## Chemical Reactor Design:

## Catalysts

The reforming catalyst, one of the most important factors in reactor design, must be durable enough for severe reacting conditions. A decrease in the catalytic activity is due to a reduction of the surface area caused by nickel sintering. This is prevented by providing the catalysts, which are made of porous carriers impregnated with nickel, with a suitable pore distribution and sufficient thermal resistance. The catalyst particle size and shape should be optimized to achieve maximum activity and maximum heat transfer, while minimizing the pressure drop. The high mass velocities in steam reforming reactor necessitate a relatively large catalyst particle size to obtain a low pressure drop across the catalyst bed; but the particle size is limited by another requirement for effective packing. The pressure drop depends strongly on the void fraction of the packed bed and decreases with the size of the packed particle.



Fig. 1. Industrial Catalyst Types

Fig. 1. Shows some types industrial catalyst where the internal surface areas are $10^7$-$10^9$ m$^{-1}$ for industrial catalysts. The choice of catalyst porosity is, therefore, very important. A high internal surface area is desirable to give high local reaction rates, but if, in achieving the high surface area, the pore size is reduced to the point where diffusion rates are hindered, then the overall performance will suffer.

**1**

The amount of catalyst used is that which will give the residence time needed for the reactants to be sufficiently converted at the operating temperature and pressure. In addition, carbon deposition on the catalyst surface can be a serious problem, thus its prevention is essential. Carbon tends to be formed under high temperatures and low hydrogen partial pressures. Unless the product gas is recycled, no hydrogen exists in the reacting gas at the inlet of the reactor. This raises the technical issue of what inlet temperature should be set to prevent carbon deposition. The problem can be solved by consideration based on chemical thermodynamics.

Hydrotreating is one of the key technologies in petroleum refining, covering a series of processes with different objectives. The process is commonly employed to reduce or saturate organic compounds. Various petroleum fractions are treated with hydrogen in the presence of catalyst (Fig. 2), to decompose and eliminate unfavourable impurities such as sulphur, nitrogen and metals in order to produce clean fuel oil or feed stock for fluid catalytic cracking or to hydrogenate olefin and aromatics into saturated hydrocarbons. Commercial hydrogenation catalysts are generally composed of cobaltmolybdenum supported on alumina, and if larger hydrogenation activity is required, then nickel is employed instead of cobalt.
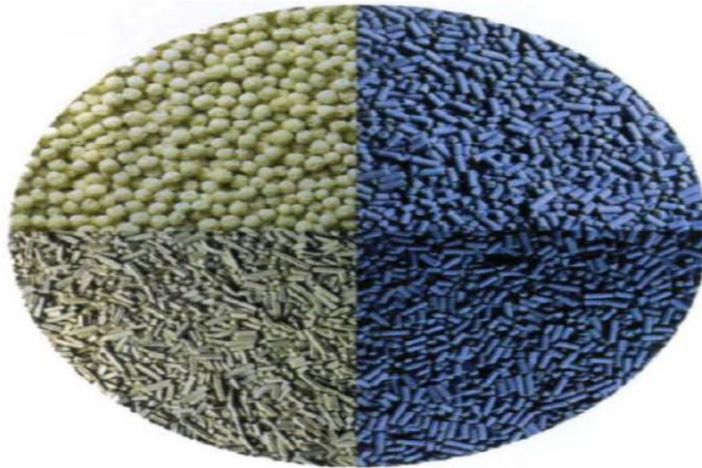


Fig. 2. Catalysts for Hydroprocessing

There are a large number of commercial catalysts available for hydrotreating. Typically, the supports are extruded alumina cylinders. Some, as shown on Fig. 3, are 'shaped', to give extended surfaces.
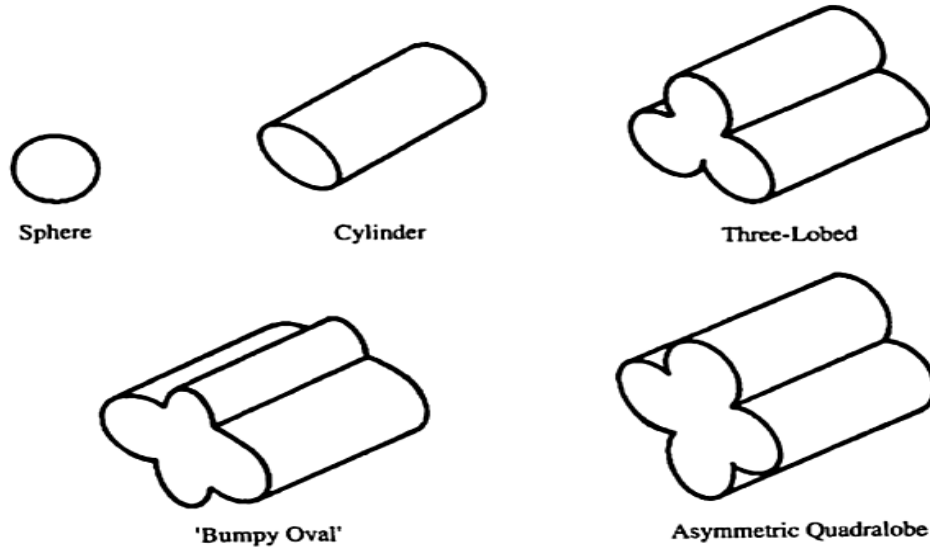
Fig. 3. Common catalyst shapes

In addition to the above metal oxides (sulphides in practical usage) as active components, control of pore diameter and acidity of the alumina as carrier are the important factors for preparation of the catalyst with excellent performance. The catalyst activity degrades gradually during the operating time because of metals and carbon produced from the heavy ends in the feed. to supplement its activity loss, the reactor is operated at temperatures which are increased gradually, and finally shut down either for replacement of the catalyst or regeneration of the catalyst while holding it within the reactor (in situ). Catalyst regeneration is carried out by adding air little by little into the inert gas which is charged into the reactor to burn (carefully) the carbon deposited on the catalyst. Catalysts do not change before or after a reaction, and neither give energy to raw molecules, but reduce the value of the activation energy. Since the activation energy is fed as heat, catalytic reactions are a kind of thermal reaction. The list of examples of catalytic reactions is endless: hydrogenation of the unsaturated hydrocarbons using palladium as a catalyst; synthesis of polymers from olefins using the Ziegler-Natta catalyst; and production of gasoline by zeolite (Fig. 4). It is more likely that catalysts are used in the majority of industrial reaction processes.
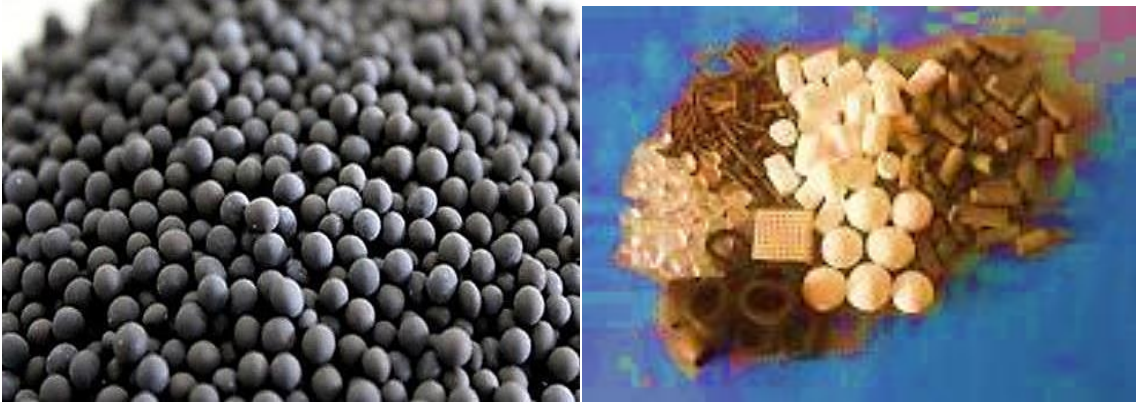
**3**

Fig. 4. Palladium and zeolite catalyst

Enzymes are also a kind of catalyst (Enzymes are protein as well as a catalyst existing in a living body). In the process that converts cane sugar into glucose through hydrolysis, either sulphuric acid or an enzyme called Alpha-amylase is available for accelerating the reaction; thus processes using either of them as a catalyst become widespread in industrial applications.

Diameters of the catalyst particles can vary from 0.8 mm to 5.0 mm. Small diameter catalysts have a larger external surface area per unit volume when compared to large diameter catalysts. However, there are limitations. Very small diameter catalysts can have two serious problems. One is crushing strength, an important catalyst property. Pressure drop through a bed of small diameter catalyst will be greater than that through larger diameter particles, and if too great, can exceed the mechanical strength of the supports. Larger diameter catalysts have greater strength and can resist the crushing effects of pressure drop. The other problem with very small diameter catalysts is their filtering ability, i.e., any discrete solid particles, such as scale, entering the catalyst bed will be trapped at the top of the bed by the fine catalyst. This, in turn, can raise pressure drop over the catalyst bed causing either catalyst crushing or increased operating costs. If scale is a serious problem it can be alleviated by using larger diameter catalyst in the top bed and smaller diameter in the lower bed or beds. Also, external filters are sometimes used on raw feed to remove particulate matter, especially when the stock comes from tankage. Although the actual composition of commercial hydrotreating catalysts is proprietary information, it can be said that a typical CoMo catalyst will contain about 2-5 wt% Co

and 4-8 wt% Mo. A typical NiMo catalyst will contain about 2-5 wt% Ni and 4-8 wt% Mo. These compositions can vary widely depending on the selectivity desired in the hydrotreating process. One chemical reaction can be encouraged and another discouraged by changes in catalyst components. The products must meet certain specifications, but exceeding them may consume valuable hydrogen that could be used elsewhere in the refinery. Selectivity can be influenced both by variations in catalyst properties and by variations in operating conditions.

Reactor internal arrangements will vary depending on the reactant phases, catalyst and type of operation. Fig. 5. shows typical reactor internals for hydroprocessing units.
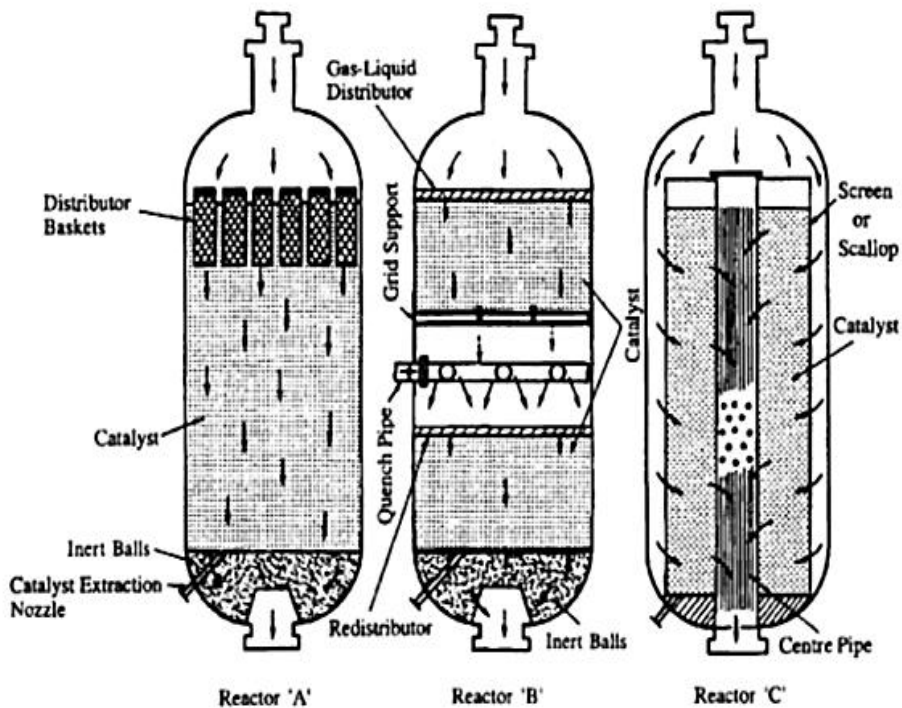


Fig. 5. Reactor internals

(I) Reactor A with distributor baskets at the catalyst top is used for both single-phase and two-phase operations. The purpose of the baskets is to give uniform distribution of the phase and/or to collect any particulate matter present in the feed which would otherwise clog the top of the catalyst bed and cause increasing pressure drop.

(2) Reactor B has multiple beds, each requiring support grids. Multiple beds are used to redistribute the liquid phase, and are needed when (1) pressure drop across a single bed would be excessive, or (2), as shown, where a cold quench stream must be introduced to control temperature. Multiple beds are used in hydrotreating units because the exothermic heat of reaction is high. Quench streams are inserted between beds to limit temperature rise. Temperature rise is usually limited to about $25^0$C.

(3) Reactor C is used only for vapour-phase reactions, particularly where a low pressure drop is desired (which is typical in catalytic reforming units). The reactants distribute over the outer periphery of the catalyst bed (which is contained by a cylindrical screen or perforated sheet metal), then flow radially through a shallow bed into a perforated centre pipe and then out of the reactor bottom.

Catalysts are usually applied in fixed beds where there are several types of fixed bed reactors as shown in Fig. 6. The fixed bed reactors are most commonly used as catalytic reactors.
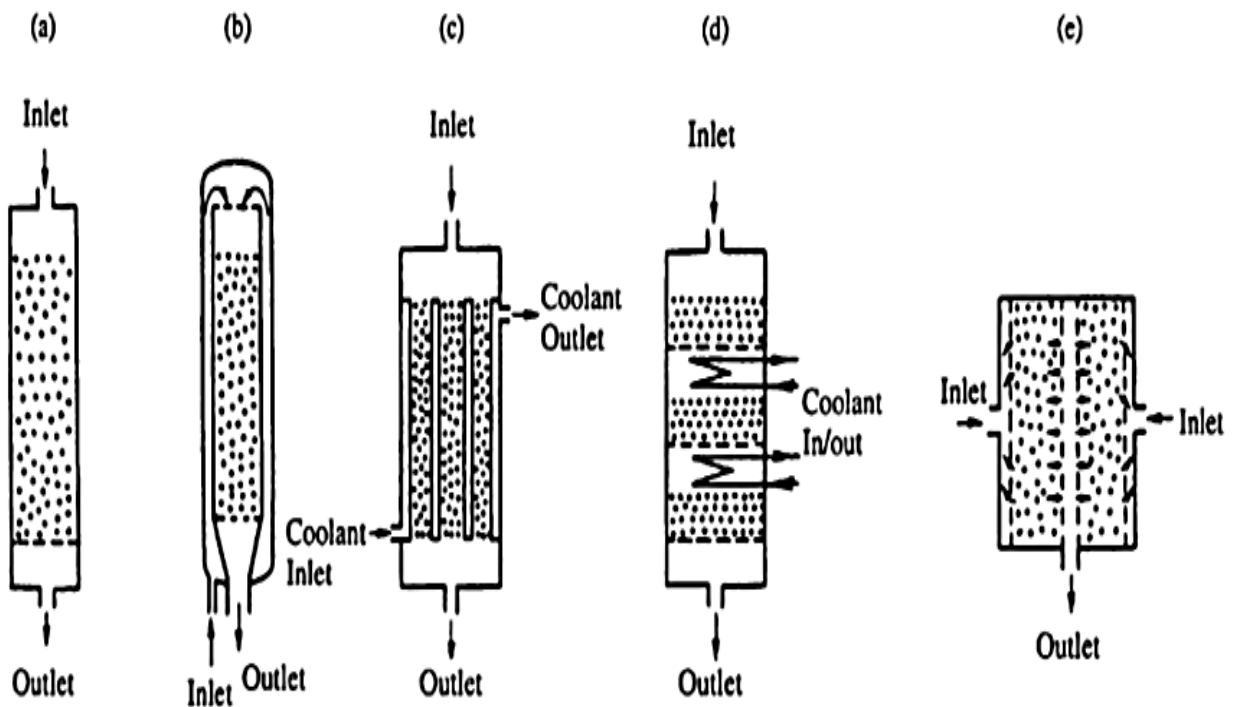


Fig. 6. Several types of fixed bed reactors. (a) Down flow type. (b) Self-thermal-exchange Type. (c) Cooling Type. (d) Intermediate Cooling Type. (e) Radial Flow Type.

