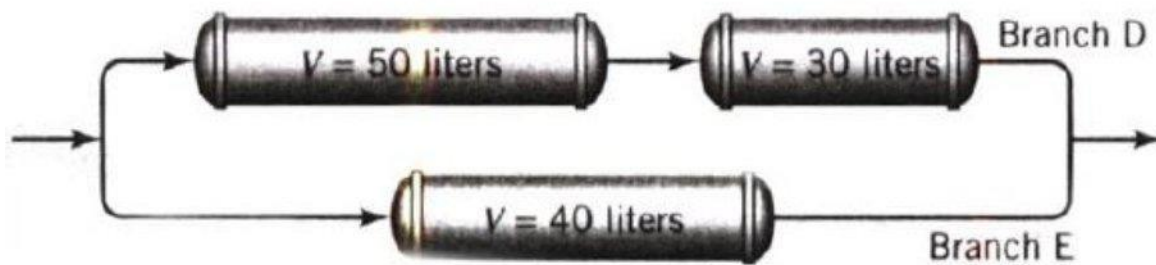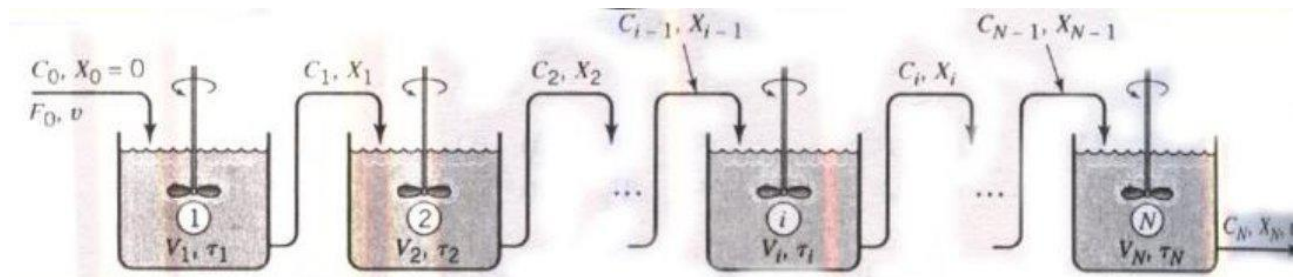
Branch D consists of two reactors in series; hence, it may be considered to be a single reactor of volume

$$V_D = 50 + 30 = 80 \text{ liters}$$

Now for reactors in parallel V/F must be identical if the conversion is to be the same in each branch. Therefore, two-thirds of the feed must be fed to branch D.

## 3.3 Equal-Size Mixed Flow Reactors in Series

In plug flow, the concentration of reactant decreases progressively through the system; in mixed flow, the concentration drops immediately to a low value. Because of this fact, a plug flow reactor is more efficient than a mixed flow reactor for reactions whose rates increase with reactant concentration, such as nth-order irreversible reactions, $n > 0$. Consider a system of N mixed flow reactors connected in series. Though the concentration is uniform in each reactor, there is, nevertheless, a change in concentration as fluid moves from reactor to reactor. This stepwise drop in concentration, illustrated in above figure, suggests that the larger the number of units in series, the closer should the behavior of the system approach plug flow. This will be shown to be so. Quantitatively evaluate the behavior of a series of N equal-size mixed flow reactors. Density changes will be assumed to be negligible; hence $\rho = 0$. As a rule, with mixed flow reactors it is more convenient to develop the necessary equations in terms of concentrations rather than fractional conversions.

3.4 Comparison Charts

At present 90% of reactant A is converted into product by a second-order reaction in a single mixed flow reactor. We plan to place a second reactor similar to the one being used in series with it.

(a) For the same treatment rate as that used at present, how will this addition affect the conversion of reactant?

For the same 90% conversion, by how much can the treatment rate be increased?
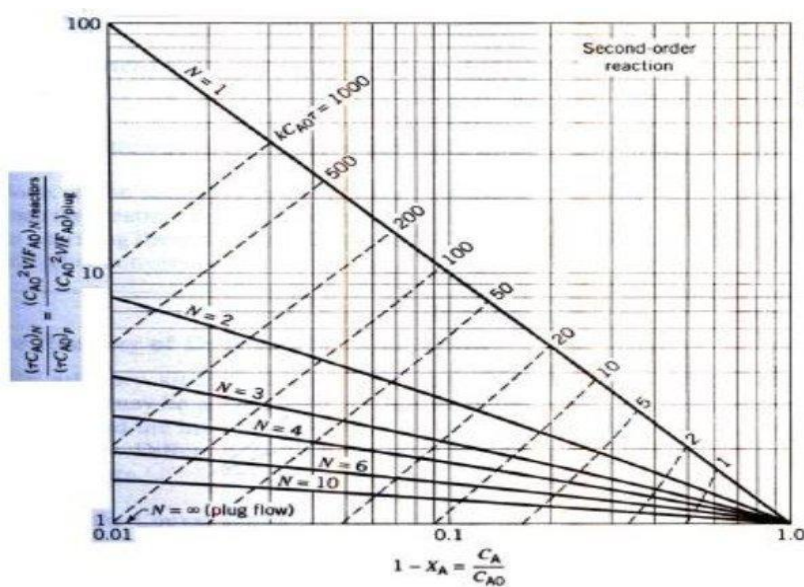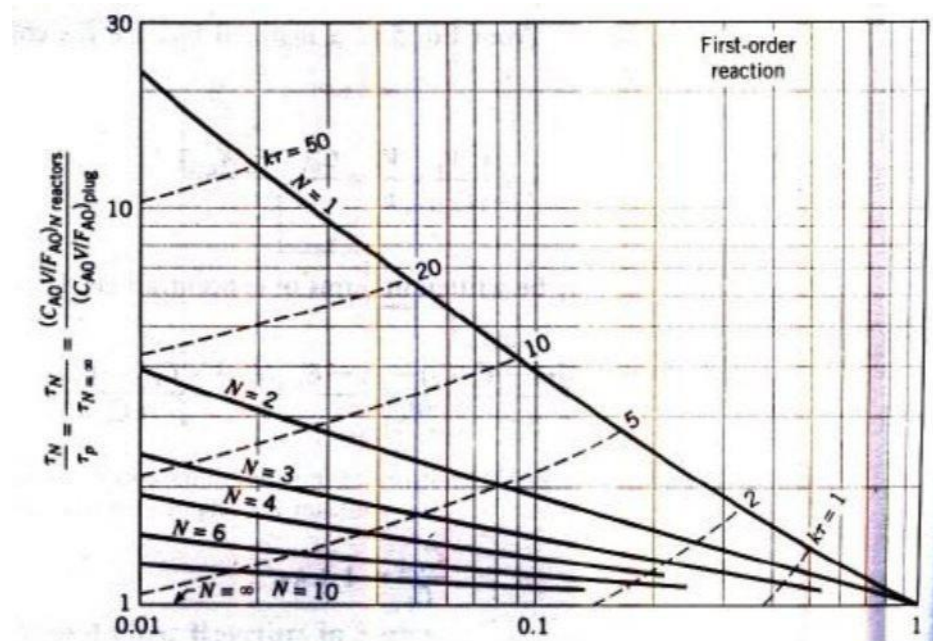
(a) Find the conversion for the same treatment rate. For the single reactor at 90% conversion we have from chart

$kC_o\tau = 90$

For the two reactors the space-time or holding time is doubled; hence, the operation will be represented by the dashed line of chart where

$kC_o\tau = 180$

This line cuts the $N = 2$ line at a conversion $X = 97.4\%$, point a.

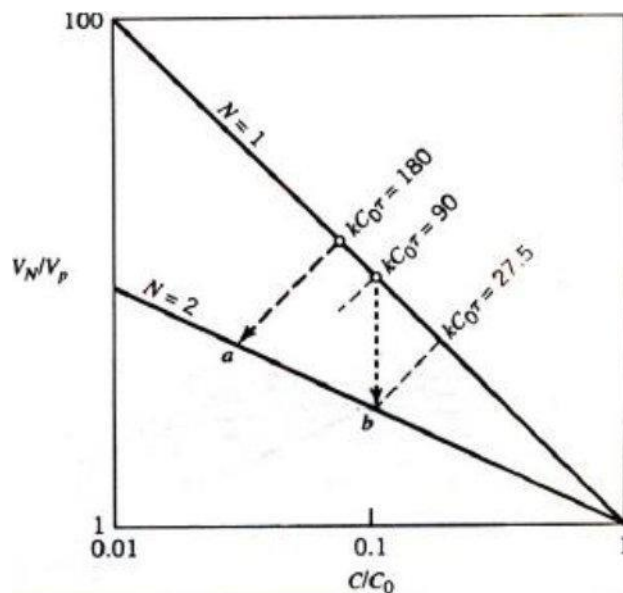*(b) Find the treatment rate for the same conversion.* Staying on the 90% conversion

line, we find for $N = 2$ that

$kC_o\tau = 27.5$, point b

Comparing the value of the reaction rate group for $N = 1$ and $N = 2$, we find
Since $V_2 = 2V_1$ the ratio of flow rates becomes

Thus, the treatment rate can be raised to 6.6 times the original.

3.5 Mixed Flow Reactors of Different Sizes in Series

For arbitrary kinetics in mixed flow reactors of different size, two types of questions may be asked: how to find the outlet conversion from a given reactor system, and the inverse question, how to find the best setup to achieve a given conversion. Different procedures are used for these two problems.