## Chemical Reactor Design:

## Fundamental Concepts Used in Chemical Reactor Design

Reactor design is primarily concerned with the type and size of reactor and its method of operation for the required process. Designers must first consider the thermodynamics involving the equilibrium of reaction before investigating the chemical kinetics in relation to the reaction mechanisms. Figure 2.1 illustrates the logic of this approach. In this figure, consideration is given to the possibility of using either a gas phase or liquid phase reaction, whether the reaction is endothermic (i.e., absorbing heat) or exothermic (i.e., releasing heat), and whether or not the reaction is reversible.

There are advantages to using the liquid phase rather than the gas phase operation. For example, for the desired product the reactor may be smaller. This is because the physical properties of liquids are greater than those for gases, namely the heat capacities and thermal conductivities, factors which increase the heat transfer. Additionally, the equipment size is small resulting in lower power requirements and capital costs. The main disadvantages are corrosion and catalyst losses. In considering a liquid system, all operating conditions must fall within the two-phase region. If the critical temperature is not significantly above the desired reaction temperature, high operating pressures are potentially hazardous and expensive to contain, especially if one of the reactants is a non-condensable gas, which is required at high partial pressure.

In the case of thermodynamics, the designer can investigate the nature of the reaction heat and whether the reaction is reversible. If these exothermic reactions are irreversible, attention may be focused on the influence of reactor design on conversion and with heat transfer control. An objective of reactor design is to determine the size and type of reactor and mode of operation for the required job. The choice of reactors depends on many factors such as safety, environment, and profit. Optimization techniques are often employed during the design stage to establish the optimum design from the profit viewpoint. This includes factors such as raw materials, initial and operating costs, and the market value of the finished products. The designer also requires knowledge of reactor performance before reviewing an optimization technique.
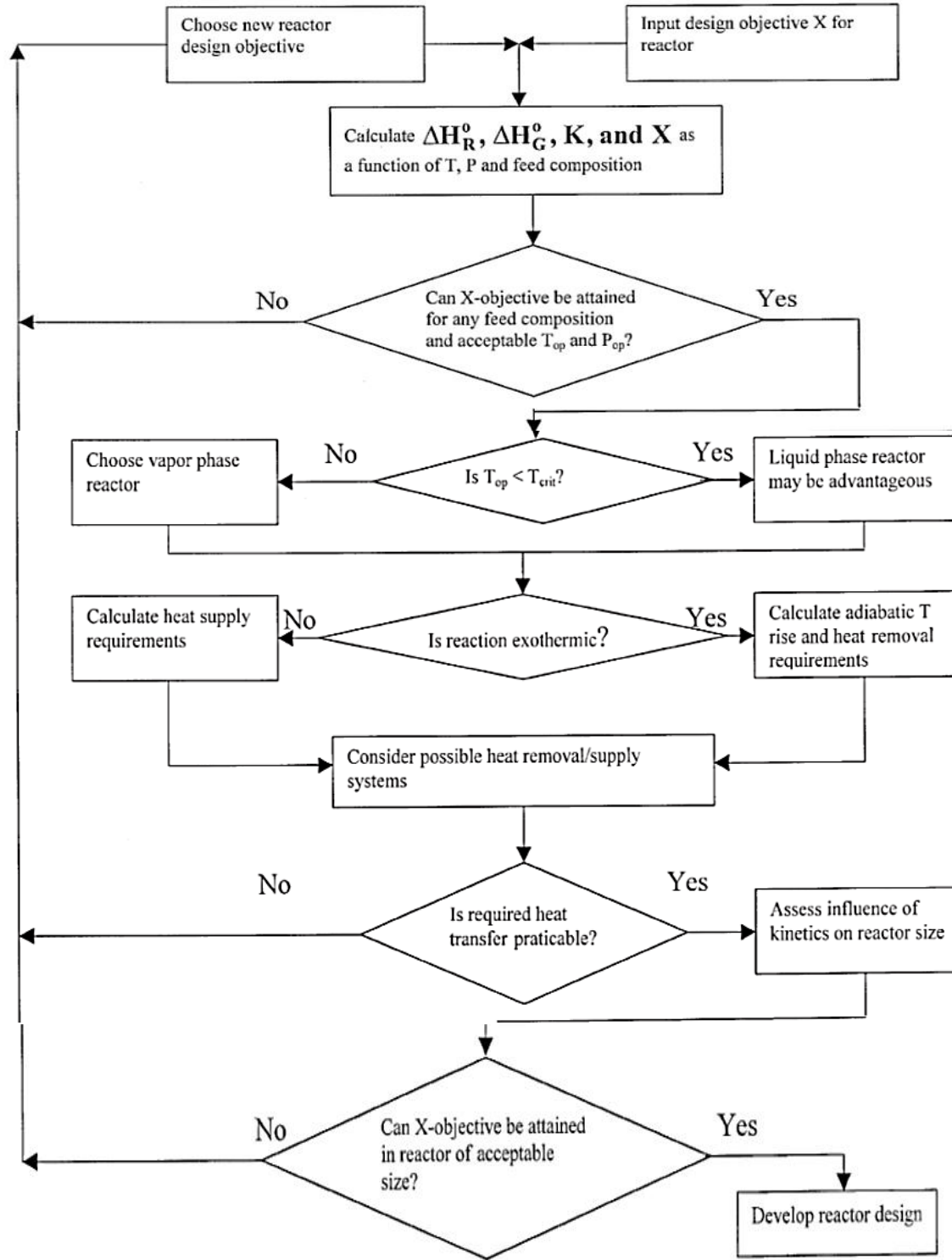
**Fig. 2.1.** Flowchart of reactor design

Chemical reactions are performed in reactor systems that are derived from one of the following basic types of model reactors:

• The well-mixed reaction system with uniform composition that is operated batchwise.

• The semibatch reactor where the incoming and outgoing mass flows are not equal to each other, and the total mass of the reacting mixture is not constant.

• The continuously operated stirred tank reaction in which the composition of the reaction mixture is assumed uniform and equal to the composition at the outlet.

• The tubular (plug flow) reactor in which piston flow of the reacting mixture is assumed, and there is neither mixing nor diffusion in the flow direction.

The rate equation involves a mathematical expression describing the rate of progress of the reaction. To predict the size of the reactor required in achieving a given degree of conversion of reactants and a fixed output of the product, the following information is required:

• Composition changes

• Temperature changes

• Mixing patterns

• Mass transfer

• Heat transfer

Information on the composition and temperature changes is obtained from the rate equation, while the mixing patterns are related to the intensity of mixing and reactor geometry. Heat transfer is referred to as the exothermic or endothermic nature of the reactions and the mass transfer to the heterogeneous systems.

*Material and Energy Balances in the Design of Industrial Reactors.*

The analysis of chemical reactors in terms of material and energy balances differs from the analysis of other process equipment in that one must take into account the rate at which molecular species are converted from one chemical form to another and the rate at which energy is transformed by the process. When combined with material and energy balances on the reactor, the reaction rate expression provides a means of determining the production rate and the composition of the products as functions of time. Both steady-state and time varying situations may be analyzed using the same fundamental relations. Differences in the analyses result from the retention of different terms in the basic balance equations. A material balance on a reactant species of interest for an element of volume $\Delta V$ can be written as:

$$\begin{pmatrix} \text{Rate of flow} \\ \text{of reactant into} \\ \text{volume element} \end{pmatrix} =$$

$$\begin{pmatrix} \text{Rate of flow} \\ \text{of reactant out of} \\ \text{volume element} \end{pmatrix} + \begin{pmatrix} \text{Rate of disappearance} \\ \text{of reactant by} \\ \text{chemical reactions} \\ \text{within the} \\ \text{volume element} \end{pmatrix} + \begin{pmatrix} \text{Rate of accumulation} \\ \text{of reactant within} \\ \text{the volume element} \end{pmatrix} \qquad (2.1)$$

or, in shorter form,

**Input = output + disappearance by reaction + accumulation** (2.2)

In the analysis of batch reactors the two flow terms in equation 1 are omitted. For continuous flow reactors operating at steady state, the accumulation term is omitted. However, for the analysis of continuous flow reactors under transient conditions and for semibatch reactors it may be necessary to retain all four terms. For ideal well-stirred reactors the composition and temperature are uniform throughout the reactor and all volume elements are identical. Hence the material balance may be written over the entire reactor in these cases.

For tubular flow reactors the composition is not independent of position and the balance must be written on a differential element of reactor volume and then integrated over the entire reactor using appropriate flow conditions and concentration and

temperature profiles. Where nonsteady-state conditions are involved, it will be necessary to integrate over time as well as over volume in order to determine the performance characteristics of the reactor.

Since the rate of a chemical reaction is normally strongly temperature dependent, it is essential to know the temperature at each point in the reactor in order to be able to utilize equation (2.1) properly. When there are temperature gradients within the reactor, it is necessary to utilize an energy balance in conjunction with the material balance in order to determine the temperature and composition prevailing at each point in the reactor at a particular time. The general energy balance for an element of volume $\Delta V$ over a time $\Delta t$ can be written as:

$$
\begin{pmatrix} \text{Accumulation of} \\ \text{energy within the} \\ \text{volume element} \end{pmatrix} =
$$

$$
\begin{pmatrix} \text{Energy transferred} \\ \text{from surroundings to} \\ \text{volume element} \\ \text{by heat and shaft} \\ \text{work interactions} \end{pmatrix} + \begin{pmatrix} \text{Energy effects} \\ \text{associated with the} \\ \text{entry of matter into} \\ \text{the volume element} \end{pmatrix} + \begin{pmatrix} \text{Energy effects} \\ \text{associated with the} \\ \text{transfer of matter out} \\ \text{of the volume element} \end{pmatrix} \quad (2.3)
$$

The chemical reaction rate does not appear explicitly in equation 2.3, but its effects are implicit in all terms except the second. The first, third, and fourth terms reflect differences in temperature and/or in composition of the entering and leaving streams. The energy effects associated with composition changes are a direct reflection of the enthalpy change associated with the reaction.

There are a variety of limiting forms of equation 2.3 that are appropriate for use with different types of reactors and different modes of operation. For stirred tanks the reactor contents are uniform in temperature and composition throughout, and it is possible to write the energy balance over the entire reactor. In the case of a batch reactor, only the first two terms need be retained. For continuous flow systems operating at steady state, the accumulation term disappears.

For adiabatic operation in the absence of shaft work effects the energy transfer term is omitted. For the case of semibatch operation it may be necessary to retain all four terms.

For tubular flow reactors neither the composition nor the temperature need be independent of position, and the energy balance must be written on a differential element of reactor volume. The resultant differential equation must then be solved in conjunction with the differential equation describing the material balance on the differential element.

*Important terms used in reactor design:*

- **Steady-state operation**: Large-scale industrial reactions are almost invariably carried out on a continuous basis with reactants entering at one end of the reactor network and products leaving at the other.

- **Transient operation**: that will invariably be incurred during start-up and shut-down periods.

- **Equilibrium**: It is restricted to isolated systems that undergo no net change with time.

- **Adiabatic operation** implies that there is no heat interaction between the reactor contents and their surroundings.

- **Isothermal operation** implies that the feed stream, the reactor contents, and the effluent stream are equal in temperature and have a uniform temperature throughout.

## Chemical Reactor Design:

## Ideal Isothermal Reactors

Batch reactors are widely used in the chemical industry for producing materials that are needed in limited quantity, particularly in those cases where the processing cost represents only a small fraction of the total value of the product.

The starting point for the development of the basic design equation for a well-stirred batch reactor is a material balance involving one of the species participating in the chemical reaction. For convenience we will denote this species as *A* and we will let (*- $r_A$*) represent the *rate of disappearance* of this species by reaction. For a well-stirred reactor the reaction mixture will be uniform throughout the effective reactor volume, and the material balance may thus be written over the entire contents of the reactor. For a batch reactor equation 2.1 becomes

$$\begin{pmatrix} \textbf{Rate of accumulation} \\ \textbf{of reactant within} \\ \textbf{the volume element} \end{pmatrix} = - \begin{pmatrix} \textbf{Rate of disappearance} \\ \textbf{of reactant by} \\ \textbf{chemical reactions} \\ \textbf{within the} \\ \textbf{volume element} \end{pmatrix} \qquad (3.1)$$

The accumulation term is just the time derivative of the number of moles of reactant *A* contained within the reactor (**$dN_A/dt$**). This term also may be written in terms of either the extent of reaction ($\zeta$) or the fraction conversion of the limiting reagent (**$X_A$**) where *A* is presumed to be the limiting reactant. Thus,

$$Rate\ of\ accumulation = \frac{dN_A}{dt} \qquad (3.2)$$

$$Rate\ of\ disappearance = (\ -\ r_A)V_R \qquad (3.3)$$

Equation 3.1 becomes

$$-\ (\ -\ r_A)V_R = \frac{dN_A}{dt} \qquad (3.4)$$

Rearranging Equation 3.4 gives

$$-(-r_A) = \frac{1}{V_R} \frac{dN_A}{dt} \tag{3.5}$$

In terms of the fractional conversion $X_A$

$$X_A = \frac{N_{Ao} - N_A}{N_{Ao}} \tag{3.6}$$

Rearranging Equation 3.6 gives

$$N_A = N_{A0} (1 - X_A) \tag{3.7}$$

where $N_{A0}$ is number of moles of species $A$ present when the fraction conversion is zero.

Differentiating Equation 3.7 gives

$$dN_A = -N_{A0} \, dX_A \tag{3.8}$$

Substituting Equation 3.8 into Equation 3.5 gives

$$(-r_A) = \frac{N_{A0}}{V_R} \frac{dX_A}{dt} \tag{3.9}$$

Rearranging and integrating Equation 3.9 between the limits at: $t = 0$, $X_A = 0$ and at $t = t$, $X_A = X_{AF}$ results in

$$\int_0^t dt = N_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)V_R}$$

$$t = N_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)V_R} \tag{3.10}$$

Both the reaction rate and the reactor volume should be retained inside the integral sign, since either or both may change as the reaction proceeds.

The concentration equals

$$C_A = \frac{N_A}{V_R} \left(\frac{moles}{volume}\right)$$

The fractional conversion $X_A$ at constant volume is

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \tag{3.11}$$

Equation 3.10 becomes

$$t = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)} \tag{3.12}$$

**H.W. 3.1**: *Derive equation 3.12*

Equation 3.12 is the time required to achieve a conversion $X_A$ for either isothermal or non-isothermal operation. Equation 3.12 can also be expressed in terms of concentration at constant fluid density as

$$t = - \int_{C_{A0}}^{C_{AF}} \frac{dC_A}{(-r_A)} \qquad \text{for } \mathcal{E} = 0 \tag{3.13}$$

Equations 3.10, 3.12, and 3.13 are the performance equations for a batch reactor. Figure 3.1 illustrates the performance equations for batch reactors.

When the volume of reacting mixture changes proportionately with conversion, as in the case of gas phase reactions, this implies working volume changes with time,

$$V_R = V_0 (1 + \mathcal{E}_A X_A) \tag{3.14}$$

where $V_0$ = initial volume of the reactor (i.e. the volume occupied by the reacting fluid at zero fraction conversion) and $V_R$ = volume at time t. Equation 3.10 becomes

$$t = N_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)\, V_0\, (1 + \mathcal{E}_A\, X_A)} =$$

$$\frac{N_{A0}}{V_0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)\, (1 + \mathcal{E}_A\, X_A)} = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)\, (1 + \mathcal{E}_A\, X_A)} \tag{3.15}$$

This equation would be appropriate for use when low-pressure gas phase reactions involving a change in the number of moles on reaction take place in a batch reactor *at constant pressure.* However, gas phase reactions are rarely carried out batch-wise on a

commercial scale because the quantity of product that can be produced in a reasonably sized reactor is so small. The chief use of batch reactors for gas phase reactions is to obtain the data necessary for the design of continuous flow reactors.
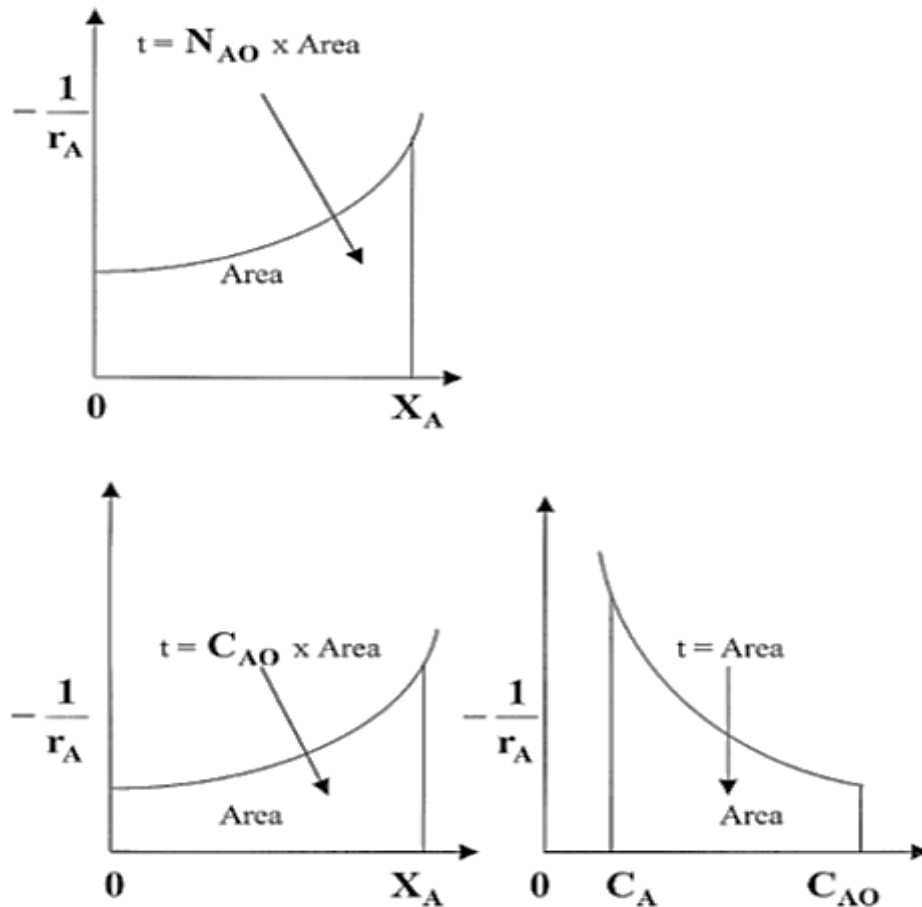


**Figure 3.1**. The performance equations for batch reactors

The degree of difficulty associated with evaluating the integral in any of the batch reactor design equations depends on the composition and temperature dependence of the reaction rate expression.

For nonisothermal systems an energy balance must be employed to relate the system temperature (and through it the reaction rate) to the fraction conversion. While for isothermal systems it is not necessary to utilize an energy balance to determine the holding time necessary to achieve a given fraction conversion. One merely substitutes rate constants evaluated at the temperature in question directly into the rate expression.

One merely substitutes rate constants evaluated at the temperature in question directly into the rate expression.

Batch reactors are charged with reactants, closed, and heated to the reaction temperature, which may be maintained (i.e., isothermally) for the duration of the reaction. After the reaction is completed, the mixture cooled, and the reactor opened, the product is discharged and the reactor is cleaned for the next batch. In industrial operations, the cycle time is constant from one batch to the next. The time required for filling, discharging, heating, cooling, and cleaning the reactor forms an integral part of the total batch cycle time ($t_b$). The total batch cycle time $t_b$ is the reaction $t_r$ time plus the turnaround time $t_t$. This is expressed as:

$$t_b = t_r + t_t \tag{3.16}$$

From these various estimates, the total batch cycle time $t_b$ is used in batch reactor design to determine the productivity of the reactor. Batch reactors are used in operations that are small and when multi-products are required. However, batch reactors are seldom employed on an industrial scale for gas phase reactions. This is due to the limited quantity produced, although batch reactors can be readily employed for kinetic studies of gas phase reactions.

Next, some illustrations will be studied to know how the basic design relations developed above are used to answer the two questions with which the reactor designer is most often faced.

1. What is the time required for converting a quantity of material to the desired level under specified reaction conditions?
2. What reactor volume is required to achieve a given production rate?

## Chemical Reactor Design:

## Ideal Isothermal Batch Reactors

The following examples explain how to find the holding time and the batch reactor volume.

***Example 4.1***.  The Diels-Alder reaction of benzoquinone *(B)* and cyclopentadiene (C) is occurred at 25 °C as follows:
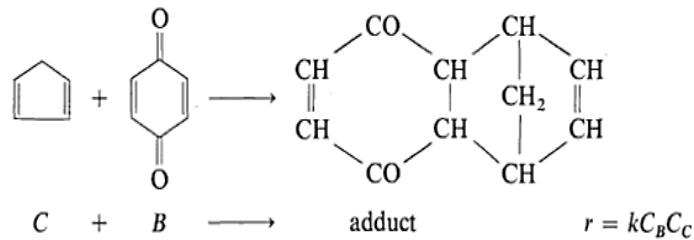


Volume changes on reaction may be neglected. At 25 °C the reaction rate constant is equal to 9.92 x $10^{-3}$ $m^3$/kmole • sec. If one employs a well-stirred isothermal batch reactor to carry out this reaction, determine the holding time necessary to achieve 95% conversion of the limiting reagent using initial concentrations of 0.1 and 0.08 kmole/$m^3$ for cyclopentadiene and benzoquinone, respectively.

**Solution**

The limiting reagent is benzoquinone. The rate of disappearance of this species can be written in terms of the initial concentrations and the fraction conversion as

$-r_B = k\,[C_{B0}\,(1 - X_B\,)]\,(\,C_{C0} - X_B\,C_{B0})$

Since the reaction takes place at constant volume, the pertinent design equation is equation 3.12.

$$t = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)} \tag{3.12}$$

$$t = C_{B0} \int_0^{X_{BF}} \frac{dX_B}{(-r_B)} = C_{B0} \int_0^{X_{BF}} \frac{dX_B}{kC_{B0}(1-X_B)(C_{Co}-X_B C_{Bo})}$$

Since the reaction occurs under isothermal conditions, the rate constant could be taken outside the integral sign. Integration and simplification then gives

$$t = \frac{\ln\left[\left(\dfrac{\frac{C_{Co}}{C_{Bo}} - X_B}{1 - X_B}\right)\left(\dfrac{C_{Bo}}{C_{Co}}\right)\right]}{k(C_{Co} - C_{Bo})}$$

Substitution of numerical values gives

$$t = \frac{\ln\left[\left(\dfrac{\frac{0.1}{0.08} - 0.95}{1 - 0.95}\right)\left(\dfrac{0.08}{0.1}\right)\right]}{9.92 \times 10^{-3}(0.1 - 0.08)}$$

$$t = 7.91 \times 10^3 \sec \quad or \quad 2.20 \ hr$$

***Example 4.2***.  The Consider an isothermal batch reactor for a given conversion of the reactant

**aA + bB → cC + dD**                                                                                                   (4.1)

where component *A* is the limiting reactant. The stoichiometric coefficients are: **a** = 1, **b** = 2, **c** = 1, and **d** = 0. The initial moles of components *A, B, C*, and *D*; are $N_A$ = 0.001 gmol, $N_B$ = 0.003 gmol, $N_C$ = 0.0 gmol, $N_D$ = 0.0 gmol, respectively. The mixture of *A* and *B* is charged into a 1-liter reactor. Determine the holding time required to achieve 90% fractional conversion of *A* ($X_A$ = 0.9). The rate constant is $k$ = $1.0 \times 10^5$ [(liter)$^2$/(gmol$^2$ • min)] and the reaction is first order in *A*, second order in *B* and third order overall.

**Solution**:

Assuming a constant volume batch system, from the stoichiometric coefficients of Equation 3.1:

$$A + 2B \xrightarrow{k} C \tag{4.2}$$

where component $A$ is the limiting reactant. The material balance on component $A$ in the batch reactor is

$$(-r_A) = -\frac{1}{V_R}\frac{dN_A}{dt} \tag{3.5}$$

where the concentration $C_A = N_A/V_R$ and the rate Equation 3.5 becomes

$$(-r_A) = -\frac{dC_A}{dt} = kC_A C_B^2 \tag{4.3}$$

The concentrations of A and B can be expressed in terms of the fractional conversion and the stoichiometry of the reaction as:

| Component | A | B |
|---|---|---|
| At time t = 0 | $C_{AO}$ | $C_{BO}$ |
| At time t = t | $C_A$ | $C_B$ |
| Amount reacted | $(C_{AO} - C_A)$ | $(C_{BO} - C_B)$ |

From the stoichiometry,

$$2(C_{A0} - C_A) = C_{B0} - C_B \tag{4.4}$$

The concentration of $B$ is expressed as

$$C_B = C_{B0} - 2(C_{A0} - C_A) \tag{4.5}$$

Using the fractional conversion $X_A$ at constant volume

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \tag{3.11}$$

Therefore, the amount reacted

$$C_{A0} - C_A = C_{A0}\,X_A \tag{4.6}$$

Or

$$C_A = C_{A0}\,(1 - X_A) \tag{4.7}$$

Differentiation of A in Equation 3.6 gives

$$-dC_A = C_{A0}\, dX_A \tag{4.8}$$

Substituting Equations 4.5, 4.7, and 4.8 into Equation 4.3 gives

$$C_{A0}\frac{dX_A}{dt} = kC_{A0}(1 - X_A)\{C_{B0} - 2(C_{A0} - C_A)\}^2 \tag{4.9}$$

$$C_{A0}\frac{dX_A}{dt} = kC_{A0}(1 - X_A)(C_{B0} - 2C_{A0}X_A)^2 \tag{4.10}$$

$$C_{A0}\frac{dX_A}{dt} = kC_{A0}(1 - X_A)\{C_{A0}\left[\frac{C_{B0}}{C_{A0}} - 2X_A\right]\}^2 \tag{4.11}$$

$$\frac{dX_A}{dt} = kC_{A0}{}^2(1 - X_A)(\theta_B - 2X_A)^2 \tag{4.12}$$

Where $\theta_B = (C_{B0}/C_{A0}) = 3$. Rearranging Equation 4.12 and integrating between the limits $t = 0$, $X_A = 0$, $t = t_{holding\ time}$, $X_A = X_{AF=0.9}$ gives

$$\int_{X_{A=0}}^{X_{A=0.9}}\frac{dX_A}{(1-X_A)(\theta_B-2X_A)^2} = kC_{A0}{}^2\int_{t=0}^{t=t_{holding\ time}}dt \tag{4.13}$$

The integral on the left side of Equation 4.13 can be expressed by partial fraction to give

$$\frac{1}{(1-X_A)(\theta_B-2X_A)^2} = \frac{A}{1-X_A} + \frac{B}{\theta_B-2X_A} + \frac{C}{(\theta_B-2X_A)^2} \tag{4.14}$$

Rearranging Equation 4.14 gives

$$1 = A(\theta_B - 2X_A)^2 + B(1 - X_A)(\theta_B - 2X_A) + C(1 - X_A) \tag{4.15}$$

After solving, the value of constants are:

$$A = \frac{1}{(\theta_B-2)^2}\ ; \qquad B = -\frac{2}{(\theta_B-2)^2} \qquad ; \qquad C = \frac{2}{(2-\theta_B)}$$

The integral of Equation 4.13 between the limits becomes

$$I =$$

$$\int_{X_A=0}^{X_A=0.9} \frac{dX_A}{(1-X_A)(\theta_B-2X_A)^2} =$$

$$\frac{1}{(\theta_B-2)^2} \int_0^{X_A} \frac{dX_A}{1-X_A} - \frac{2}{(\theta_B-2)^2} \int_0^{X_A} \frac{dX_A}{(\theta_B-2X_A)} + \frac{2}{(2-\theta_B)} \int_0^{X_A} \frac{dX_A}{(\theta_B-2X_A)^2} \qquad (4.16)$$

The holding time $t_{holding\ time}$ is given by the expression

$$t_{holding\ time} = \frac{1}{kC_{A0}^2} \frac{1}{(\theta_B-2)^2} \left[ \ln\left\{ \frac{(\theta_B-2X_A)}{\theta_B(1-X_A)} \right\} - \frac{2X_A(\theta_B-2)}{\theta_B(\theta_B-2X_A)} \right] \qquad (4.17)$$

After substituting the given data, the holding time required equals

$$t_{holding\ time} = 8.86\ min$$

In other words, it would take approximately 9 minutes to convert 90% of reactant **A** charged to the 1-liter reactor.