3.5.1 Finding the Conversion in a Given System

A graphical procedure for finding the outlet composition from a series of mixed flow reactors of various sizes for reactions with negligible density change has been presented by Jones (1951). All that is needed is an r versus C curve for component A to represent the reaction rate at various concentrations. It is illustrated by the use of this method by considering three mixed flow reactors in series with volumes, feed rates, concentrations, space-times (equal to residence timesbecause ρ = O), and volumetric flow rates as shown in figure below. Now from equation noting that $\rho = 0$, we may write for component **A** in the first reactor
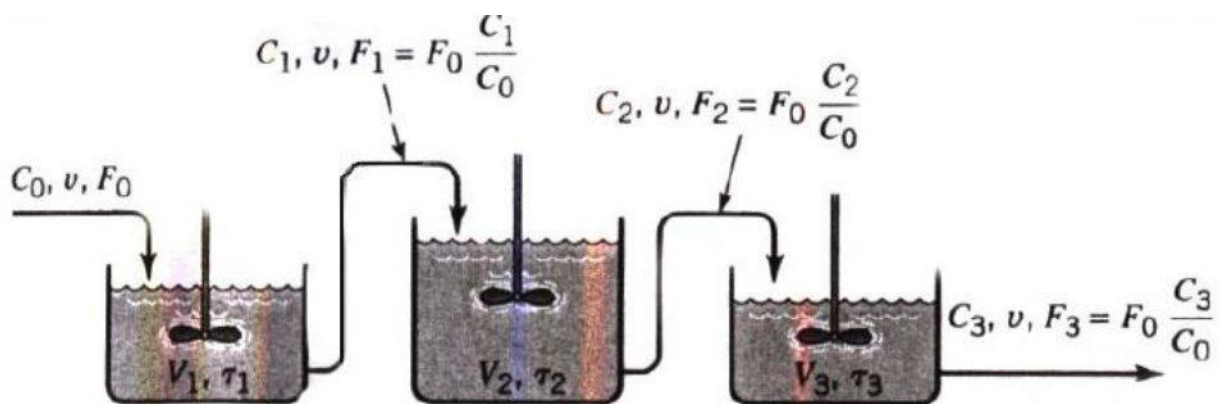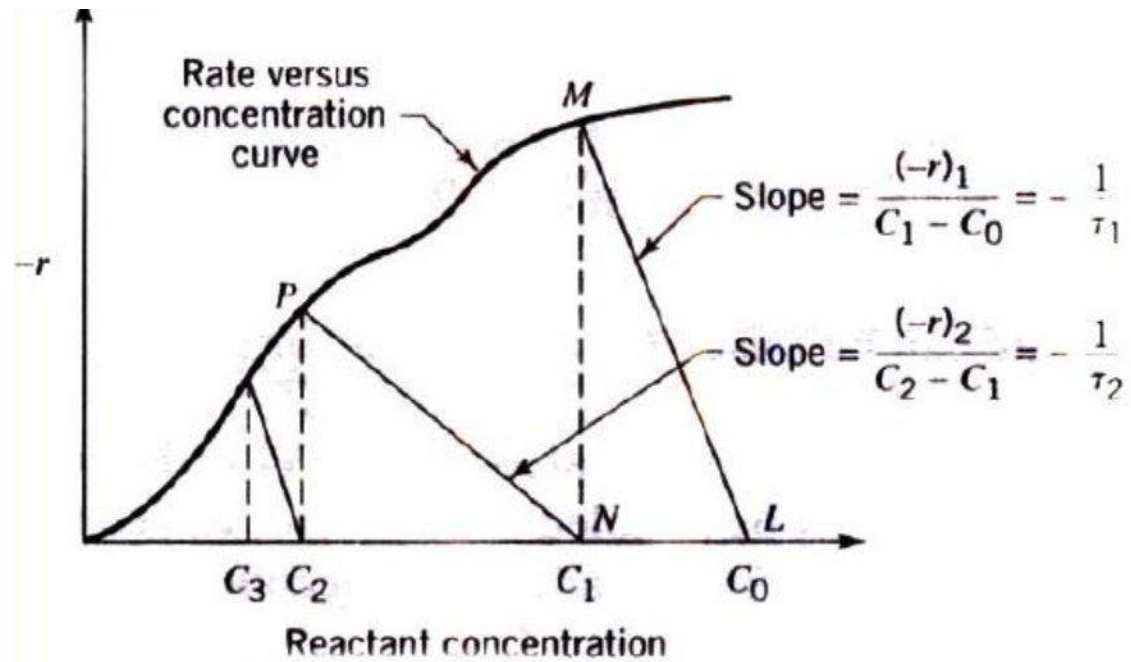
$\tau_1 = V_1/ v = C_0-C_1/(-r_1)$ $-1/ \tau_1 = (-r_1) / C_1-C_0$

For i th reactor

$-1/ \tau_i = (-r_i) / C_i-C_{i-1}$

Rate versus concentration curve

$\text{Slope} = \dfrac{(-r)_1}{C_1 - C_0} = -\dfrac{1}{\tau_1}$

$\text{Slope} = \dfrac{(-r)_2}{C_2 - C_1} = -\dfrac{1}{\tau_2}$

Reactant concentration

Plot the C versus r curve for component A and it is as shown in figure above. To find the conditions in the first reactor note that the inlet concentration Co is known (point L), that C, and $(-r)$, correspond to a point on the curve to be found (point M), and that the slope of the line LM = MNINL = (-r),l (C, - Co) = -(l/rl) from equation. Hence, from Co draw a line of slope - (l/r,) until it cuts the rate curve; this gives C1. Similarly, we find from equation, that a line of slope -(1/r2) from point N cuts the curve at P, giving the concentration C2 of material leaving the second reactor. This procedure is then repeated as many times as needed. With slight modification this graphical method can be extended to reactions in which density changes are appreciable.

3.5.2 Determining the Best System for a Given Conversion

To find the minimum size of two mixed flow reactors in series to achieve a specified conversion of feed which reacts with arbitrary but known kinetics, the following procedure is followed. The basic performance expressions, from equations, give, in turn, for the first reactor

$$\frac{\tau_1}{C_0} = \frac{V_1}{F_0}$$

$$\tau_1/C_0 = X_1/(-r_1)$$
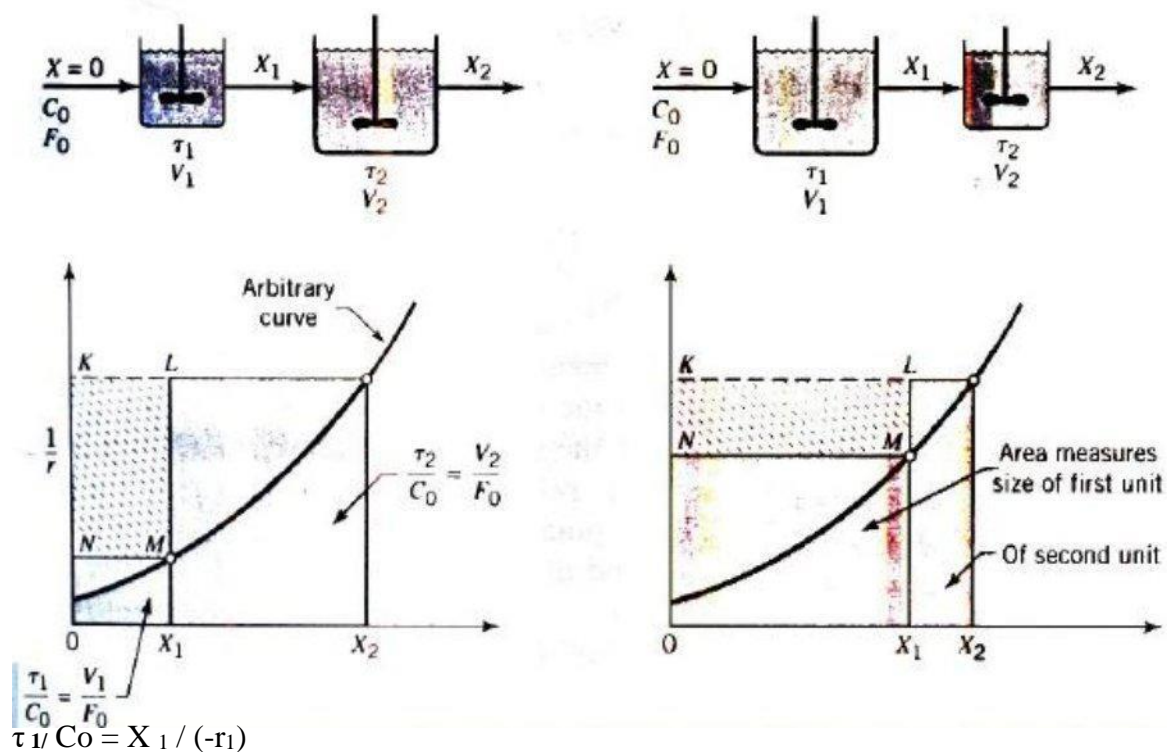
and for the second reactor

$$\tau_2 / Co = X_2 - X_1 / (-r_2)$$

as the intermediate conversion *XI* changes, so does the size ratio of the units (represented by the two shaded areas) as well as the total volume of the two vessels required (the total area shaded). Figure shows that the total reactor volume is as small as possible (total shaded area is minimized) when the rectangle KLMN is as large as possible. This brings us to the problem of choosing *XI* (or point M on the curve) so as to maximize the area of this rectangle. This is done according to Maximization of Rectangles concept.In the below figure, construct a rectangle between the x-y axes and touching the arbitrary curve at point M(x, y). The area of the rectangle is then

$$A = xy$$

This area is maximized when

$$da = 0 = xdy + ydx$$

or when $-dy/dx = y/x$
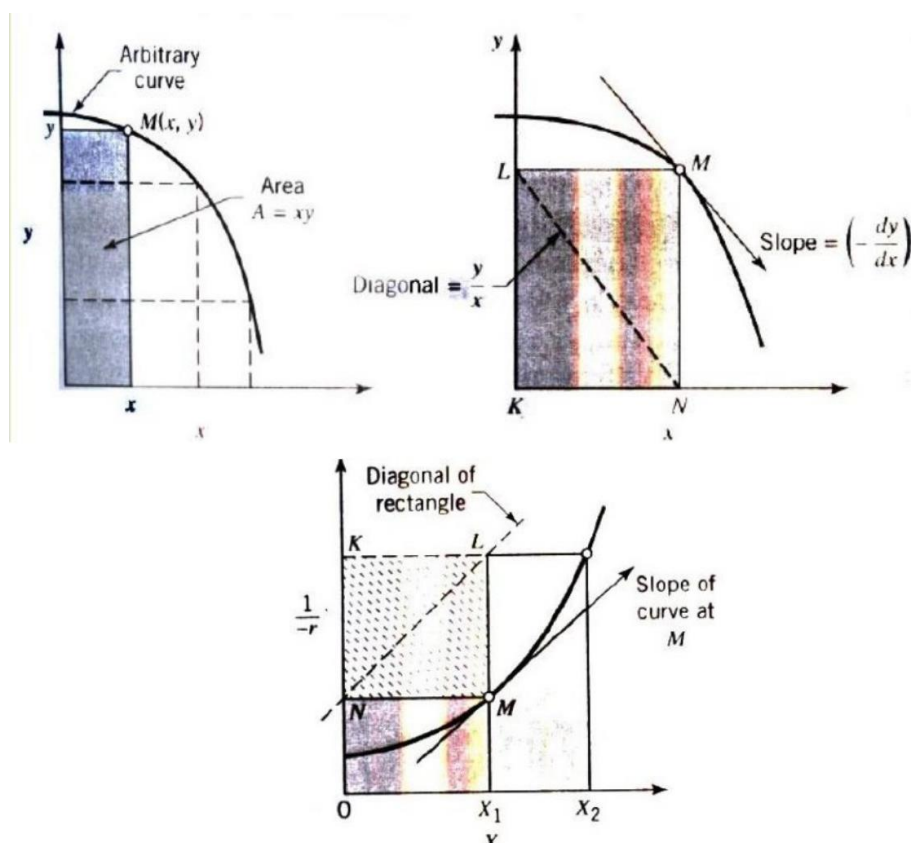
In words, this condition means that the area is maximized when M is at that point where the slope of the curve equals the slope of the diagonal NL of the rectangle. Depending on the shape of the curve, there may be more than one or there may be no "best" point. However, for nth-order kinetics, $n > 0$, there always is just one "best" point. The optimum size ratio of the two reactors is achieved where the slope of the rate curve at M equals the diagonal NL. The best value of M is shown in figure, and this determines the intermediate conversion X, as well as the size of units needed. The optimum size ratio for two mixed flow reactors in series is found in general to be dependent on the kinetics of the reaction and on the conversion level. For the special case of first-order reactions equal-size reactors are best; for reaction orders $n > 1$ the smaller reactor should come first; for $n < 1$ the larger should come first. However, Szepe and Levenspiel (1964) show that the advantage of the minimum size system over the equal-size system is quite small, only a few percent at most. Hence, overall economic consideration would nearly always recommend using equal-size units.

3.6 Best Arrangement of a Set of Ideal Reactors
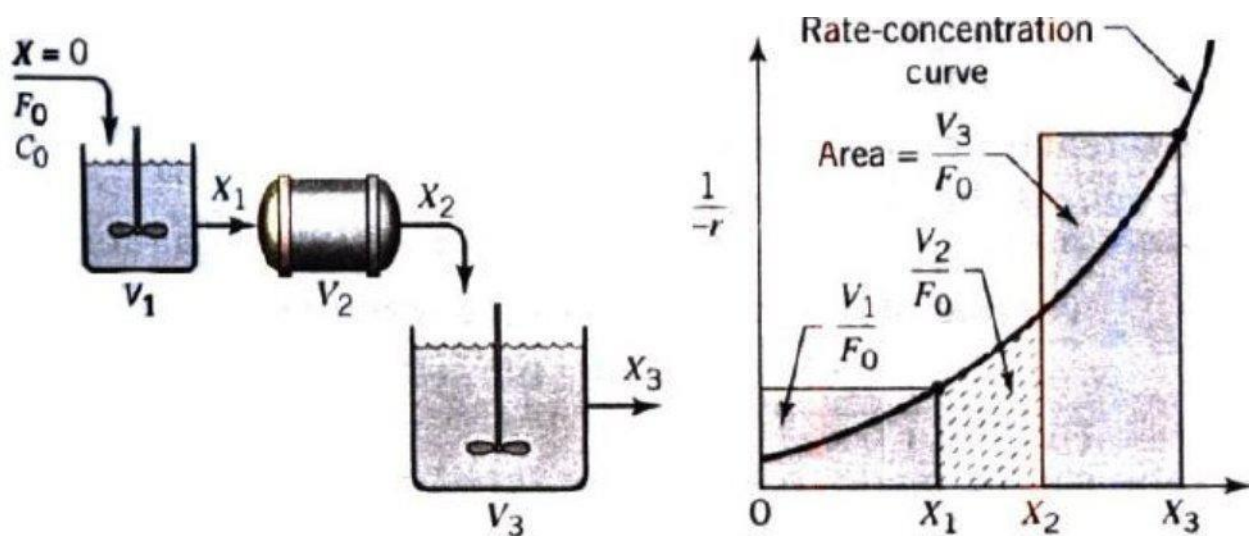
For the most effective use of a given set of ideal reactors we have the following general rules:

1. For a reaction whose rate-concentration curve rises monotonically (any nth-order reaction, n >

0) the reactors should be connected in series. They should be ordered so as to keep the concentration of reactant as high as possible if the rate-concentration curve is concave (n > I), and as low as possible if the curve is convex (n < 1). As an example, for the case of above figure the ordering of units should be plug, small mixed, large mixed, for n > 1; the reverse order should be used when $n < 1$.

2. For reactions where the rate-concentration curve passes through a maximum or minimum the arrangement of units depends on the actual shape of curve, the conversion level desired, and the units available. No simple rules can be suggested.

3. Whatever may be the kinetics and the reactor system, an examination of the l/(-r) vs. CA curve is a good way to find the best arrangement of units.

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

**UNIT – IV - Chemical Reaction Engineering-1 – SCHA1402**

DESIGN OF SINGLE AND MULTIPLE REACTORS FOR MULTIPLE REACTIONS

More than one reaction occurs within a chemical reactor. Minimization of undesired side reactions that occur with the desired reaction contributes to the economic success of a chemical plant. The distinction between a single reaction and multiple reactions is that the single reaction requires only one rate expression to describe its kinetic behavior whereas multiple reactions require more than one rate expression. Multiple reactions are of two primary types: parallel reactions and series reactions.
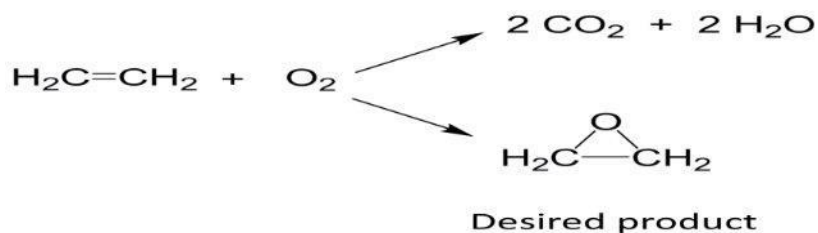
4.1 Multiple Reactions

Parallel or competing reactions

When a reactant gives two product (desired, and undesired) simultaneously with different rate constant then this is called a parallel reaction.
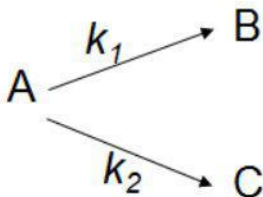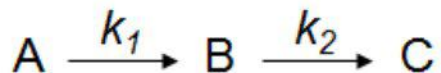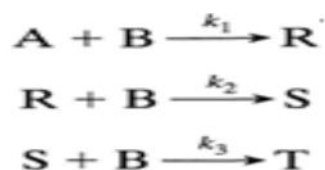

With an example

Series reactions

When a reactant gives an intermediate (desired product) which decomposes to product

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Series-Parallel reactions

Multiple reaction that consist of steps in series and steps in parallel reaction. In these reaction proper contacting pattern is very important.

The general representation of these reaction are

$$A + B \xrightarrow{k_1} R$$
$$R + B \xrightarrow{k_2} S$$
$$S + B \xrightarrow{k_3} T$$

Here the reaction is parallel with respect to reactant B and in series with A.

$$A \xrightarrow{+B,\, k_1} R \xrightarrow{+B,\, k_2} S \xrightarrow{+B,\, k_3} T$$
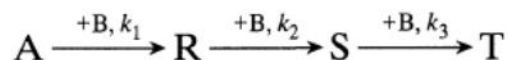
With an example

Halogenations of alkane is a example of this kind of reaction where reaction is parallel with respect to halogen

$$C_6H_6 \xrightarrow{+Cl_2} C_6H_5Cl \xrightarrow{+Cl_2} \cdots \xrightarrow{+Cl_2} C_6Cl_6$$

$$C_6H_6 \xrightarrow{+HNO_3} C_6H_5NO_2 \xrightarrow{+HNO_3} \cdots \xrightarrow{+HNO_3} C_6H_3(NO_2)_3$$

$$CH_4 \xrightarrow{+Cl_2} CH_3Cl \xrightarrow{+Cl_2} \cdots \xrightarrow{+Cl_2} CCl_4$$
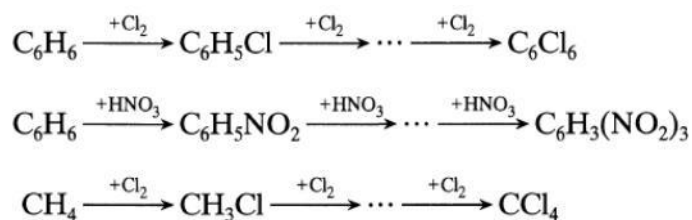
4.2 PARALLEL REACTIONS

4.2.1 Qualitative Discussion About Product Distribution

Consider the decomposition of A by either one of two paths

$$A \xrightarrow{k_1} D \quad \text{(Desired)} \quad r_D = k_1 C_A^{\alpha}$$
$$A \xrightarrow{k_2} U \quad \text{(Undesired)} \quad r_U = k_2 C_A^{\beta}$$
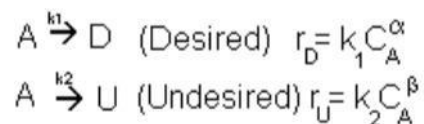
The net rate of disappearance of A

$$r_A = r_D + r_U$$

$$S_{D/W} = \frac{r_D}{r_U} = \frac{k_1 C_A^{\alpha}}{k_2 C_A^{\beta}} = \frac{k_1}{k_2} C_A^{(\alpha-\beta)}$$

gives a measure of the relative rates of formation of D and U. This ratio is adjusted to be as large as possible

If $\alpha > \beta$ use high concentration of A. Use PFR.