---

**H.W. 4.1**. *Starting from equation 4.16, find equation 4.17.*

---

## Chemical Reactor Design:

## Isothermal Plug flow Reactors

Tubular reactors are normally used in the chemical industry for extremely large-scale processes. When filled with solid catalyst particles, such reactors are referred to as fixed or packed bed reactors. This section treats general design relationships for tubular reactors in which isothermal homogeneous reactions take place. The simplest model of the behavior of tubular reactors is the plug flow model. Consider the segment of tubular reactor shown in Figure 5.1.
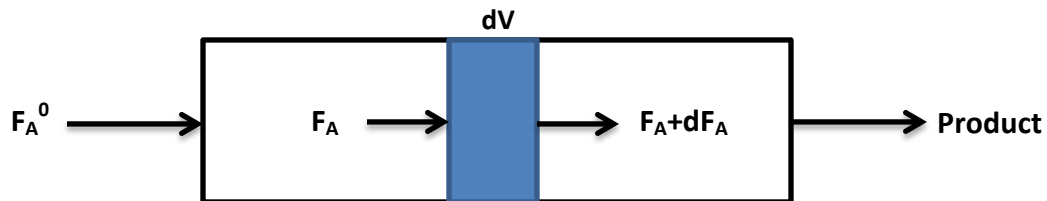


**Fig. 5.1.** Schematic representation of differential volume element of plug flow reactor

Since the fluid composition varies with longitudinal position, we must write our material balance for a reactant species over a different element of reactor ($dV_R$). Moreover, since plug flow reactors are operated at steady state except during start-up and shut-down procedures, the relations of major interest are those in which the accumulation term is missing from equation 2.1. Thus

$$\begin{pmatrix} \text{Rate of flow} \\ \text{of reactant into} \\ \text{volume element} \end{pmatrix} = \begin{pmatrix} \text{Rate of flow} \\ \text{of reactant out of} \\ \text{volume element} \end{pmatrix} + \begin{pmatrix} \text{Rate of disappearance} \\ \text{of reactant by} \\ \text{chemical reactions} \\ \text{within the} \\ \text{volume element} \end{pmatrix} \qquad (5.1)$$

$$F_A = (F_A + dF_A) + (-r_A)\, dV_R \qquad (5.2)$$

Or    $dF_A = r_A\, dV_R$ \qquad (5.3)

At any point the molal flow rate of reactant $A$ can be expressed in terms of the fraction conversion $X_A$ and the molal flow rate corresponding to zero conversion $F_{A0}$.

$F_A = F_{A0} (1 - X_A)$ (5.4)

Differentiating

$dF_A = - F_{A0} \, dX_A$ (5.5)

Combining equations 5.3 and 5.5 gives

$F_{A0} \, dX_A = (-r_A) \, dV_R$

$$\frac{dV_R}{F_{A0}} = \frac{dX_A}{(-r_A)}$$ (5.6)

which may be integrated over the entire reactor volume to give

$$\int_0^{V_R} \frac{dV_R}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$V_R = F_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$ (5.7)

This equation is a very useful relation that indicates the reactor size necessary to accomplish a specified change in the degree of conversion for a fixed molal flow rate. It does require, however, a knowledge of the relationship between the reciprocal rate of reaction and the fraction conversion.

The value of $F_{A0}$ may also be written as the product of a volumetric flow rate and a reactant concentration where both are measured at some reference temperature and pressure and correspond to zero fraction conversion. Thus

$$\frac{V_R}{F_{A0}} = \frac{V_R}{C_{A0} v_0} = \frac{\tau}{C_{A0}}$$ (5.8)

where $\tau$ is the space time. Combining equations 5.7 and 5.8 gives

$$\tau = \frac{V_R}{v_0} = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$ (5.9)

Reactor inlet conditions are particularly useful as reference conditions for measuring the input volumetric flow rate in that they not only give physical meaning to $C_{A0}$ and $v_0$ but also usually lead to cancellation of $C_{A0}$ with a similar term appearing in the reaction rate expression.

If the temperature is constant throughout the reactor volume, the rate constant k may be removed from the integral and an analytic solution obtained. In more general terms it will be necessary to evaluate the integrals in equations 5.7 and 5.9 using graphical or numerical methods. Figure 5.2 indicates this schematically.
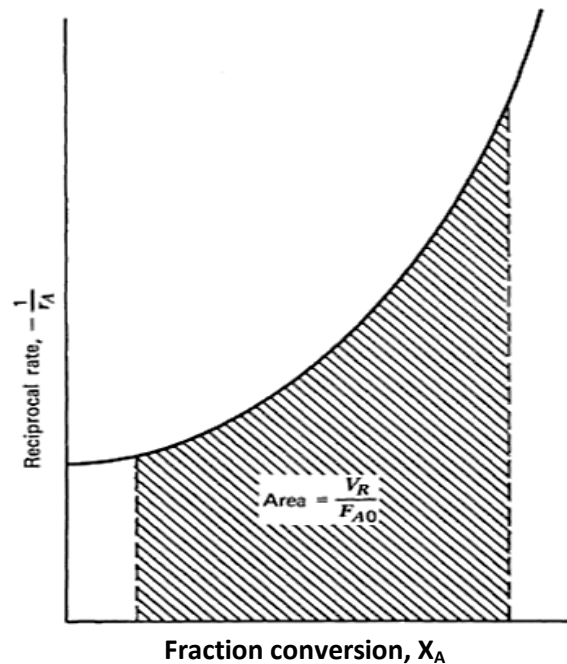


**Fig. 5.2**. Determination of $V_R/F_{A0}$ from plot of reciprocal rate versus fraction conversion

Equation 5.9 could be written in the form of

$$\tau = - \int_{C_{A0}}^{C_A} \frac{dC_A}{(-r_A)} \tag{5.10}$$

For variable density systems it is more convenient to work in terms of the fraction conversion (equation 5.9), but for constant density systems either equation 5.9 or equation 5.10 is appropriate.

So, if $(-r_A)$ is given as data in a table, the integration of equations 5.9 and 5.10 could be solved graphically. While if $(-r_A)$ is given as equation, the integration could be solved directly.
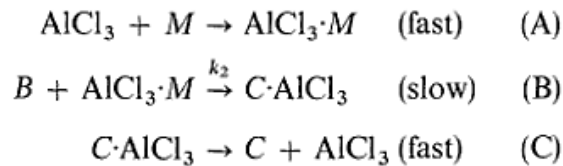
For preliminary design calculations involving tubular reactors, the usual procedure is to assume plug flow with constant pressure over the length of the reactor. However, the above analysis is appropriate regardless of whether or not a pressure drop exists. The pressure enters only through its influence on the reaction rate term.

For liquid phase reactions the influence of pressure variations is usually insignificant but, for gas phase reactions or when mixtures of gases and liquids are present, the pressure drop across a given segment of the reactor must be taken into account in arriving at the reactor volume required to accomplish a given task.

***Example 5.1.*** Two scientist have studied the aluminum chloride catalyzed diene condensation of butadiene and methyl acrylate in benzene solution. The stoichiometry for this Diels-Alder reaction is



butadiene $(B)$          methyl acrylate $(M)$  $\longrightarrow$          adduct $(C)$
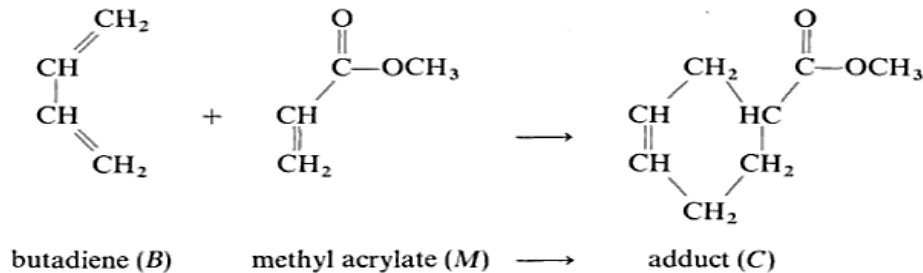
The following set of mechanistic equations is consistent with their experimental results:

$$AlCl_3 + M \rightarrow AlCl_3{\cdot}M \quad \text{(fast)} \quad \text{(A)}$$
$$B + AlCl_3{\cdot}M \xrightarrow{k_2} C{\cdot}AlCl_3 \quad \text{(slow)} \quad \text{(B)}$$
$$C{\cdot}AlCl_3 \rightarrow C + AlCl_3 \text{ (fast)} \quad \text{(C)}$$

where reaction B is the rate limiting step. These investigators report that the second-order rate constant for reaction B is equal to 1.15 x $10^3$ m$^3$/mole-ksec at 20 °C. Determine the volume of plug flow reactor that would be necessary to achieve 40% conversion of the

**4**

input butadiene assuming isothermal operating conditions and a liquid feed rate of 0.50 m³/ksec. The feed composition is as follows.

| | | |
|---|---|---|
| Butadiene ($B$) | 96.5 | moles/m³ |
| Methyl acrylate ($M$) | 184 | moles/m³ |
| $AlCl_3$ | | 6.63 moles/m³ |

**Solution**

The butadiene is the limiting reagent and conversions will be expressed in terms of this species. Over the composition range of interest there will always be sufficient methyl acrylate present to tie up the aluminum chloride. Consequently the concentration of the complex (AlCl$_3$·M) will remain constant throughout the length of the reactor at a value equal to the initial AlCl$_3$ concentration. For these conditions the reaction rate expression is the form

$$-r_B = kC_B C_{AlCl_3.M} = kC_{B0}(1-X_B)C_{AlCl_3,0} \qquad \text{(D)}$$

since the volume change accompanying liquid phase reactions is negligible. Equation 5.9 may be used as the basic design relationship.

$$\tau = C_{B0}\int_0^{X_B}\frac{dX_B}{(-r_B)} = C_{B0}\int_0^{X_B}\frac{dX_B}{kC_{B0}(1-X_B)C_{AlCl_3,0}} \qquad \text{(E)}$$

Since the quantities $C_{AlCl3,0}$ and $k$ are constant for the conditions cited, equation **E** may be integrated to give

$$\tau = \frac{ln(\frac{1}{1-X_B})}{kC_{AlCl_3,0}}$$

Substitution of numerical values gives

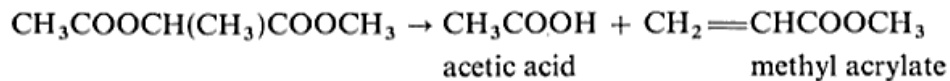$$\tau = \frac{ln(\frac{1}{1-0.4})}{(1.15\times10^{-3})(6.63)} = 67.0\ ksec \approx 18.6\ hr$$

From the definition of the space time and the inlet volumetric flow rate,

$$V_R = \tau \, v_0 = 67.0 \, (0.500) = 33.5 \, m^3$$

The space time and reactor volume required to accomplish the specified conversion in a plug flow reactor are sufficiently high that they make the use of a tubular reactor impractical for the specified operating conditions. For these conditions a cascade of stirred tank reactors would be more appropriate.

***Example 5.2***. Two scientist have the pyrolysis of methyl acetoxypropionate at temperatures near 500 °C and a variety of pressures.

$$CH_3COOCH(CH_3)COOCH_3 \rightarrow CH_3COOH + CH_2\!=\!\!=\!CHCOOCH_3$$
$$\text{acetic acid} \qquad\qquad \text{methyl acrylate}$$

Below 565 °C the pyrolysis reaction is essentially first order with a rate constant given by

$k = 7.8 \times 10^9 \, e^{-19220/T} \, sec^{-1}$ ; where **T** is expressed in degrees Kelvin.

If one desires to design a pilot scale tubular reactor to operate isothermally at 500 °C, what length of 6-in. pipe will be required to convert 90% of the raw feedstock to methyl acrylate?. The feedstock enters at 5 atm at a flow rate of 500 lb/hr. Ideal gas behavior may be assumed. A 6-in. pipe has an area of 0.0388 ft2 available for flow. Pressure drop across the reactor may be neglected.

**Solution**

From equation 5.9 and the fact that the reaction is first order,

$$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{kC_A} \qquad\qquad\qquad (A)$$

For the case where the feed is pure methyl acetoxypropionate, $(\mathcal{E}_A = 1)$

***H.W. 5.1***. *Prove that $\mathcal{E}_A = 1$.*

Since there is a change in the number of moles of gaseous species on reaction, the concentration corresponding to a given fraction conversion is

$$C_A = C_{A0}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right) = C_{A0}\left(\frac{1-X_A}{1+X_A}\right) \qquad (B)$$

Combining equations A and B gives

$$\tau = \int_0^{X_A} \frac{(1+X_A)dX_A}{k(1-X_A)}$$

Since the reaction takes place isothermally at 500 °C, the reaction rate constant may be moved outside the integral sign. At this temperature it is equal to 0.124 sec$^{-1}$ . Thus

$$0.124\,\tau = \int_0^{X_A} \frac{dX_A}{(1-X_A)} + \int_0^{X_A} \frac{X_A dX_A}{(1-X_A)}$$

Evaluation of the integrals gives

$$0.124\,\tau = -ln(1-X_A) - X_A - ln(1-X_A)$$

$$0.124\,\tau = -2ln(1-X_A) - X_A$$

For $X_A = 0.9$,

$$\tau = [-2ln(1-0.9) - 0.9]/0.124$$

$$\tau = 29.9\,sec$$

**H.W. 5.2**. *What will be the space time at constant volume?*

If the gas behaves ideally the volumetric flow rate at the reactor inlet is given by the product of the molal flow rate [(500/146) lb moles/hr] and the molal volume at the pressure and temperature in question. The latter may be calculated by correcting the standard molal volume (359 ft$^3$/lb mole) for variations in temperature and pressure between the reactor inlet and standard conditions. Hence

$$v_0 = \left(\frac{500}{146}\right)(359)\left(\frac{773}{273}\right)\left(\frac{1}{5}\right) = 696\frac{ft^3}{hr} = 0.193\,\frac{ft^3}{sec}$$

From the definition of the space time,

$$V_R = \tau\,v_0 = (29.9)(0.193) = 5.78\,ft^3$$

From geometric considerations the required length of 6-in. pipe is equal to (5.78 ft$^3$)/(0.0388 ft$^2$) or 149 ft.

## Chemical Reactor Design:

## The Continuous Flow Stirred Tank Reactor (CSTR)

Continuous flow stirred tank reactors are widely used in the chemical process industry. Although individual reactors may be used, it is usually preferable to employ a battery of such reactors connected in series. The effectiveness of such batteries depends on the number of reactors used, the sizes of the component reactors, and the efficiency of mixing within each stage. Continuous flow stirred tank reactors are normally just what the name implies—tanks into which reactants flow and from which a product stream is removed on a continuous basis. CFSTR, CSTR, C-star, and back-mix reactor are only a few of the names applied to the idealized stirred tank flow reactor.

The virtues of a stirred tank reactor lie in its simplicity of construction and the relative ease with which it may be controlled. These reactors are used primarily for carrying out liquid phase reactions in the organic chemicals industry, particularly for systems that are characterized by relatively slow reaction rates. The most important feature of the CSTR is its mixing characteristics. The idealized model of reactor performance presumes that the reactor contents are perfectly mixed so that the system properties are uniform throughout. The effluent composition and temperature are thus identical with those of the reactor contents. Moreover, because of the simplicity of their construction, stirred tank reactors normally cost much less per unit of volume than tubular reactors. Thus, in many cases, it is more economical to employ a large stirred tank reactor or a battery of such reactors than it is to use a tubular reactor.