If $\alpha < \beta$ use low concentration of A. Use CSTR

Now concentration is the only factor in this equation which we can adjust and control (k_1, k_2, $a_1(\alpha)$ and $a_2(\beta)$) are all constant for a specific system at a given temperature) and we can keep concentration, low throughout the reactor by any of the following means: by using a mixed flow reactor, maintaining high conversions, increasing inerts in the feed, or decreasing the pressure in gas-phase systems. On the other hand, we can keep CA high by using a batch or plug flow reactor, maintaining low conversions, removing inerts from the feed, or increasing the pressure in gas phase systems. For the reactions of whether the concentration of A should be kept high or low.

If $a_1 > a_2$ or the desired reaction is of higher order than the unwanted reaction, Equation shows that a high reactant concentration is desirable since it increases the R/S ratio. As a result, a batch

or plug flow reactor would favor formation of product R and would require a minimum reactor size.

If $a_1 < a_2$ or the desired reaction is of lower order than the unwanted reaction, we need a low reactant concentration to favor formation of R. But this would also require large mixed flow reactor.
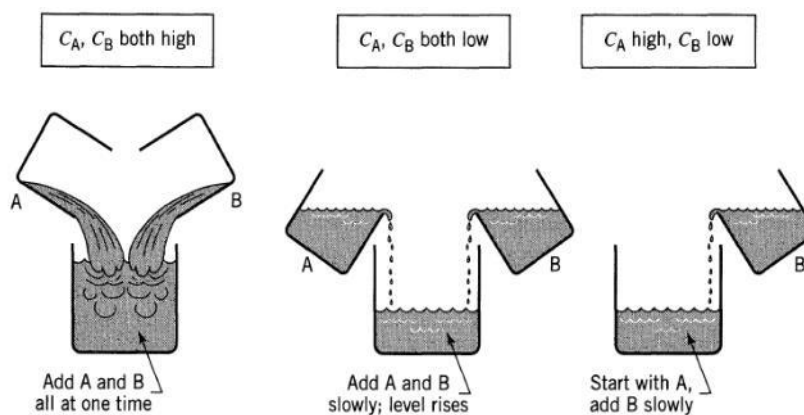
If $a_1 = a_2$ or the two reactions are of the same order, then only rate constant is the deciding authority

Hence, product distribution is fixed by k_2/k_1 alone and is unaffected by type of reactor used. We also may control product distribution by varying k_2/k_1. This can be done in two ways:

1. By changing the temperature level of operation. If the activation energies of the two reactions are different, k_2/k_1can be made to vary.

2. By using a catalyst. One of the most important features of a catalyst is its selectivity in depressing or accelerating specific reactions. This may be a much more effective way of controlling product distribution than any of the methods .

For reactions in parallel, the concentration level of reactants is the key to proper control of product distribution. A high reactant concentration favors the reaction of higher order, a

low concentration favors the reaction of lower order, while the concentration level has no effect on the product distribution for reactions of the same order.

| C_A, C_B both high | C_A, C_B both low | C_A high, C_B low |

Add A and B all at one time   Add A and B slowly; level rises   Start with A, add B slowly

For example, another case in maximizing the desired product in parallel reactions

$$A+B \begin{array}{c} \xrightarrow{k_D} D \\ \xrightarrow{k_U} U \end{array}$$

$r_D \quad k_D C_A{}^{a1} C_B{}^{b1}$

$$\frac{-E_D}{}$$
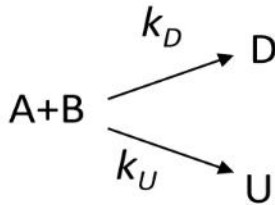
$$Æ\ r_D = A_D e^{\ RT}\ C_A{}^{a1} C_B{}^{b1}$$

$r_U \quad k_U C_A{}^{a2} C_B{}^{b2}$

$-E_U$

$$Æ\ r_U = A\ _U e^{\ RT}\ C_A{}^{a2} C_B{}^{b2}$$

Rate of disappearance of A: $-r_A = {}_{rD} + {}_{rU}$

Let α1 be the order of the desired reaction A + B → D and α2 be the order of the undesired reaction A + B → U. Let ED be the activation energy of the desired reaction and EU be the activation of the undesired reaction. We want to maximize selectivity. If α1 > α2: We want the concentration of the reactant to be as high as possible since C α1−α2 A has a positive exponent . If in the gas phase, the reaction should be run without inerts and at high pressure . If in the liquid phase, the reaction should be run without dilutents . A batch or PFR should be used since CA starts at a high value and drops over the course of the reaction whereas it is always at the lowest concentration in a CSTR (i.e. the outlet concentration) . If α2 > α1: We want the concentration of the reactant to be as low as possible since C α1−α2 .A has a negative exponent . If in the gas phase, the reaction should be run with inerts and at low pressure .If in the liquid phase, the reaction should be run without dilutents . A CSTR or recycle reactor should be used . If ED > EU

High temperature should .If EU > ED Low temperature should be used (but not so low that the desired reaction never proceeds) .For analyzing the effect of activatoin energies on selectivity, one can state the following if the reaction is A → D and A → U SD/U ~ kD kU = AD AU e −[(ED−EU)/(RT)] . Let α1 and β1 be the order of the desired reaction A + B → D and α2 and β2 be the order of the desired reaction A + B → D if the reaction rates can be described by r = kCα AC β B. We want to maximize the selectivity of the desired product: If α1 > α2 and β1 > β2: Since C α1−α2 A and C β1−β2 B. Both have positive exponents, the concentration of both A and B should be maximized. Therefore, a tubular reactor or batch reactor should be used .High pressure for a gas phase reaction and a minimization of inerts should be considered .If α1 > α2 but β2 > β1: Since C α1−α2 .A has a positive exponent but C β1−β2 B has a negative exponent, the concentration of A should be maximized, but the concentration of B should be minimized.

4.2.2 Quantitative Treatment of Product Distribution and of Reactor Size.

If rate equations are known for the individual reactions, we can quantitatively determine product distribution and reactor-size requirements. For convenience in evaluating product distribution we introduce two terms, φ and Φ. First, consider the decomposition of reactant A, and let φ be the fraction of A disappearing at any instant which is transformed into desired product R. This is called as instantaneous fractional yield of R.

Thus at any CA .

φ = moles R formed/ moles A reacted

For any particular set of reactions and rate equations φ is a function of CA, and since CA in general varies through the reactor, φ will also change with position in the reactor. So let us define

Φ as the fraction of all the reacted A that has been converted into R, and let us call this the overall fractional yield *of* R. The overall fractional yield is then the mean of the instantaneous fractional yields at all points within the reactor; thus we may write

φ = all R formed / all A reacted

It is the overall fractional yield that really concerns us for it represents the product distribution at the reactor outlet. Now the proper averaging for φ p depends on the type of flow within the reactor.

The Selectivity

The selectivity, is often used in place of fractional yield. It is usually defined as follows:

Selectivity = moles of desired product formed/moles of undesired material formed

4.3 SERIES REACTIONS

4.3.1 Qualitative Discussion About Product Distribution.

Consider the following two ways of treating a beaker containing A: First, the contents are uniformly irradiated; second, a small stream is continuously withdrawn from the beaker, irradiated, and returned to the beaker; the rate of absorption of radiant energy is the same in the two cases. During this process A disappears and products are formed. In the first beaker, when the contents are being irradiated all at the same time, the first bit of light will attack A alone because only A is present at the start. The result is that R is formed. With the next bit of light both A and R will compete; however, A is in very large excess so it will preferentially absorb the radiant energy to decompose and form more R. Thus, the concentration of R will rise while the concentration of A will fall. This process will continue until R is present in high enough concentration so that it can compete favorably with A for the radiant energy. When this happens, a maximum R concentration is reached. After this the decomposition of R becomes more rapid than its rate of formation and its concentration drops. In the alternative way of treating A, a small fraction of the beaker's contents is continuously removed, irradiated, and returned to the beaker. Although the total absorption rate is the same in the two cases, the intensity of radiation received by the removed fluid is greater, and it could well be, if the flow rate is not too high, that the fluid being irradiated reacts essentially to completion. In this case, then, A is removed and S is returned to the beaker. So, as time passes the concentration of A slowly decreases in the beaker, S rises, while R is absent. These two methods of reacting the contents of the beaker yield different product distributions and represent the two extremes in possible operations, one with a maximum possible formation of R and the other with a minimum, or no formation, of R. We note in the first method that the contents of the beaker remain homogeneous throughout, all changing slowly with time, whereas in the second a stream of highly reacted fluid is continually being mixed with fresh fluid. In other words, we are mixing

two streams of different compositions. This discussion suggests the following rule governing product distribution for reactions in series.

For irreversible reactions in series the mixing of fluid of different composition is the key to the formation of intermediate. The maximum possible amount of any and all intermediates is obtained if fluids of different compositions and at different stages of conversion are not allowed to mix. As the intermediate is frequently the desired reaction product, this rule allows us to evaluate the effectiveness of various reactor systems. For example, plug flow and batch operations should both give a maximum R yield because here there is no mixing of fluid streams of different compositions. On the other hand, the mixed reactor should not give as high a yield of R as possible because a fresh stream of pure A is being mixed continually with an already reacted fluid in the reactor.
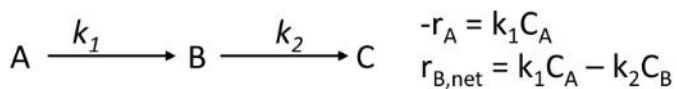
4.3.2 Quantitative Treatment of Product Distribution and of Reactor Size.

A→R→S
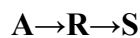
The concentration- time curves for this reaction when it takes place in a mixed flow reactor. Again, the derivation will be limited to a feed which contains no reaction product R or S. By the steady-state material balance we obtain for any component input = output + disappearance by reaction

which for reactant A becomes

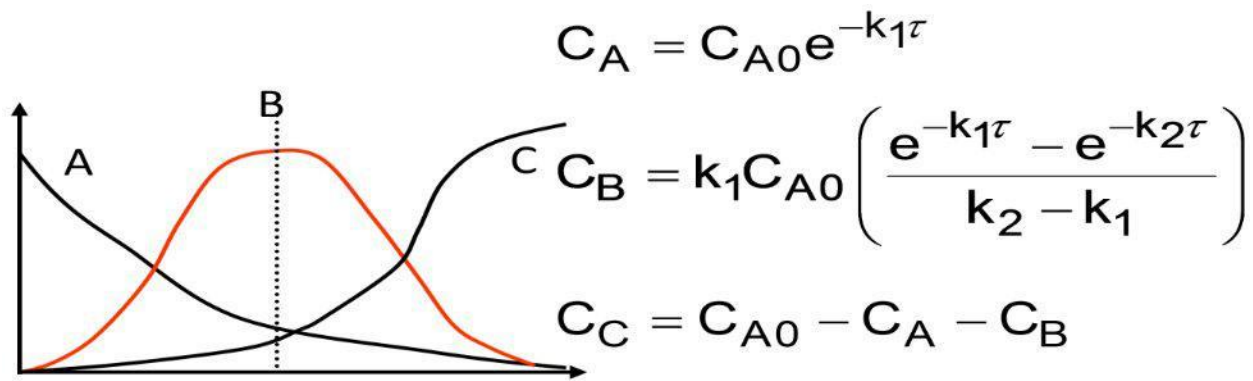Noting that we obtain for A, on rearranging,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \begin{aligned} -r_A &= k_1 C_A \\ r_{B,net} &= k_1 C_A - k_2 C_B \end{aligned}$$

$$\frac{dF_A}{dV} = -k_1 C_A \; \text{Æ} u_0 \frac{dC_A}{dV} = -k_1 C_A \; \text{Æ} \; C_A = C_{A0} e^{-k_1 t} \frac{dF_B}{dV}$$
$$= k_1 C_A - k_2 C_B$$

$$\rightarrow C_B = k_1 C_{A0} \left(\frac{e^{-k_1 \tau} - e^{-k_2 \tau}}{k_2 - k_1} \right)$$

$$C_C = C_{A0} - C_A - C_B$$

$$C_A = C_{A0}e^{-k_1\tau}$$

$$C_B = k_1 C_{A0}\left(\frac{e^{-k_1\tau} - e^{-k_2\tau}}{k_2 - k_1}\right)$$

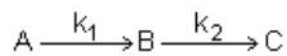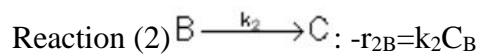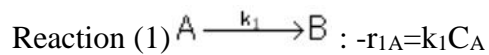$$C_C = C_{A0} - C_A - C_B$$

$$\tau_{opt} = \frac{1}{k_1 - k_2}\ln\frac{k_1}{k_2}$$

Example: Series Reaction in a batch reactor

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

This series reaction could also be written as

Reaction (1) $A \xrightarrow{k_1} B$: $-r_{1A} = k_1 C_A$

Reaction (2) $B \xrightarrow{k_2} C$: $-r_{2B} = k_2 C_B$

Mole Balance on every species

Species A:

Combined mole balance and rate law for a control volume batch reactor.

Batch Reactor $V = V_0$

$$\frac{1}{V_0}\frac{dN_A}{dt} = r_A$$

Net Rate of Reaction of A

$$r_A = r_{1A} + 0$$

Rate Law

$r_{1A} = -k_{1A}C_A$

Relative Rates

$$r_{1B} = -r_{1A}$$

$$\frac{dC_A}{dt} = -k_{1A}C_A$$

Integrating   with
$C_A = C_{A0}$ at t=0 and
then rearranging

$$C_A = C_{A0}\exp(-k_1 t)$$

Mole Balance

$$\frac{dC_B}{dt} = r_B$$

Species B:

Net Rate of Reaction of B

$$r_B = r_{B\,NET} = r_{1B} + r_{2B}$$

Rate Law

$$r_{2B} = -k_2 C_B$$

Combine

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} \exp(-k_1 t)$$

Using
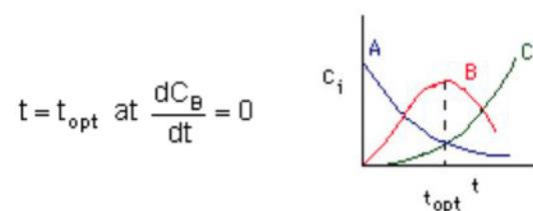
the integrating
factor, i.f.:

$$\text{i.f.} = \exp\int k_2 \, dt = \exp(k_2 t)$$

$$\frac{d[C_B \exp(k_2 t)]}{dt} = k_1 C_{A0} \exp(k_2 - k_1)t$$

$$\boxed{C_B = \frac{k_1 C_{A0}}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]}$$

at $t = 0$, $C_B = 0$

Optimization of the Desired Product B

$$t = t_{opt} \text{ at } \frac{dC_B}{dt} = 0$$

Then

Species C $C_C = C_{A0} - C_B - C_A$

$$C_C = \frac{C_{A0}}{k_2 - k_1}\left[k_2\left(1 - e^{-k_1 t}\right) - k_1\left(1 - e^{-k_2 t}\right)\right]$$

The series reaction is when the reactant forms an intermediate product, which reacts further to form another product (e.g.. $A \rightarrow B \rightarrow C$) . The parallel reaction occurs when the reactant is consumed by two different reaction pathways to form different products (e.g. A breaks down to both B and C) .Complex reactions are multiple reactions that involve a combination of both series and parallel reactions . Independent reactions occur are reactions that occur at the same time but neither the products nor reactants react with themselves or one another (e.g. $A \rightarrow B + C$ and $D \rightarrow E + F$) The selectivity is defined as S = rate of formation of desired product rate of formation of undesired product. The overall selectivity is defined as $S^\sim$ = exit molar flow rate of desired product exit molar flow rate of undesired product. For a CSTR, the overall selectivity and selectivity are identical . For a CSTR, the highest overall yield (i.e. most product formed)occurs when the rectangle under the rate vs. CA curve has the largest area .For a PFR, the highest overall yield (i.e. most product formed) occurs when the area under the (rate) vs, CA curve is maximized . If unreacted reagent can be separated from the exit stream and recycled, the highest overall yield (i.e. most product formed) is at the maximum of the (rate) vs. CA curve.

4.4 SERIES-PARALLEL REACTIONS
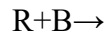
Multiple reactions that consist of steps in series and steps in parallel are called series-parallel reactions.

k1

A+B→ R

k_2

R+B→
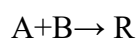
S
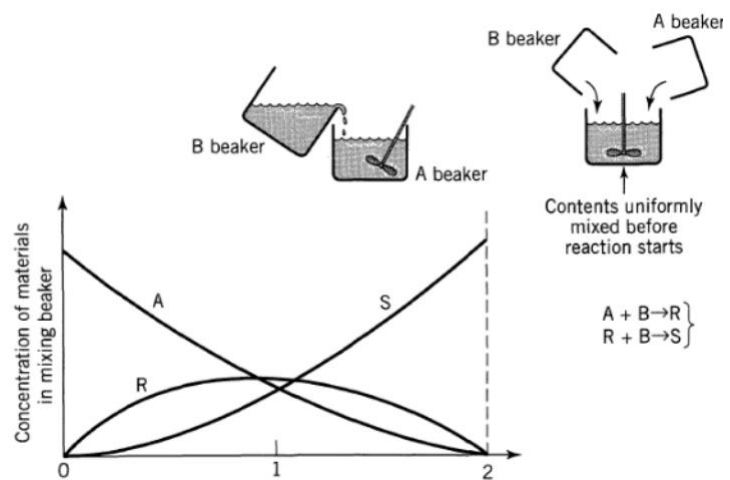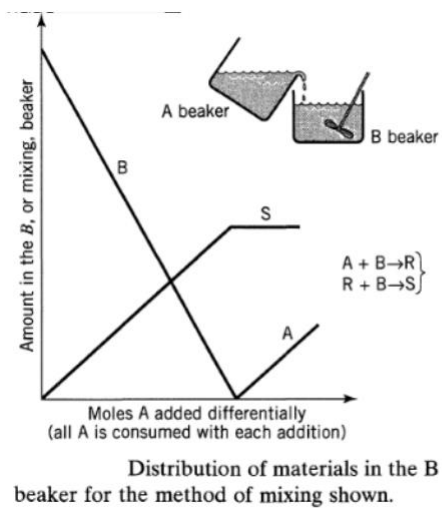
$d[A]/dt = -k_1[A][B]$

$d[B]/dt = -k_1[A][B]-k_2[R][B]$

$d[R]/dt = k_1[A][B]-k_2[R][B]$

$d[S]/dt = k_2[R][B]$

4.4.1 Qualitative Discussion About Product Distribution.

Distribution of materials in the B
beaker for the method of mixing shown.

There are two beakers, one containing A and the other containing B. Consider the following ways of mixing the reactants: (a) add A slowly to B, (b) add B slowly to A, and finally (c) mix A and B together rapidly.

(a) Add A *Slowly to B.* For the first alternative pour A a little at a time into the beaker containing B, stirring thoroughly and making sure that all the A is used up and that the reaction stops before the next bit is added. With each addition a bit of R is produced in the beaker. But this R finds itself in an excess of B so it will react further to form S. The result is that at no time during the slow addition will A and R be present in any appreciable amount. The mixture becomes progressively richer in S and poorer in B. This continues until the beaker contains only S.