Consider the schematic representation of a continuous flow stirred tank reactor shown in Figure 6.1. The starting point for the development of the fundamental design equation is again a generalized material balance on a reactant species. For the steady-state case the accumulation term in equation 2.1 is zero. Furthermore, since conditions are uniform throughout the reactor volume, the material balance may be written over the entire reactor. Hence,

**1**

$$\begin{pmatrix} \text{Rate of flow} \\ \text{of reactant into} \\ \text{reactor} \end{pmatrix} = \begin{pmatrix} \text{Rate of flow} \\ \text{of reactant out of} \\ \text{reactor} \end{pmatrix} + \begin{pmatrix} \text{Rate of disappearance} \\ \text{of reactant by} \\ \text{reaction} \\ \text{in the} \\ \text{reactor} \end{pmatrix} \qquad (6.1)$$



Entry: $F_{A0}$, $C_{A0}$, $X_{A0} = 0$

$V_R$ = Reactor volume
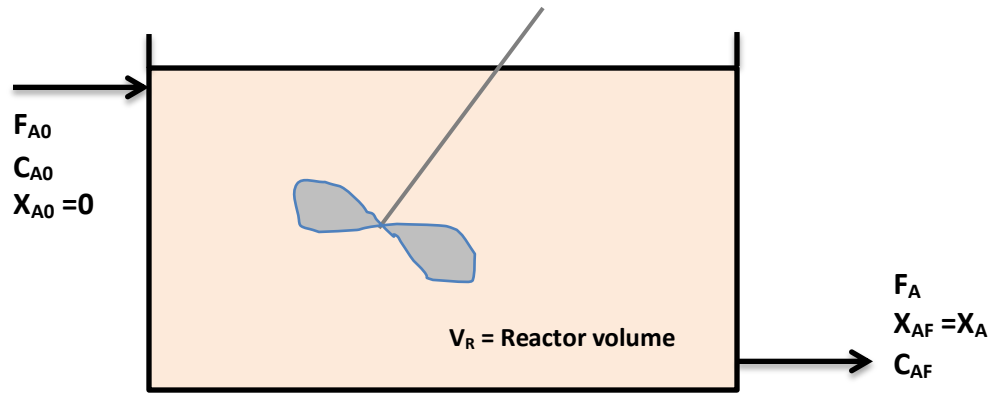
Exit: $F_A$, $X_{AF} = X_A$, $C_{AF}$

**Fig. 6.1.** Schematic representation of CSTR

$$F_{A0} = F_A + (-r_A) \, V_R \qquad (6.2)$$

where we again emphasize that the appropriate volume is that physically occupied by the reacting fluid. The quantity ($-r_A$) is the rate of disappearance of reactant $A$ evaluated at reactor outlet conditions. The last equation may be rewritten in terms of the fraction conversion as

$$F_{A0} = F_{A0} \, (1 - X_A) + (-r_A) \, V_R \qquad (6.3)$$

$$F_{A0} = F_{A0} - F_{A0} \, X_A + (-r_A) \, V_R$$

$$F_{A0} \, X_A = (-r_A) \, V_R \qquad (6.4)$$

$$V_R = \frac{F_{A0} X_A}{-r_A} \qquad (6.5)$$

Since,

$$F_{A0} = C_{A0} \, v_0 \qquad (6.6)$$

So, equation (6.5) could be written as

$$V_R = \frac{C_{A0} v_0 X_A}{-r_A} \tag{6.7}$$

$$\frac{V_R}{v_0} = \tau = \frac{C_{A0} X_A}{-r_A} = \frac{C_{A0} - C_A}{-r_A} \tag{6.8}$$

$$\tau = \frac{1}{s} \tag{6.9}$$

Where $\tau$ is the space time, or time required to process one reactor volume of feed measured at specified conditions. While the space velocity (s) is the number of reactor volumes of feed at specified conditions which can be treated in unit time and it equals the reciprocal of the space time. Both of the space-time and space-velocity are characterized as the proper performance measures of flow reactors while the reaction time $t$ is the natural performance measure for a batch reactor.

Thus, a space-velocity of 3 min$^{-1}$ means that three reactor volumes of feed at specified conditions are being fed into the reactor per hour. A space-time of 4 min means that every 4 min one reactor volume of feed at specified conditions is being treated by the reactor.

Figure 6.2 is a graphical representation of these continuous stirred tank reactor performance equations.
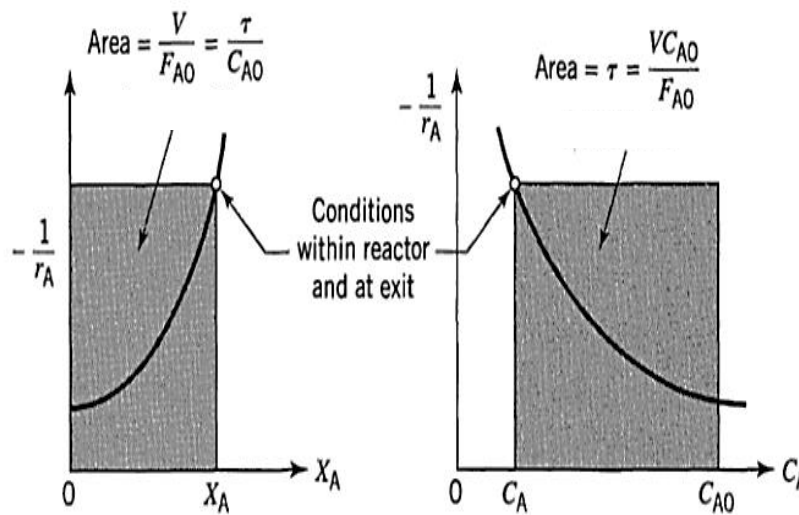


**Fig. 6.2.** Graphical representation of the design equations for CSTR

As an example, for constant density systems $C_A/C_{A0} = 1 - X_A$, thus the performance expression *for first-order reaction* becomes

$$k\tau = \frac{X_A}{1-X_A} = \frac{C_{A0}-C_A}{C_A} \tag{6.10}$$

---

**H.W. 6.1**. *Write an equation of $X_A$ as a function of $k\tau$ .*

---

While for variable volume ($\varepsilon_A \neq 0$)

$$V_R = V_{R0}(1 + \varepsilon_A X_A)$$

$$\frac{C_A}{C_{A0}} = \frac{1-X_A}{1+\varepsilon_A X_A} \tag{6.11}$$

thus *for first-order reaction* the performance expression for flow reactors becomes

$$k\tau = \frac{X_A(1+\varepsilon_A X_A)}{1-X_A} \tag{6.12}$$

For *second-order reaction,* A → products, *$-r_A = kC_A^2$*, ($\varepsilon_A = 0$) the performance equation becomes

$$k\tau = \frac{C_{A0}-C_A}{C_A^2} \tag{6.13}$$

Similar expressions can be written for any other form of rate equation. These expressions can be written either in terms of concentrations or conversions. Using conversions is simpler for systems of changing density, while either form can be used for systems of constant density.

The residence time ($t_r$) for CSTR could be represented as follows:

$$t_r = \frac{V_R}{v} = \frac{V_R}{v_0(1+\varepsilon_A X_A)} = \frac{\tau}{(1+\varepsilon_A X_A)} \tag{6.14}$$

While for PFR, the residence time is

$$t_r = C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)} \tag{6.15}$$

The CSTR can make products 24 hours a day for weeks at a time, whereas for a typical cycle, the batch reactor is producing only about half the time. Moreover, conversion and selectivity may vary from day to day with a batch reactor, and they are more likely to be constant with a CSTR and a good control system.

The main disadvantage of continuous operation is that the reaction rate is nearly always lower than the average rate for a batch reaction. In most cases, the batch reaction rate decreases as the conversion increases, and in the CSTR the reaction rate is the same as the final reaction rate in the batch reactor. For high conversions, the final rate may be several-fold lower than the average rate, and the average residence time in the CSTR must then be several-fold greater than the reaction time in a batch reactor.

To compare the batch and CSTR times, the equation for a batch first-order reaction is used with equation (6.10):

$$k\tau = \ln\left(\frac{1}{1-X_A}\right)$$

$$\frac{\tau_{CSTR}}{t_{Batch}} = \frac{X_A/(1-X_A)}{\ln\left(\frac{1}{1-X_A}\right)} \tag{6.16}$$

> **H.W. 6.2**. *Try a few values of $X_A$ (0.5, 0.8, 0.9, 0.95) in the case of first-order reaction to find the ratio of equation (6.16) and list the results in a table.*

The ratio of actual reactor volumes for the CSTR and the batch reactor is smaller than the ratio of reaction times, because the total time for a batch reactor is considerably greater than the reaction time. If the CSTR is compared with a PFR, the ratio of times is the same as the ratio of reactor volumes. (*Why?*)

Similar comparisons could be presented for second-order reactions, but several tables or plots would be needed, because most such reactions involve two reactants, with one fed in excess. The ratio of reaction times is higher than for a first-order reaction, but not much higher when there is a large excess of one reactant. For half-order reactions, there

is less change in rate with conversion, and the ratio of reaction times is less than for first-order kinetics.

When batch data are presented as a plot of conversion versus time, the comparison of CSTR and batch reaction times can be made graphically without knowing the reaction order. As shown in Figure 6.3, a tangent to the conversion curve is extended to intersect the time axis. The distance from this intersection to the batch time represents the residence time for the CSTR, as shown here:

$$-r_A = -C_{A0} \frac{dx}{dt}$$

$$r_A = C_{A0} \, (slope)$$

For the CSTR,

$$V_R = \frac{C_{A0} v_0 \, X_A}{-r_A} \tag{6.7}$$

$$C_{A0} v_0 \, X_A = r_A V_R = C_{A0} \, (slope) \, V_R$$

$$\frac{V_R}{v_0} = \tau = \frac{X_A}{slope}$$

From Figure 6.1, slope= $X_A/t'$

Or

$$\frac{V_R}{v_0} = \tau = \frac{X_A}{slope} = \frac{X_A}{X_A/t'} = t' \tag{6.17}$$
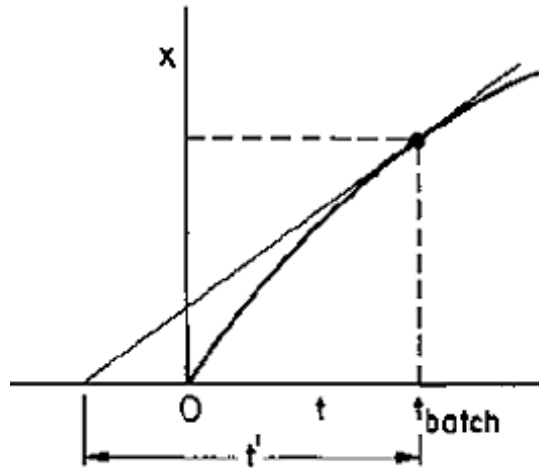
**Fig. 6.3.** Determination of residence time for a CSTR from a batch test.

If the rate in the batch reaction at first increases with time and then decreases, as in Figure 6.4, the desired conversion may be reached with a smaller residence time for the CSTR. Operating at $x_1$ would give $t_{CSTR} < t_{batch}$, but at $x_2$, $t_{CSTR} > t_{batch}$. Reaction curves of this type could result from an autocatalytic reaction or a reaction with an induction period caused by an inhibitor. Similar plots would result from an exothermic reaction in an adiabatic reactor.
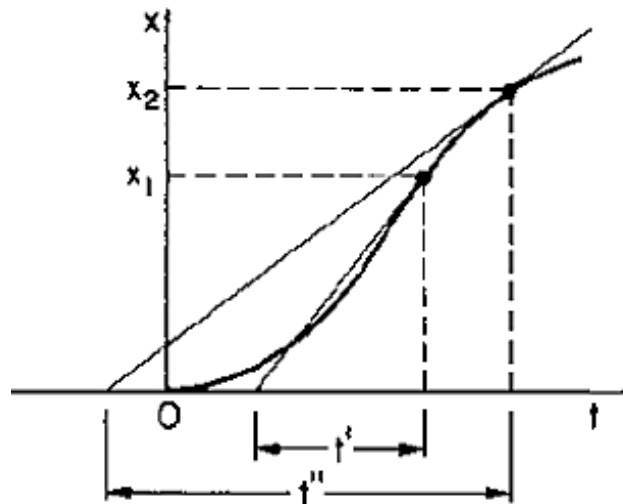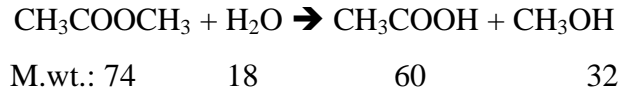


**Fig. 6.3.** Conversion plot for an autocatalytic reaction.

## Chemical Reactor Design:

## Ideal Reactors

***Example 7.1.*** In a batch reactor of 5 m³ volume used for the hydrolysis of acetate as:

$$CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$$

M.wt.: 74          18          60          32

a feed containing 4 kgmol of methyl acetate was charged. The batch was discharged when 60% of the acetate was hydrolyzed. If the reactor is shut down for a period of 30min between batches can be considered as irreversible-first-order reaction with a rate constant of $1.25 \times 10^{-4}$ sec⁻¹. Determine the quantity of acetic acid produced per day.