(b) **Add *B Slowly to* A.** Now pour B a little at a time into the beaker containing A, again stirring thoroughly. The first bit of B will be used up, reacting with A to form R. This R cannot react further for there is now no B present in the mixture. With the next addition of B, both A and R will compete with each other for the B added, and since A is in very large excess it will react with most of the B, producing even more R. This process will be repeated with progressive build up of R and depletion of A until the concentration of R is high enough so that it can compete favorably with A for the B added. When this happens, the concentration of R reaches a maximum, then decreases. Finally, after addition of 2 moles of B for each mole of A, we end up with a solution containing only S.

*(c) **Mix A and B Rapidly.*** Now consider the third alternative where the contents of the two beakers are rapidly mixed together, the reaction being slow enough so that it does not proceed to any appreciable extent before the mixture becomes uniform. During the first few reaction

(d) increments R finds itself competing with a large excess of A for B and hence it is at a disadvantage. Thus, when A is kept uniform in composition as it reacts, then R is formed. However, when fresh A is mixed with partly reacted mixture, then no intermediate R forms. But this is precisely the behavior of reactions in series. Thus, as far as A, R, and S are concerned, the concentration level of B, whether high or low, has no effect on the path of the reaction and on the distribution of products. But this is precisely the behavior of parallel reactions of the same order. So it can be looked at as Irreversible series-parallel reactions can be analyzed in terms of their constituent series reactions and parallel reactions in that optimum contacting for favorable product distribution is the same as for the constituent reactions.

4.4.2 Quantitative Treatment, Plug Flow or Batch Reactor.

Quantitatively treat the reactions with the understanding that R, the intermediate, is the desired product, and that the reaction is slow enough so that we may ignore the problems of partial reaction during the mixing of reactants. In general, taking the ratio of two rate equations eliminates the time variable and gives information on the product distribution. We obtain the first-order linear differential equations . With no R present in the feed the limits of integration are CAO to C_A for A and CRO = 0 for R, and the solution of this differential equation is given by mathematical calculation. This gives the relationship between CR and CA in a batch or in a plug flow reactor. To find the concentrations of the other components, simply make a material balance. An A balance gives

$$C_{AO} + C_{RO} + C_{SO} = C_A + C_R + C_S$$

from which C_S can be found as a function of C_A and C_R. Finally, a balance about B gives C_B.

4.4.3 Quantitative Treatment, Mixed Flow.

Writing the design equation for mixed flow in terms of A and R gives rate equations. Rearranging, we obtain which the difference equation is corresponding to the differential equation. Writing CR in terms of CA then gives equations which can be solved mathematically. Material balances about A and B in plug flow, hold equally well for mixed flow and serve to complete the set of equations giving complete product distribution in this reactor.

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – V - Chemical Reaction Engineering-1 – SCHA1402

NON-ISOTHERMAL REACTOR DESIGN

The reaction temperature and pressure also influence the progress of reactions. A three-step procedure is followed: 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 for single reactions and follow this with the special considerations of multiple reactions.

5.1 Single Reactions

With single reactions conversion level and reactor stability are the important criteria. Questions of product distribution do not occur. Thermodynamics gives two important pieces ofinformation, the first being the heat liberated or absorbed for a given extent of reaction, the second being the maximum possible conversion.

5.2 Heats of Reaction from Thermodynamics

The heat liberated or absorbed during reaction at temperature $T,$ 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 $H,$ 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 $H,$ or heats of combustion $H,$ of the reacting materials. These are tabulated at some standard temperature, $T1,$ usually 25°C. As a brief reminder, consider the reaction

aA + 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 + rR + **sS,** *AHrT* { positive, endothermic

negative, exothermic

$$aA \rightarrow rR + sS, \qquad \Delta H_{rT} \begin{cases} \text{positive, endothermic} \\ \text{negative, exothermic} \end{cases}$$
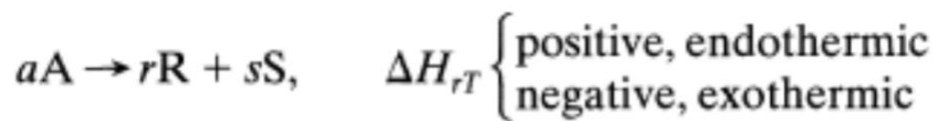
$$\begin{pmatrix} \text{heat absorbed} \\ \text{during reaction} \\ \text{at temperature} \\ T_2 \end{pmatrix} = \begin{pmatrix} \text{heat added to} \\ \text{reactants to} \\ \text{change their} \\ \text{temperature} \\ \text{from } T_2 \text{ to } T_1 \end{pmatrix} + \begin{pmatrix} \text{heat absorbed} \\ \text{during reaction} \\ \text{at temperature} \\ T_1 \end{pmatrix} + \begin{pmatrix} \text{heat added to} \\ \text{products to} \\ \text{bring them} \\ \text{back to } T_2 \\ \text{from } T_1 \end{pmatrix}$$

5.3 Heats of Reaction and Temperature.

The first problem is to evaluate the heat of reaction at temperature *T2* knowing the heat of reaction at temperature *T1*. This is found by the law of conservation of energy .

    – a_i activity of component I

Gas Phase, $a_i = \varphi_i y_i P,$

    – $\varphi_{i==}$ fugacity coefficient of i Liquid

Phase, $a_i = \gamma_i x_i \exp[V_i (P-P_i{}^S)/RT]$

    – γ_i = activity coefficient of i

Energy Balance with "dissected" enthalpies:

$$\dot{Q} - \dot{W}_s - F_{A0} \int_{T_R}^{T} \sum \Theta_i C_{Pi} \, dT - F_{A0} X \left[\Delta H_R^\circ(T_R) + \int_{T_R}^{T} \Delta C_P \, dT \right] = 0$$

For constant or mean heat capacities:

$$\dot{Q} - \dot{W}_s - F_{A0} X \left[\Delta H_R^\circ(T_R) + \Delta \hat{C}_P(T - T_R) \right] = F_{A0} \sum \Theta_i \tilde{C}_{Pi}(T - T_{i0})$$

V_i = Partial Molar Volume of i

$$\Delta H_{r2} = -(H_2 - H_1)_{\text{reactants}} + \Delta H_{r1} + (H_2 - H_1)_{\text{products}}$$

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

$$C_{pA} = \alpha_A + \beta_A T + \gamma_A T^2$$
$$C_{pR} = \alpha_R + \beta_R T + \gamma_R T^2$$
$$C_{pS} = \alpha_S + \beta_S T + \gamma_S T^2$$

Knowing the heat of reaction at any one temperature as well as the specific heats of reactants and products in the temperature range concerned allows us to calculate the heat of reaction at any other temperature. From this the heat effects of the reaction can be found.

5.4 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.

$$\delta = 0$$

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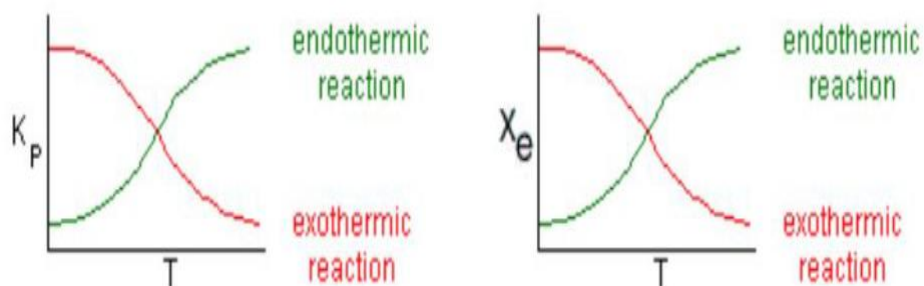
5.5 Equilibrium Conversion

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

$$\frac{d\ln K_P}{dT} = \frac{\Delta H_R(T)}{RT^2} = \frac{\Delta H_R^0(T_R) + \Delta \hat{C}_P (T - T_R)}{RT^2}$$

On integrating , we see how the equilibrium constant changes with temperature. When the heat of reaction H, can be considered to be constant in the temperature interval, integration yields

$$K_P(T_2) = K_P(T_1) \exp\left[\frac{\Delta H_R^0(T_R)}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

These expressions allow us to find the variation of the equilibrium constant, hence, equilibrium conversion, with temperature.
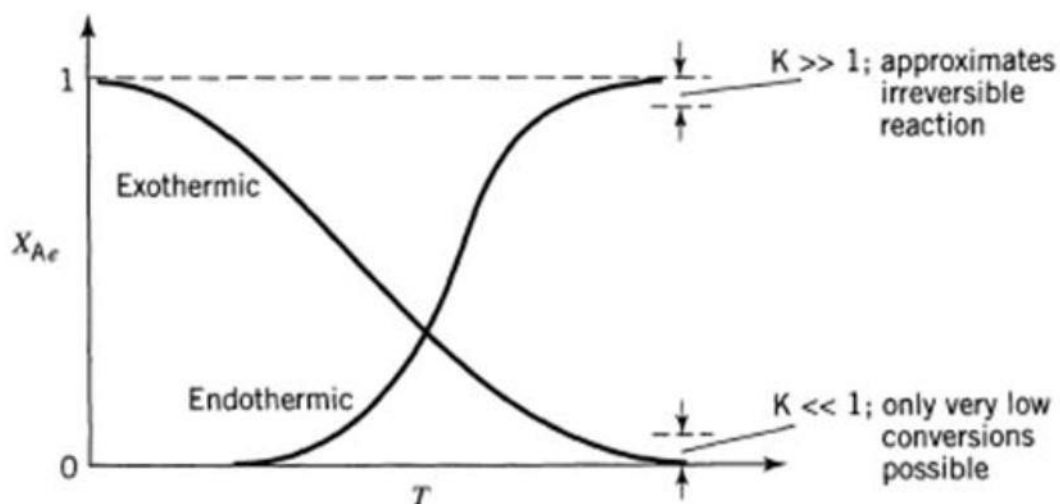
1. The thermodynamic equilibrium constant is unaffected by the pressure of the system, by the presence or absence of inerts, or by the kinetics of the reaction, but is affected by the temperature of the system.

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.