***Ans.:***

For batch reactor and constant volume,

$$t = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)} \qquad (3.12)$$

For first-order reaction,

$$-r_A = kC_A$$

For constant volume,

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

So,

$$-r_A = kC_{A0}(1 - X_A)$$

$$t = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)} = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{kC_{A0}(1 - X_A)} = \frac{1}{k} \int_0^{X_{AF}} \frac{dX_A}{(1 - X_A)}$$

1

$$t = \frac{1}{k}\ln\left(\frac{1}{1 - X_{AF}}\right)$$

$$t = \frac{1}{1.25 \times 10^{-4}}\ln\left(\frac{1}{1 - 0.6}\right) = 7330 \; sec = 122.17 \; min$$

Total time of one batch = reaction time + period of shut down

Total time of one batch = 122.17 + 30 = **152.17 min**

Mass of acetic acid produced per batch = 4 × 0.6 × 60 = **144 kg/batch** of 152.17 min

The quantity per one day= (144 × 24 × 60) / (152.17) = **1362.69 Kg acetic acid/day**

***Example 7.2.*** The homogeneous gas reaction (A➔2B) is run at $100^0$C and constant pressure of 1 atm in an experimental batch reactor. The data listed in the table below were obtained starting with pure A. What size of plug flow reactor operated at $100^0$C and 10 atm would yield 90% conversion of A for a feed rate of 10 mol/sec where the feed containing 40% inert?

| Time (min) | $V/V^0$ | Time (min) | $V/V^0$ |
|------------|---------|------------|---------|
| 0 | 1.00 | 8 | 1.82 |
| 1 | 1.20 | 9 | 1.86 |
| 2 | 1.35 | 10 | 1.88 |
| 3 | 1.48 | 11 | 1.91 |
| 4 | 1.58 | 12 | 1.92 |
| 5 | 1.66 | 13 | 1.94 |
| 6 | 1.72 | 14 | 1.95 |
| 7 | 1.78 | 15 | 1.96 |

***Ans.:***

Assume a first-order reaction, for variable volume

$$-\ln(1 - \frac{\Delta V}{\varepsilon_A V^0}) = kt$$

$$\ln\left(\frac{1}{1 - \frac{\Delta V}{\varepsilon_A V^0}}\right) = kt \quad \Rightarrow \quad \ln\left(\frac{1}{1 - X_A}\right) = kt$$

$$\varepsilon_A = \left(\frac{\Delta n}{a}\right) y_A = \left(\frac{2 - 1}{1}\right) 1 = 1$$

$$V = V^0(1 + \varepsilon_A X_A) \quad \Rightarrow \quad X_A = \frac{V}{V^0} - 1$$

Now, we will apply these equations to find the rate constant for each time. For example, at time = 1 min

$$\frac{V}{V^0} = 1.20 \quad \Rightarrow \quad X_A = \frac{V}{V^0} - 1 = 1.20 - 1 = 0.2$$

$$\ln\left(\frac{1}{1 - X_A}\right) = kt \quad \Rightarrow \quad \ln\left(\frac{1}{1 - 0.2}\right) = k(1)$$

$$k = 0.223 \ min^{-1}$$

| Time (min) | $V/V^0$ | $X_A$ | $k(min^{-1})$ | Time (min) | $V/V^0$ | $X_A$ | $k(min^{-1})$ |
|---|---|---|---|---|---|---|---|
| 0 | 1.00 | 0.0 | - | 8 | 1.82 | 0.82 | 0.214 |
| 1 | 1.20 | 0.20 | 0.223 | 9 | 1.86 | 0.86 | 0.218 |
| 2 | 1.35 | 0.35 | 0.215 | 10 | 1.88 | 0.88 | 0.212 |
| 3 | 1.48 | 0.48 | 0.218 | 11 | 1.91 | 0.91 | 0.219 |
| 4 | 1.58 | 0.58 | 0.217 | 12 | 1.92 | 0.92 | 0.210 |
| 5 | 1.66 | 0.66 | 0.216 | 13 | 1.94 | 0.94 | 0.216 |
| 6 | 1.72 | 0.72 | 0.212 | 14 | 1.95 | 0.95 | 0.214 |
| 7 | 1.78 | 0.78 | 0.216 | 15 | 1.96 | 0.96 | 0.215 |

The average rate constant ($k_{av}$) equals (0.216 min$^{-1}$), so the assumption of first-order reaction is correct.

3

For plug flow reactor

$$V_R = F_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)} \tag{5.7}$$

For variable volume

$$C_A = C_{A0} \left( \frac{1 - X_A}{1 + \varepsilon_A X_A} \right)$$

For first-order reaction,

$$-r_A = kC_A$$

$$-r_A = kC_{A0} \left( \frac{1 - X_A}{1 + \varepsilon_A X_A} \right)$$

$$V_R = F_{A0} \int_0^{X_A} \frac{dX_A}{kC_{A0} \left( \frac{1 - X_A}{1 + \varepsilon_A X_A} \right)} = \frac{F_{A0}}{kC_{A0}} \int_0^{X_A} \frac{(1 + \varepsilon_A X_A) dX_A}{1 - X_A}$$

$$V_R = \frac{F_{A0}}{kC_{A0}} \left[ (1 + \varepsilon_A) \ln \left( \frac{1}{1 - X_A} \right) - \varepsilon_A X_A \right]$$

A➔2B   ; 60% A and 40% inert

$$\varepsilon_A = \left( \frac{\Delta n}{a} \right) y_A = \left( \frac{2 - 1}{1} \right) 0.6 = 0.6$$

$$F_{A0} = 10 \frac{mol}{sec} = 600 \frac{mol}{min}$$

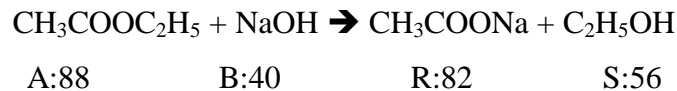$$C_{A0} = \frac{p_{A0}}{RT} = \frac{y_A P_{T0}}{RT}$$

$$P_{T0} = 10 \, atm = 1013 \, kPa$$

$$C_{A0} = \frac{0.6 \times 1013}{8.314 \times 373} = 0.196 \frac{kgmol}{m^3} = 0.196 \frac{mol}{lit}$$

$$V_R = \frac{F_{A0}}{kC_{A0}}\left[(1 + \varepsilon_A)\ln\left(\frac{1}{1 - X_A}\right) - \varepsilon_A X_A\right]$$

$$V_R = \frac{600}{0.216 \times 0.196}\left[(1 + 0.6)\ln\left(\frac{1}{1 - 0.9}\right) - 0.6 \times 0.9\right]$$

$$V_R = 44560\ lit = 44.56\ m^3$$

***Example 7.3.*** An aqueous solution of ethyl acetate is to be saponified with sodium hydroxide in a batch reactor.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$
$$A{:}88 \qquad\quad B{:}40 \qquad\quad R{:}82 \qquad\quad S{:}56$$

The initial concentration of ethyl acetate is **5 g/lit** and that of caustic soda is 0.1 gmol/lit. Values of the second-order rate constant in (lit/gmol.min) are 23.5 at $0^0C$ and 92.4 at $20^0C$. The reaction is essentially irreversible. Estimate the time required to saponify 95% of the ester at $40^0C$.

***Ans.:***

Since the reaction occurred at $40^0C$, the rate constant should be estimated. Initially, the activation energy must measure as follows,

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

At temperatures 0 and $20^0C$

$$\ln\left(\frac{92.4}{23.5}\right) = \frac{E}{R}\left(\frac{1}{273} - \frac{1}{293}\right)$$

$$\frac{E}{R} = 5475.75\ K$$

At temperatures 20 and $40^0C$

$$\ln\left(\frac{k_2}{92.4}\right) = \frac{E}{R}\left(\frac{1}{293} - \frac{1}{313}\right)$$

$$k_2 = 305 \frac{lit}{gmol.\,min}$$

The limiting reactant should be characterized

$$C_{A0} = \frac{5\ g/lit}{88\ g/gmol} = 0.057\ gmol/lit$$

$$C_{B0} = 0.1\ gmol/lit$$

So, the ethyl acetate is the limiting reactant. The aqueous solution refers to a constant volume. For a batch reactor

$$t = C_{A0} \int_{0}^{X_{AF}} \frac{dX_A}{(-r_A)}$$

$$-r_A = kC_A C_B$$

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

$$C_B = C_{B0} - C_{A0}X_A = C_{A0}\left(\frac{C_{B0}}{C_{A0}} - X_A\right) = C_{A0}(M - X_A)$$

$$-r_A = kC_{A0}^2(1 - X_A)(M - X_A)$$

$$t = C_{A0} \int_{0}^{X_{AF}} \frac{dX_A}{kC_{A0}^2(1 - X_A)(M - X_A)} = \frac{1}{kC_{A0}} \int_{0}^{X_{AF}} \frac{dX_A}{(1 - X_A)(M - X_A)}$$

$$t = \frac{1}{kC_{A0}} \frac{1}{M - 1} \ln\frac{M - X_A}{M(1 - X_A)}$$

$$M = \frac{C_{B0}}{C_{A0}} = \frac{0.10}{0.057} = 1.754$$

**6**

$$t = \frac{1}{(305 \times 0.057)} \frac{1}{(1.754 - 1)} ln \frac{1.754 - 0.95}{1.754(1 - 0.95)}$$

$$t = 0.169 \ min$$

*H.W.* **7.1.** *Study the effect of the variation of conversion on the batch time. Take (0.3,0.5,0.7,0.9, and 0.95) then draw the results of time vs. the conversion.*

## Chemical Reactor Design:

## Ideal Reactors

*Example 8.1.* An ester in aqueous solution is to be sponified in a continuous reactor system. Batch experiments showed that the reaction is first order and irreversible and 50% reaction occurred in 8 min at $40^0$C. We need to process 100 gmol/hr of 4 molar feed to 95% conversion. Calculate the reactor volume for this process in:

(a) PFR at $60^0$C.
(b) CSTR at $60^0$C.

Where the activation energy for this reaction is 40 kJ/gmol.

*Ans.:*

For batch reactor and constant volume,

$$t = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)} \tag{3.12}$$

For first-order reaction,

$$-r_A = kC_A$$

For constant volume,

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

So,

$$-r_A = kC_{A0}(1 - X_A)$$

$$t = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)} = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{kC_{A0}(1 - X_A)} = \frac{1}{k} \int_0^{X_{AF}} \frac{dX_A}{(1 - X_A)}$$

$$\ln\left(\frac{1}{1-X_{AF}}\right) = kt$$

At $40^0$C ; $X_A$=0.5 ; and time = 8 min

$$\ln\left(\frac{1}{1-0.5}\right) = 8\,k$$

$$k = 0.087\,min^{-1}$$

Since the required volume should be at $60^0$C, the rate constant must be recalculated at this temperature as follows

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

At temperatures $40^0$C (313 K), the rate constant $k_1$= 0.087 min$^{-1}$

and at $60^0$C (333 K), the rate constant $k_2$ is required.

$$\ln\left(\frac{k_2}{0.087}\right) = \frac{40000}{8.314}(\frac{1}{313} - \frac{1}{333})$$

$$k_2 = 0.219\,min^{-1} \quad at\ 60^0C$$

*(a)Volume of PFR at $60^0C$*

$$F_{A0} = 100\,gmol/hr$$

$$C_{A0} = 4\,molar = 4gmol/lit$$

For first-order reaction,

$$-r_A = kC_A$$

For constant volume,

$$-r_A = kC_{A0}(1-X_A)$$

$$k = 0.219 \, min^{-1} = 13.14 \, hr^{-1}$$

For plug flow reactor

$$V_R = F_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)} \tag{5.7}$$

$$V_R = \frac{F_{A0}}{kC_{A0}} \int_0^{X_A} \frac{dX_A}{(1 - X_A)}$$

$$V_R = \frac{F_{A0}}{kC_{A0}} \ln \frac{1}{1 - X_{AF}}$$

$$V_R = \frac{100}{(13.14)(4)} \ln \frac{1}{1 - 0.95}$$

$$V_{PFR} = 5.7 \, liter$$

*(b)Volume of CSTR at $60^0C$*

$$V_R = \frac{C_{A0} v_0 X_A}{-r_A} \tag{6.7}$$

$$V_R = \frac{F_{A0} X_A}{-r_A}$$

For first-order reaction,

$$-r_A = kC_A$$

For constant volume,

$$-r_A = kC_{A0}(1 - X_A)$$

$$V_R = \frac{F_{A0} X_A}{kC_{A0}(1 - X_A)}$$

$$V_R = \frac{(100)(0.95)}{(13.14)(4)(1-0.95)}$$

$$V_{CSTR} = 36.15 \; liter$$

The ratio of these two volumes of flow reactors are

$$\frac{V_{CSTR}}{V_{PFR}} = \frac{36.15}{5.7} = 6.34 \;\; say \; 7$$

This means that we need a CSTR having 7-fold larger than the PFR to achieve 95% of the conversion.

**H.W. 8.1.** *Find the same ratio but for the time of reaction.*

**Example 8.2.** The irreversible gas-phase reaction $A \rightarrow 3B$ is carried out isothermally at 400 K. The reaction is zero-order, the initial concentration of $A$ is 2 gmol/lit and the system contains 40% inert. The specific rate constant is 0.3805 gmol/lit.min at 450 K and the activation energy is 40 kJ/gmol. Calculate the time required to achieve 80% conversion in

(a) a constant volume batch reactor.
(b) a constant pressure batch reactor.

For a volumetric flow rate of 2 lit/min, calculate the reactor volume, space time, and space velocity to achieve 80% conversion in

(c) CSTR
(d) PFR

*Ans.:*

(a) For a constant volume batch reactor, the rate constant must be calculated at 400 K because the given value is at 450 K.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

At temperatures 400 K, the rate constant $k_1$ is required.

and at 450 K, the rate constant $k_2$=.0.3805 gmol/lit.min

$$\ln\left(\frac{0.3805}{k_1}\right) = \frac{40000}{8.314}\left(\frac{1}{400} - \frac{1}{450}\right)$$

$$k_2 = 0.10\ \frac{gmol}{lit.min}\quad at\ 400\ K$$

For batch reactor and constant volume,

$$t = -\int_{C_{A0}}^{C_{AF}} \frac{dC_A}{(-r_A)} \qquad \text{for } \mathcal{E} = 0 \tag{3.13}$$

For zero-order reaction,

$$-r_A = k$$

$$t = -\int_{C_{A0}}^{C_A} \frac{dC_A}{k}$$

So,

$$C_{A0} - C_A = kt$$

$$C_{A0} = 2\ gmol/lit$$

For constant volume,

$$C_A = C_{A0}(1 - X_A) = 2\,(1 - 0.80) = 0.4\ gmol/lit$$

$$2 - 0.4 = 0.1\ t$$

$$t = 16\ min$$

(b) For a constant pressure batch reactor,

$$\frac{C_{A0}}{C_A} ln\frac{V}{V^0} = kt$$

$$\varepsilon_A = \left(\frac{\Delta n}{a}\right) y_A$$

$$\varepsilon_A = \left(\frac{3-1}{1}\right)(0.6) = 1.2$$

$$V = V^0(1 + \varepsilon_A X_A)$$

$$\frac{V}{V^0} = 1 + \varepsilon_A X_A$$

$$\frac{V}{V^0} = 1 + (1.2)(0.8) = 1.96$$

$$\frac{2}{1.2} ln1.96 = 0.1\,t$$

$$t = 11.22\,min$$

(c) For a CSTR

$$V_R = \frac{C_{A0} v_0\,X_A}{-r_A} \tag{6.7}$$

$$V_R = \frac{(2)(2)(0.8)}{0.1} = 32\,lit$$

$$\tau = \frac{V_R}{v_0} = \frac{32}{2} = 16\,min$$

Space velocity:

$$s = \frac{1}{\tau} = \frac{1}{16} = 0.0625\,min^{-1}$$

(d)  For a PFR

$$V_R = F_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A)} \hspace{3cm} (5.7)$$

For zero-order reaction,

$$-r_A = k$$

$$F_{A0} = C_{A0} v_0$$

$$V_R = \frac{C_{A0} v_0}{k} \int_0^{X_A} dX_A$$

$$V_R = \frac{C_{A0} v_0 X_A}{k}$$

$$V_R = \frac{(2)(2)(0.8)}{0.1} = 32 \, lit$$

$$\tau = \frac{V_R}{v_0} = \frac{32}{2} = 16 \, min$$

Space velocity:

$$s = \frac{1}{\tau} = \frac{1}{16} = 0.0625 \, min^{-1}$$

> **H.W. 8.2.** *Why the values of volume, space time, and space velocity are identical for CSTR and PFR?*

## Chemical Reactor Design:

## Design for single reaction

This type of reaction could be described by using only one expression of the rate equation combined with the necessary stoichiometric and equilibrium expressions. The important parameter in comparing designs for single reactions is the reactor size, therefore, this factor will be taken into consideration in comparison of various single and multiple ideal reactor systems.