3. K > 1 indicates that practically complete conversion may be possible and that the reaction can be considered to be irreversible. K < 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.

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. *Le Chatelier's Principle*
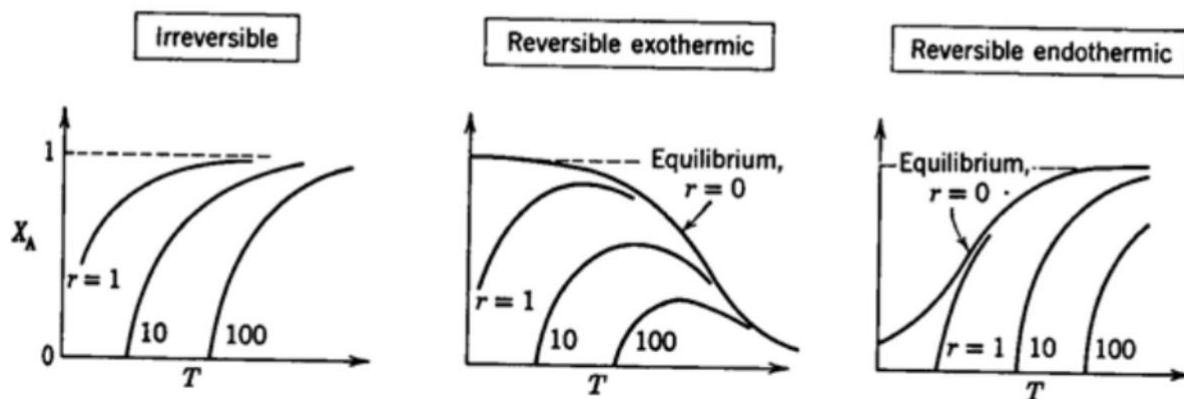
5.6 General Graphical Design Procedure

Temperature, composition, and reaction rate are uniquely related for any single homogeneous reaction, and this may be represented graphically in one of three ways, as shown in figure. The first of these, the composition-temperature plot, is the most convenient so we will use it throughout to represent data, to calculate reactor sizes, and to compare design alternatives.

For a given feed and using conversion of key component as a measure of the composition and extent of reaction, the XA versus T plot has the general shape shown in figure. This plot can be prepared either from a thermodynamically consistent rate expression for the reaction (the rate must be zero at equilibrium) or by interpolating from a given set of kinetic data in conjunction with thermodynamic information on the equilibrium. Naturally, the reliability of all the calculations and predictions that follow are directly dependent on the accuracy of this chart. Hence, it is imperative to obtain good kinetic data to construct this chart. 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 *XA* versus T plot. This is the *operating line* for the operation.

2. Find the rates at various *XA* along this path.

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

4. Find the area under this curve. This gives V/FAo.

For exothermic reactions the procedure is illustrated for three paths: path AB for plug flow with an arbitrary temperature profile, path CD for nonisothermal plug flow with 50% recycle, and 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.
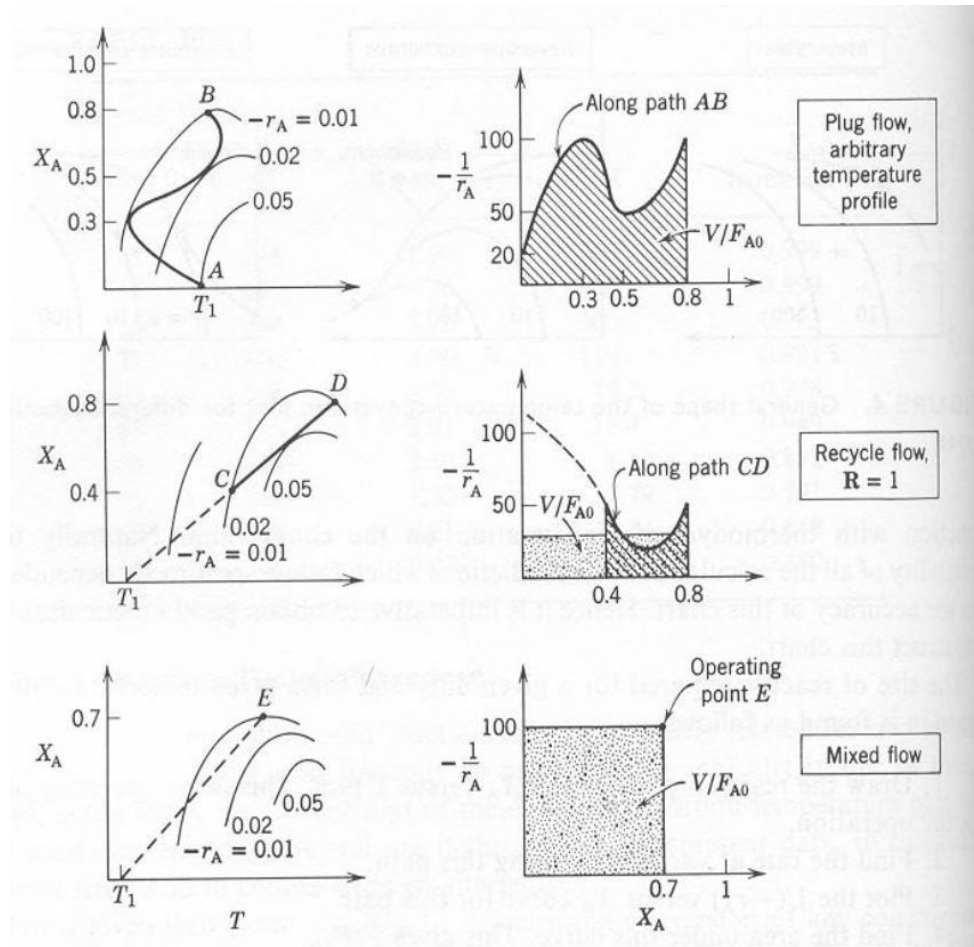
5.7 Optimum Temperature Progression

The optimum temperature progression is defined to be that progression which minimizes V/F_{A0}, 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

.Figure shows this progression. For irreversible reactions, the rate always increases with temperature at any composition, so the highest rate occurs at the highest allowable temperature. This 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. 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. This line is known as the *locus of maximum rates.*
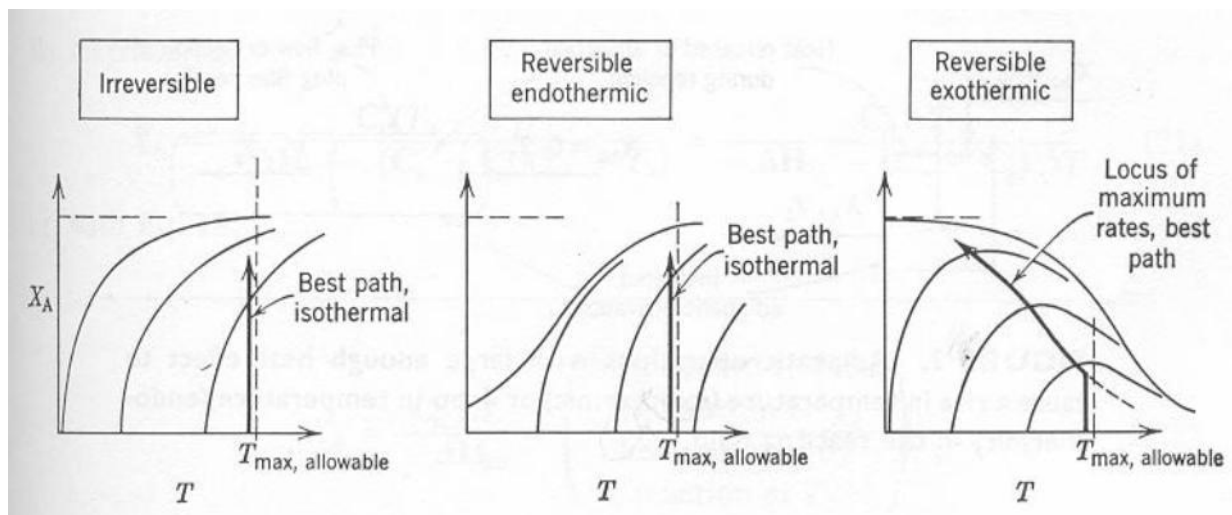
5.8 Heat Effects

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, 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.

5.9 Adiabatic Operations

Consider either a mixed flow reactor, a plug flow reactor, or a section of plug flow reactor, in which the conversion is *XA* as shown in figure. Usually the limiting reactant, is selected as the basis for all material balance calculations. The same procedure is used here, with limiting reactant A taken as the basis.

H = heat of reaction per mole of entering reacting A, and at temperature Ti.

With TI as the reference temperature on which enthalpies and heats of reaction are based . The relation between temperature and conversion, as given by the energy balances is shown in figure. The resulting lines are straight for all practical purposes . 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 Cp rises, and these curves become more closely vertical. A vertical line indicates that temperature is unchanged as reaction proceeds.

The size of reactor needed for a given duty is found as follows. For plug flow tabulate the rate for various XA along this adiabatic operating line, prepare the l/(-r,) versus XA plot and integrate. For mixed flow simply use the rate at the conditions within the reactor. Figure illustrates this procedure. 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. For exothermic reactions this means straddling the locus of maximum rates as shown in figure. A few trials will locate the best

inlet temperature, that which minimizes VIFAO. For mixed flow the reactor should operate on the locus of maximum rates.

The best reactor type, that which minimizes VIF,,, is found directly from this X, 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 XA, then falls. This behavior is characteristic of autocatalytic reactions, thus recycle operations are best.
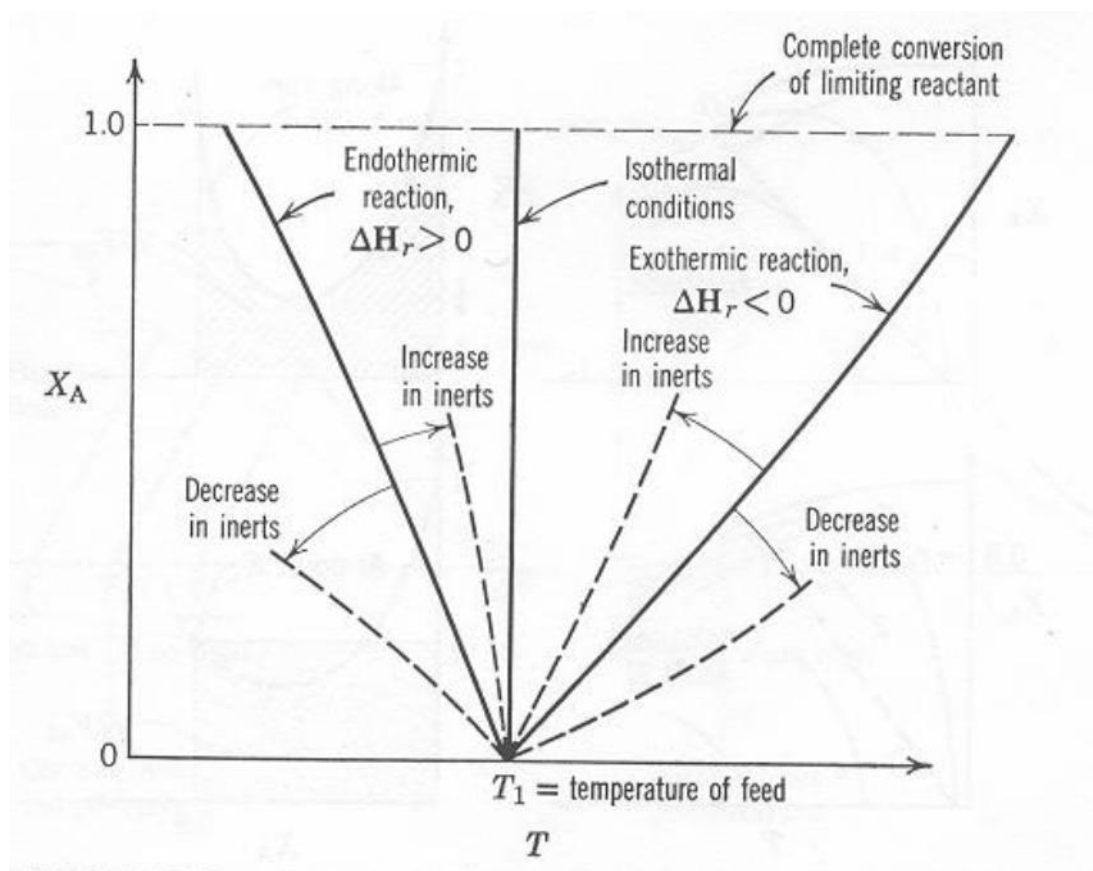
$$Q = UA\,\Delta T_{lm}$$

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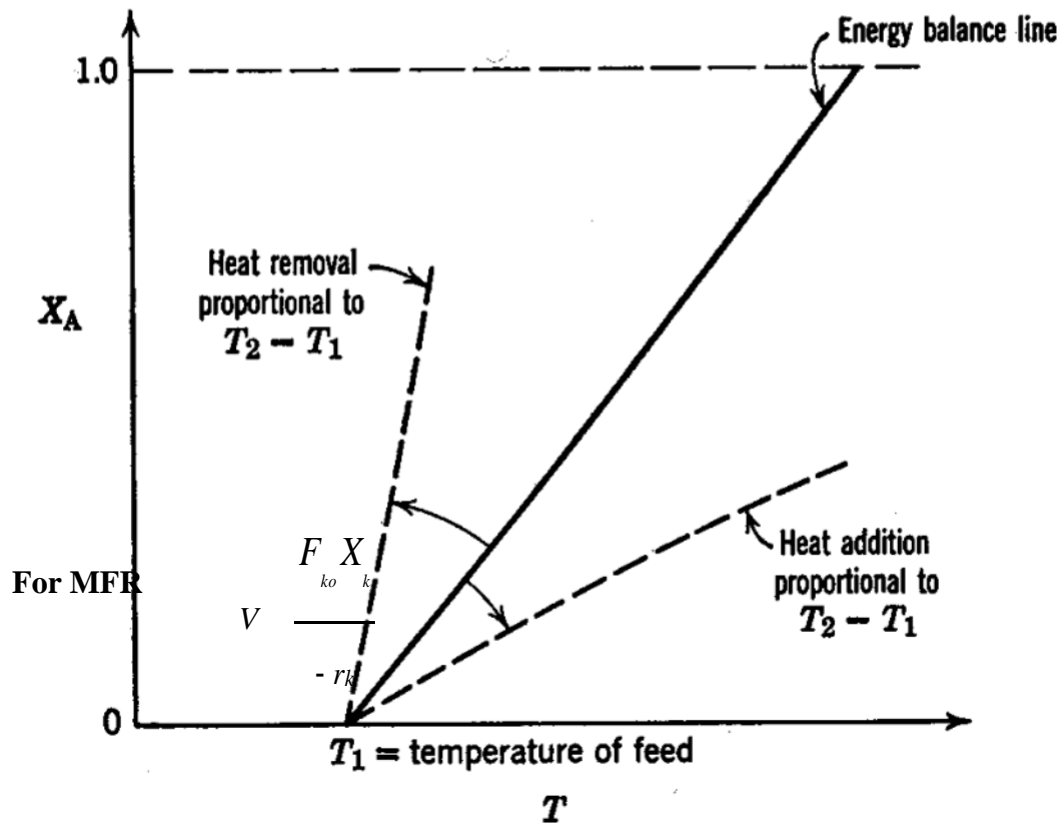
5.10 Nonadiabatic Operations

For the adiabatic operating line of above figure to more closely approach the ideals of below figure ,we may want deliberately to introduce or remove heat from the reactor. In addition, there are heat losses to the surroundings to account for. 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.

The energy balance line rotates about TI. This change is shown in figure. 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.
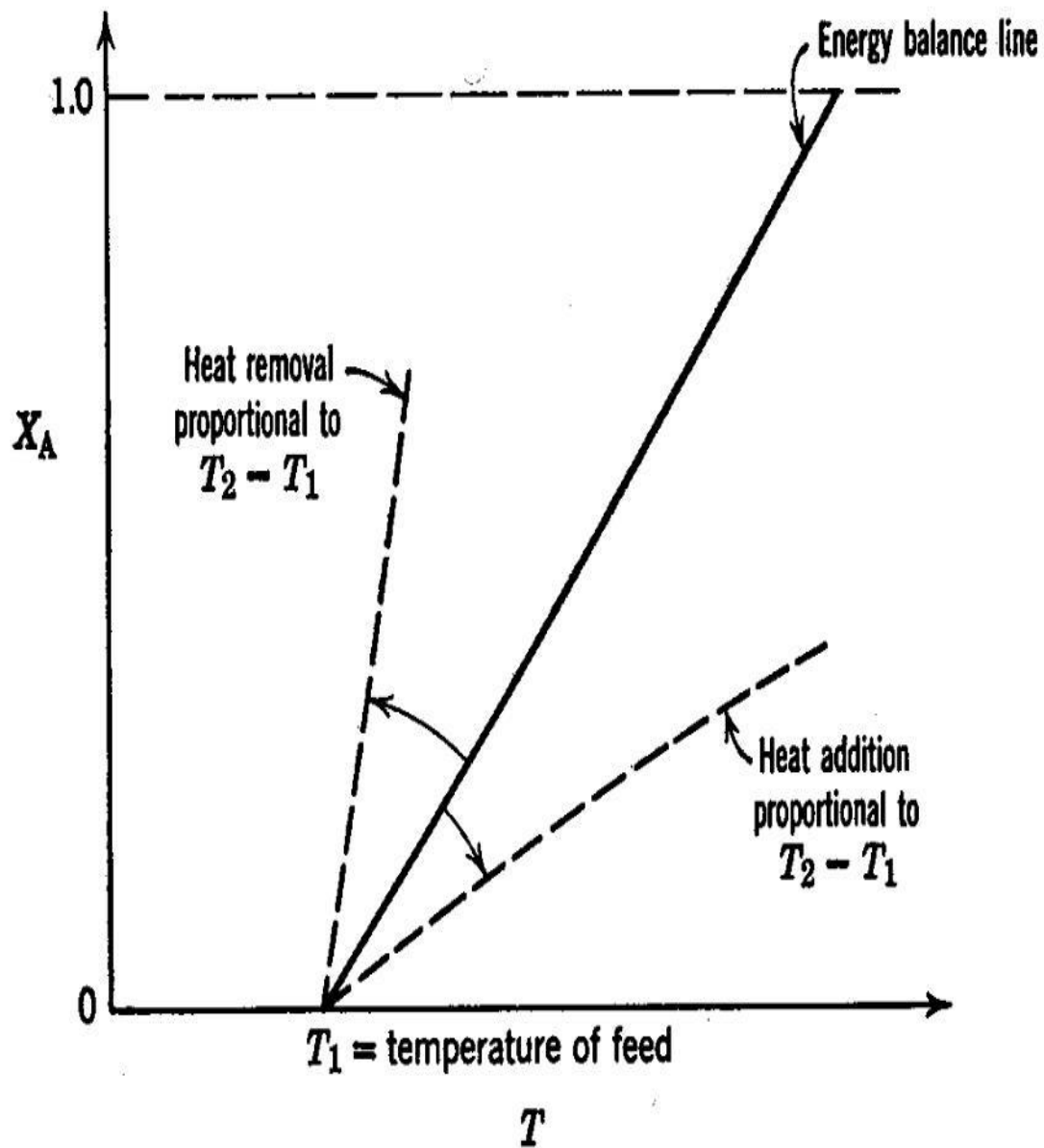
5.11 Exothermic Reactions in Mixed Flow Reactors-A Special Problem

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. Van Heerden (1953, 1958) was the first to treat this problem. First, consider reactant fluid fed at a given rate (fixed r or V/FAO) to a mixed flow reactor. At each reactor temperature there will be some particular conversion which satisfies the material balance equation. 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.

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

$$Q = UA \, \Delta T$$