## Size comparison of single reactors

### Batch reactor

This type of reactors possesses small instrumentation cost and flexibility of operation, but its disadvantages are the high labor, considerable time for filling, empty, cleanout, and refill as well as the poorer quality control of the product. In general, batch reactors are well suited to produce small amounts of material and produce several different products from one piece of equipment. The similarity between batch and plug flow reactors in the case of constant volume is that when an element of fluid reacts, it required the same length of time in both reactors as explained before in their performance equations.

$$t = - \int_{C_{A0}}^{C_{AF}} \frac{dC_A}{(-r_A)} \tag{3.13}$$

$$\tau = - \int_{C_{A0}}^{C_A} \frac{dC_A}{(-r_A)} \tag{5.10}$$

### Mixed flow versus plug flow reactors

In order to study the ratio of sizes of mixed flow and plug flow reactors, the issues of the stoichiometry of the chemical equation, the extent of reaction, and the form of the rate equation. In the case of n-order reaction:

$$-r_A = kC_A^n = kC_{A0}^n(1 - X_A)^n \qquad (n = 0 \to 3 \, ; isothermal)$$

1

For mixed flow reactors:

$$\left(\frac{V_R}{v_0}\right)_m = \tau_m = \frac{C_{A0}X_A}{-r_A} = \frac{C_{A0}X_A(1 + \varepsilon_A X_A)^n}{kC_{A0}^n(1 - X_A)^n}$$

$$\left(\frac{V_R}{v_0}\right)_m = \tau_m = \frac{1}{kC_{A0}^{n-1}} \frac{X_A(1 + \varepsilon_A X_A)^n}{(1 - X_A)^n} \qquad (9.1)$$

For plug flow reactors:

$$\left(\frac{V_R}{v_0}\right)_p = \tau_p = C_{A0} \int_0^{X_{AF}} \frac{dX_A}{(-r_A)} = C_{A0} \int_0^{X_{AF}} \frac{(1 + \varepsilon_A X_A)^n}{kC_{A0}^n(1 - X_A)^n} dX_A$$

$$\left(\frac{V_R}{v_0}\right)_p = \tau_p = \frac{1}{kC_{A0}^{n-1}} \int_0^{X_{AF}} \frac{(1 + \varepsilon_A X_A)^n}{(1 - X_A)^n} dX_A \qquad (9.2)$$

By dividing equation (9.2) by equation (9.1)

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left(\frac{C_{A0}^n V}{F_A^0}\right)_m}{\left(\frac{C_{A0}^n V}{F_A^0}\right)_p} = \frac{\left[X_A\left(\frac{1 + \varepsilon_A X_A}{1 - X_A}\right)^n\right]_m}{\left[\int_0^{X_{AF}}\left(\frac{1 + \varepsilon_A X_A}{1 - X_A}\right)^n dX_A\right]_p} \qquad (9.3)$$

For constant density ($\varepsilon_A = 0$) and ($n \neq 1$), equation (9.3) will be as follows:

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left(\frac{C_{A0}^n V}{F_A^0}\right)_m}{\left(\frac{C_{A0}^n V}{F_A^0}\right)_p} = \frac{\left[\frac{X_A}{(1 - X_A)^n}\right]_m}{\left[\frac{(1 - X_A)^{n-1} - 1}{(n - 1)}\right]_p} \qquad (9.4)$$

While, for constant density ($\varepsilon_A = 0$) and ($n = 1$), equation (9.3) will be as follows:

$$\frac{\tau_m}{\tau_p} = \frac{\left(\dfrac{C_A^0 V}{F_A^0}\right)_m}{\left(\dfrac{C_A^0 V}{F_A^0}\right)_p} = \frac{\left(\dfrac{X_A}{1-X_A}\right)_m}{[-ln(1-X_A)]_p} \qquad (9.5)$$

If the molar flow rates are identical, i.e. $(F_A^0)_m = (F_A^0)_p$ , then:

$$\frac{\tau_m}{\tau_p} = \frac{V_m}{V_p} \qquad (9.6)$$

The graphical comparison of the performance of plug flow with mixed flow reactors depending on equations (9.4) and (9.5) is shown in figure 9.1 as follows:
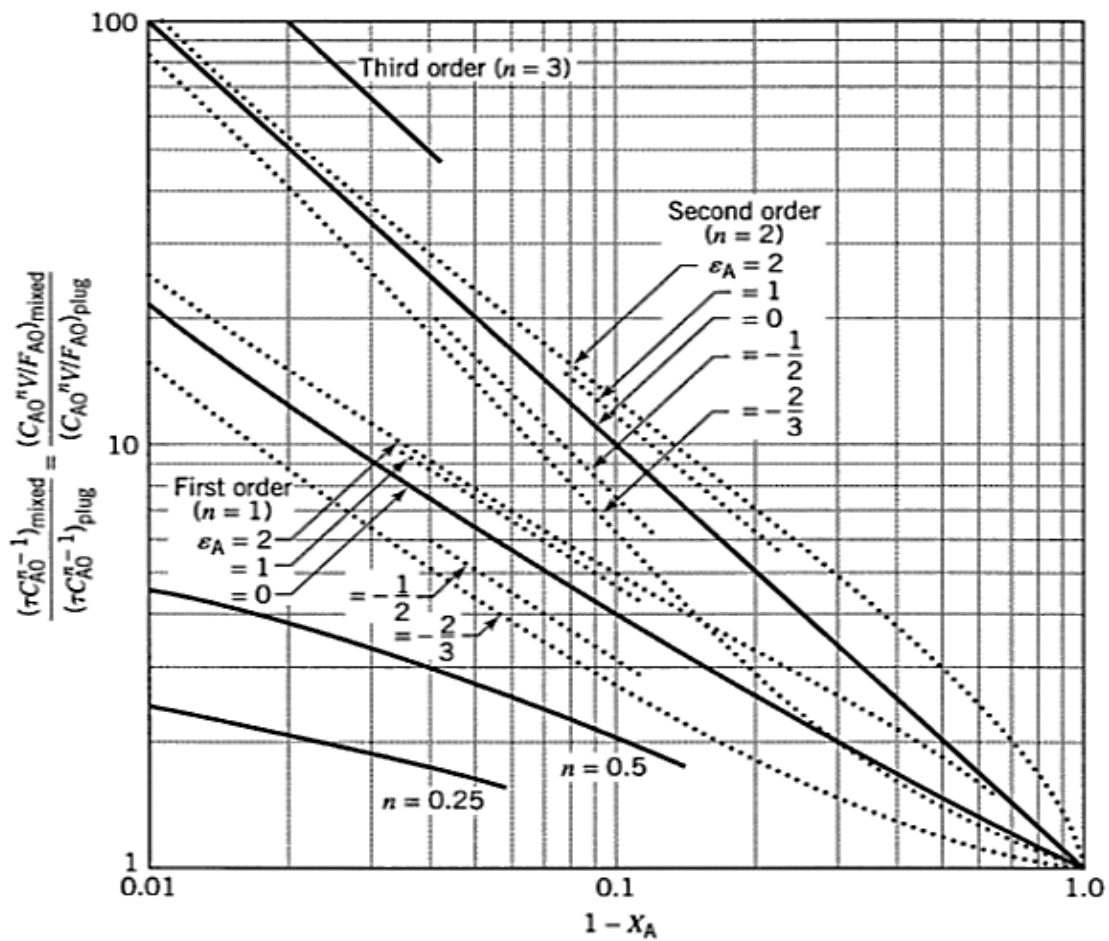


Fig. 9.1. Comparison of performance of single mixed flow and plug flow reactors for the nth-order reactions

***Example 9.1.*** Find the volume of mixed flow reactor using the following details: First order reaction, constant density, identical initial flow rates, $X_A = 0.4$, the volume of plug flow reactor equals 33.5 m³.

***Ans.*:**

Using figure 9.1. and the given data, the ratio obtained is 1.3 then

$$\frac{V_m}{V_p} = 1.3$$

$$\frac{V_m}{33.5} = 1.3$$

$$V_m = 43.7 \; m^3$$

***H.W. 9.1.*** Find the volume of mixed flow reactor using the following details: First order reaction, constant density, identical initial flow rates, $X_A = 0.9$, the volume of plug flow reactor equals 20 m³.

The following observations are important:

- If (n>0) and ($\frac{V_m}{V_p} \propto n$) then ($V_m > V_p$) for all conversion levels. But if (n=0) then the volume of reactor whither $V_m$ or $V_p$ is not a function of the type of the reactor.

- If ($\frac{V_m}{V_p} \propto X_A$) especially the higher values of conversion, then ($V_m > V_p$). But for low values of conversion, the volumes of reactor will be approximately similar, i.e. ($V_m \approx V_p$). Therefore, for any rate expression that decreases with increasing conversion, the volume of mixed reactor is always larger than the volume of plug flow reactor.

- The ratio of ($\frac{V_m}{V_p}$) is directly dependent of the value of the extent of reaction ($\xi_A$). If ($\xi_A > 0$), the ratio of volumes increases, whereas when ($\xi_A < 0$) this ratio will be decreased.

- The ratio of $(\frac{V_m}{V_p})$ is extremely affected by the order of reaction more than the extent of reaction.

- At ambient pressure, the larger volume of mixed reactor does not necessarily imply extra capital cost. But the volume increases rapidly at high conversion levels leads to some interesting optimization problems in reactor design , i.e. reactor volume costs are inversely proportional with the product separation costs.

Figure 9.2 explains clearly the a graphical comparison proving the difference in volumes between mixed and plug flow reactors for reactions with arbitrary but known rate (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.
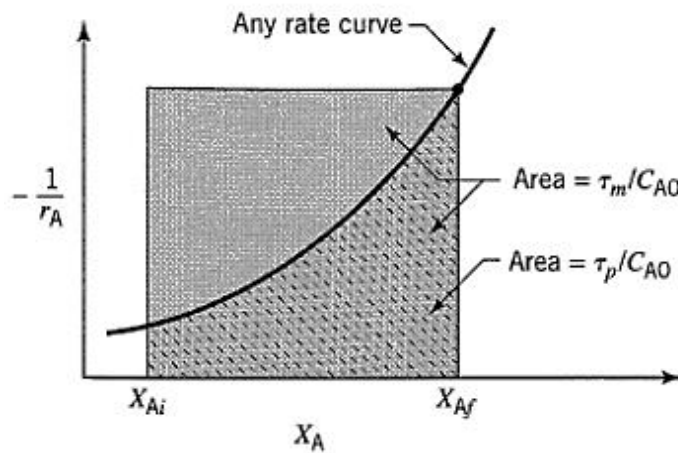


**Fig. 9.2**. Comparison of performance of mixed flow and plug flow reactors for any reaction kinetics.

## Chemical Reactor Design:

## Design for single reaction

## Variation of reaction ratio for second-order reactions

There are several cases of second-order reactions as shown below:

*Case 1*: Two different reactants such as A+B→ products, here the rate of reaction is

$$-r_A = -r_B = kC_A C_B \qquad\qquad M = \dfrac{C_{B0}}{C_{A0}} \qquad (10.1)$$

*Case 2*: One reactant only such as A → products, here the rate of reaction is

$$-r_A = kC_A^2 \qquad\qquad (10.2)$$

*Case 3*: Two different reactants such as A+B→ products, but ($C_B \approx C_{B0}$) then the order of reaction (**n**) is approximately one:

$$-r_A = kC_A C_B = (kC_{B0})C_A = k'C_A \qquad\qquad M \gg 1 \qquad (10.3)$$

In order to obtain the space time for flow reactors in the case of second-order reactions, the following equations explain that

*Case 1*: For $C_{A0} = C_{B0}$, i.e. *M=1*

$$PFR: \qquad \tau_p = \dfrac{X_A}{kC_{A0}(1 - X_A)} \qquad (10.4)$$

$$CSTR: \qquad \tau_m = \dfrac{X_A}{kC_{A0}(1 - X_A)^2} \qquad (10.5)$$

*Case 2*: For $C_{A0} \neq C_{B0}$, i.e. $M \neq 1$

$$PFR: \qquad \tau_p = \dfrac{1}{kC_{A0}(M - 1)} ln\dfrac{(M - X_A)}{M(1 - X_A)} \qquad (10.6)$$

1

$$CSTR: \qquad \tau_m = \frac{X_A}{kC_{A0}(1 - X_A)(M - X_A)} \qquad (10.7)$$

The following figure (10.1) could be used to compared the performance between a PFR and a CSTR in the case of second-order reactions:
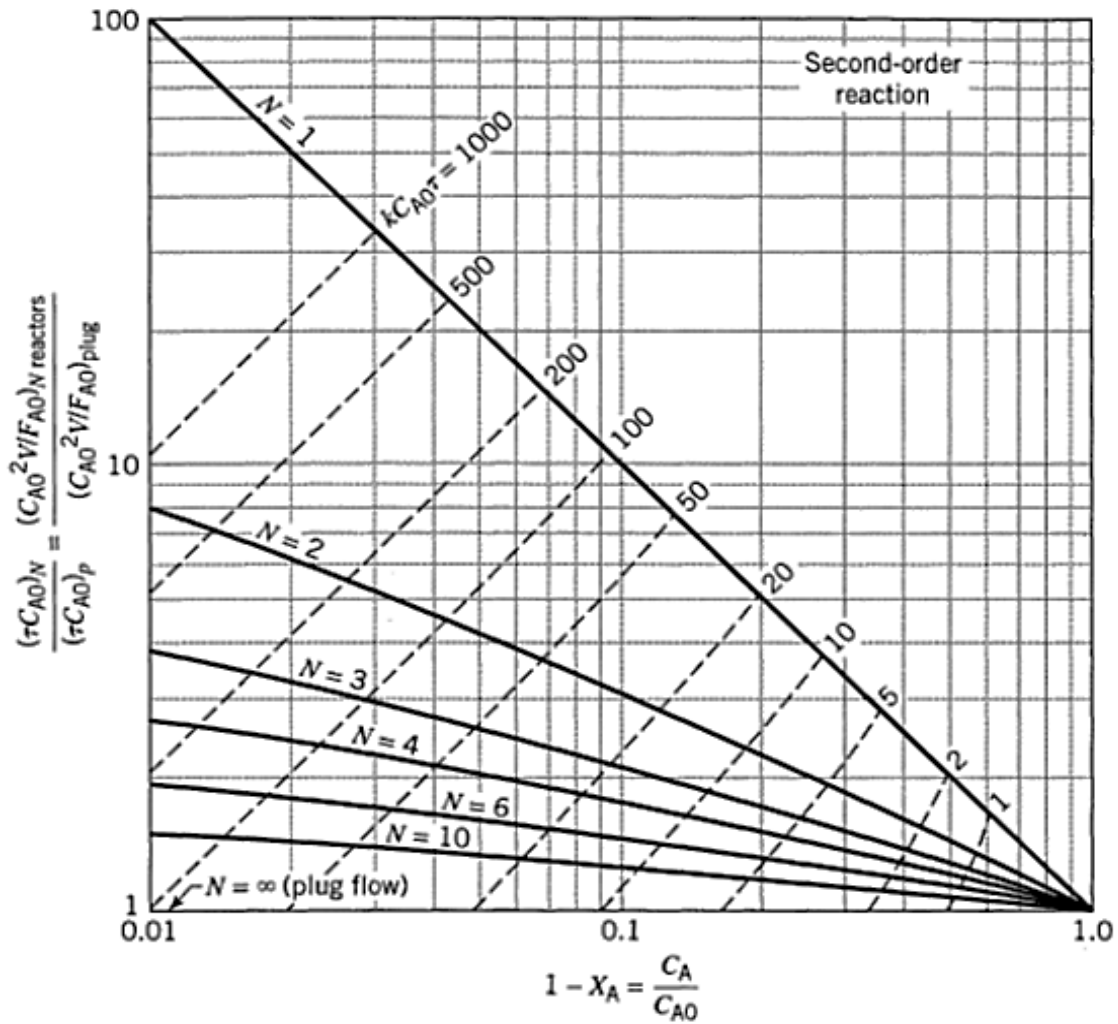


**Fig. 10.1.** Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for elementary second-order reactions

***Example 10.1***. The aqueous reaction A+B→P occurs in a **0.1 liter** plug flow reactor according to the following kinetics:

$$-r_A = 500 \, C_A C_B \qquad \left[\frac{lit}{mol.\,min}\right]$$

2

The initial concentrations of both reactants are identical (**0.01 mol/lit**) and the initial volumetric flow rate is **0.05 lit/min**.

  (a) What fractional conversion of reactants can be obtained?

  (b) What size of CSTR is needed for the same conversion obtained in (a)?

  (c) What conversion can be expected in a CSTR equal in size to the PFR?

*Ans*.:

  (a) Since the initial concentrations of reactants presented in the second-order reaction are equal, Eq. (10.4) could be used

$$\textbf{\textit{PFR}}: \qquad \tau_p = \frac{X_A}{k C_{A0}(1 - X_A)} \qquad (\textbf{10.4})$$

$$\tau_p = \frac{V_p}{v_0} = \frac{0.1}{0.05} = 2 \; min$$

$$2 = \frac{X_A}{500 \times 0.01 \, (1 - X_A)}$$

$$X_A = 0.91$$

Or by using Fig. (10.1)

$$k C_{A0} \tau_p = 500 \times 0.01 \times 2 = 10 \qquad and \qquad N = \infty$$

$$1 - X_A = 0.09 \qquad \rightarrow \qquad X_A = 0.91$$

  (b) For $X_A = 0.91$ $\;and\;$ $M = 1$, using Eq. 10.5:

$$\textbf{\textit{CSTR}}: \qquad \tau_m = \frac{X_A}{k C_{A0}(1 - X_A)^2} \qquad (\textbf{10.5})$$

$$\tau_m = \frac{0.91}{500 \times 0.01 \, (1 - 0.91)^2} = 22.46 \; min$$

$$V_m = \tau_m \, v_0 = 22.46 \times 0.05 = 1.123 \; lit$$

Or by using Fig. (10.1), **N=1** and (**1-X$_A$=0.09**):

$$\frac{(\tau C_{A0})_m}{(\tau C_{A0})_p} = \frac{\tau_m}{\tau_p} = \frac{V_m}{V_p} = 11$$

$$V_m = 11 \times 0.1 = 1.1 \; lit.$$

(c) For the same volume and volumetric flow rate, the space time will be the same, so Eq. 10.5 will be used:

$$\tau_m = \frac{X_A}{kC_{A0}(1 - X_A)^2} \qquad (10.5)$$

$$2 = \frac{X_A}{500 \times 0.01 \, (1 - X_A)^2}$$

$$X_A = 0.73$$

Or by using Fig. (10.1),

$$kC_{A0}\tau_m = 500 \times 0.01 \times 2 = 10 \qquad and \quad N = 1$$

$$1 - X_A = 0.27 \qquad \rightarrow \qquad X_A = 0.73$$

**H.W. 10.1**. *Find the conversion of a single CSTR used for a second-order chemical reaction if the $kC_{A0}\tau_m$ is (20, 40, 80, 100, 200, and 400) then tabulate the results obtained and draw it.*

## Combinations of PFRs

A PFR may take various configurational forms, as shown in Figure 10.2. The design or performance equation of PFR or its equivalent, provides a volume, V, which must then be interpreted geometrically for the purpose of fabrication. Thus, for cylindrical shape, the most common, it must be converted to a diameter (D) and length (L):

$$V = \frac{\pi D^2}{4} L = \frac{\pi D^3}{4}\left(\frac{L}{D}\right) \qquad (10.8)$$

The L/D ratio may vary from very large (L/D >> l), as in an ethane "cracker," which may consist of a very long length (i.e., many lengths connected in series) of 4-in pipe, to very small (L/D << l), as in a sulfur dioxide converter in a large-scale sulfuric acid plant, which may consist of three or four shallow beds of catalyst in series in a large diameter vessel. These situations correspond to those shown schematically in Figures 10.2 (a) and (b), respectively. The parallel-tube arrangement shown in Figure 10.2 (c), whether the tubes are packed or not, is also usually one with a relatively large L/D ratio; it facilitates heat transfer, for control of temperature, and is essentially a shell-and-tube heat exchanger in which reaction takes place either inside or outside the tubes.
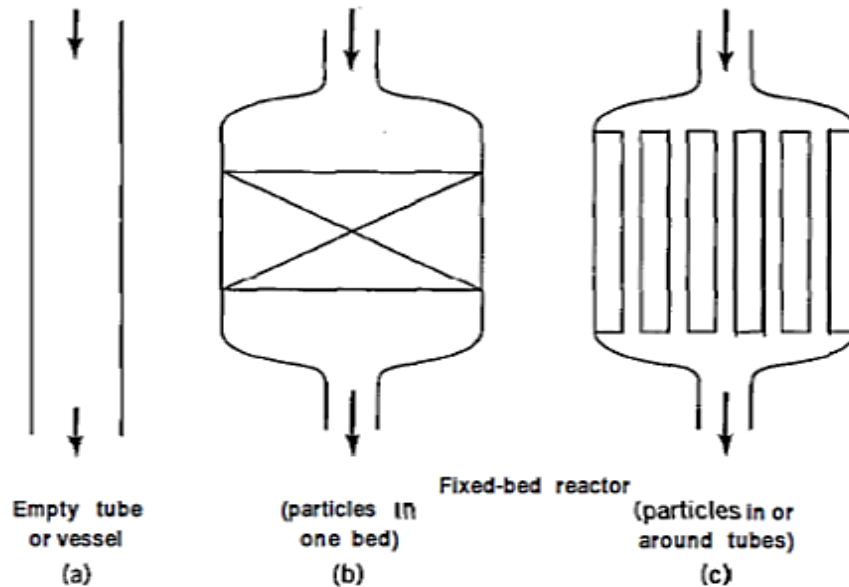


Fixed-bed reactor

| Empty tube or vessel | (particles in one bed) | (particles in or around tubes) |
|---|---|---|
| (a) | (b) | (c) |

**Fig. 10.2.** Three examples (schematic) of PFR

The volume *V* calculated by means of the design equation may be arranged into any *L/D* ratio and any series or parallel arrangement, provided:

(1) The resulting flow remains PF (to be consistent with the model on which the calculation of *V* is based).

(2) In a series arrangement, all changes in properties are taken into account, such as adjustment of *T* (without reaction) by a heat exchanger between stages (lengths). Such adjustment is more common for solid-catalyzed reactions than for homogeneous gas-phase reactions.

**5**

(3) In a parallel arrangement, streams which join at any point, most commonly at the outlet, have the same properties (e.g., composition and temperature).

For illustration of a series arrangement, point (2) above, the division of a (total) volume $(V)$ into three parts $(V1 + V2 + V_3 = V)$ in three different situations is shown in Figure 10.3.
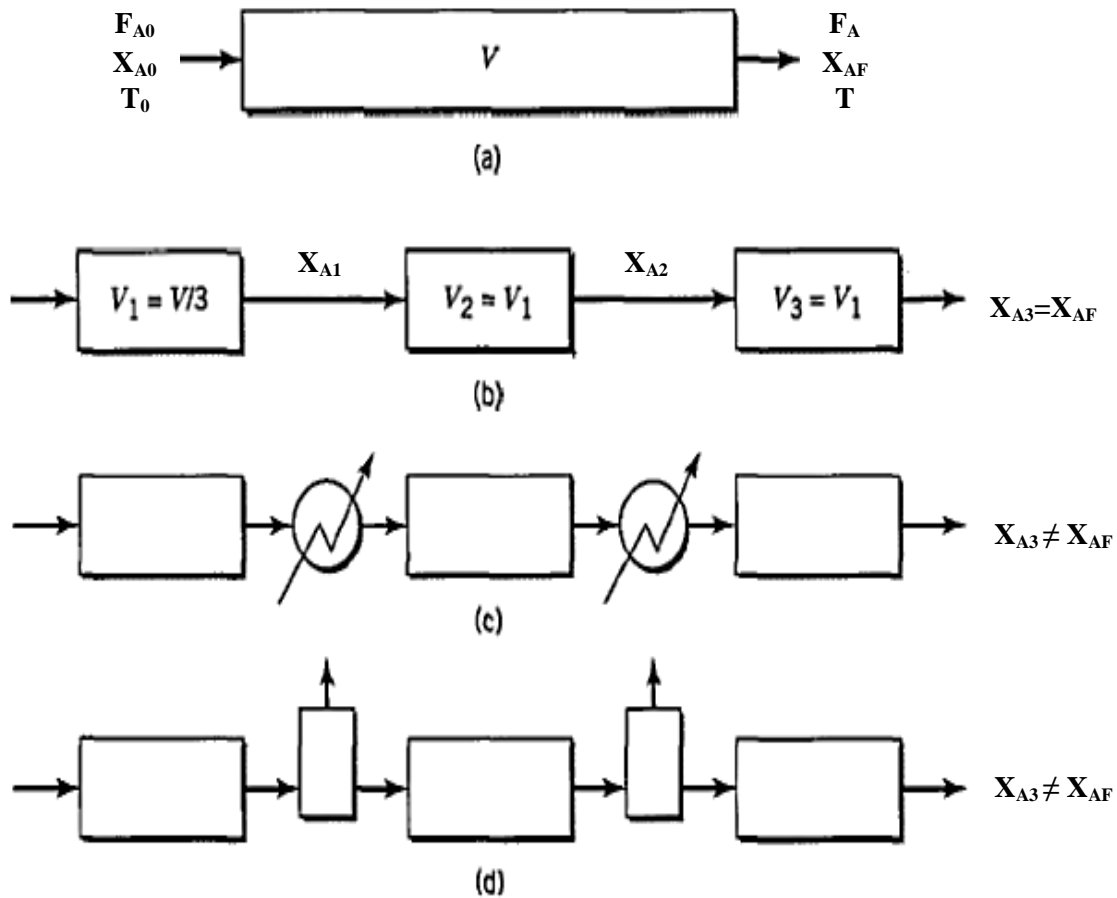


**Fig. 10.3**. Comparison of PFR and various series arrangements

Figure 10.3 (a) represents the total volume as one PFR, with reaction taking place leading to a particular fractional conversion at the outlet. Figure 10.3 (b) represents the same total volume divided into three parts, not necessarily equal, in series. Since the mere division of V into three parts does not alter the operating conditions from point to point, the two configurations are equivalent, and lead to the same final conversion.

$$\left(\frac{V_R}{F_{A0}}\right)_p = \int_0^{X_{AF}} \frac{dX_A}{(-r_A)} = \int_0^{X_{A1}} \frac{dX_A}{(-r_A)} + \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{(-r_A)} + \int_{X_{A2}}^{X_{AF}} \frac{dX_A}{(-r_A)} = \frac{V_1 + V_2 + V_3}{F_{A0}} \qquad (10.9)$$

Figure 10.3 (c) represents the same division, but with heat exchangers added between stages for adjustment of $T$. Since the $T$ profile is not the same as in (a), the performance is not the same ($X_{A3} \neq X_{AF}$). Similarly, Figure 10.3 (d) represents the same division, but with separation units added between stages to remove a rate-inhibiting product. Since the concentration profiles are not the same as in (a), the performance is not the same ($X_{A3} \neq X_{AF}$). For a parallel arrangement, point (3) above, as illustrated in Figure 10.2 (c), similar arguments can be used to show that if the space time and operating conditions (T, P, etc.) are the same for each tube, then each exhibits the same performance, and the total volume is the same as if no division took place. In this case, it is also important to show that the division of the throughput ($F_{A0}$) so that $\tau$ is the same in each tube leads to the most efficient operation (highest conversion for given total volume and throughput).

***Example 10.2.*** A system having three PFRs are connected as shown in the following figure. Find (a) the total volume of the cascade line, (b) the fraction of volumes of both streams, and (c) feed should introduce to (PFR₃) stream?
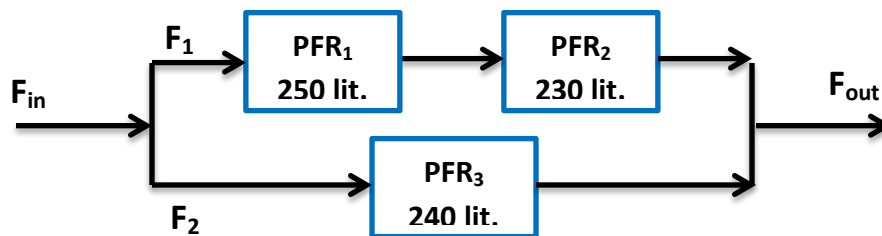


**Ans.:**

As observed in the figure, the inlet and outlet flow rates are similar. So,

$$F_{in} = F_{out}$$

(a)

$$V_{series} = V_{PFR_1} + V_{PFR_2}$$

$$V_{series} = 250 + 230 = 480 \ lit.$$

(b)

The fraction of volumes of both streams is:

$$V_{ratio} = \frac{V_{series}}{V_{PFR_3}} = \frac{480}{240} = 2$$

And (c), for parallel streams

$$\frac{V_{series}}{F_1} = \frac{V_{PFR_3}}{F_2}$$

$$\frac{F_2}{F_1} = \frac{V_{PFR_3}}{V_{series}} = \frac{1}{2}$$

$$F_2 = \frac{1}{2} F_1$$

Which means:

$$F_1 = \frac{2}{3} F_{in} \quad and \quad F_2 = \frac{1}{3} F_{in}$$

## Chemical Reactor Design:

## Design for single reaction

## Stirred Tank Reactors in Series

In order to reduce the disparities in volume or space time requirements between an individual CSTR and a plug flow reactor, batteries or cascades of stirred tank reactors are employed. These reactor networks consist of a number of stirred tank reactors connected in series with the effluent from one reactor serving as the input to the next. Although the concentration is uniform within any one reactor, there is a progressive decrease in reactant concentration as one moves from the initial tank to the final tank in the cascade, i.e. there are stepwise variations in composition as one moves from one CSTR to another. Figure 11.1 illustrates the stepwise variations typical of reactor cascades' for different numbers of CSTR's in series.
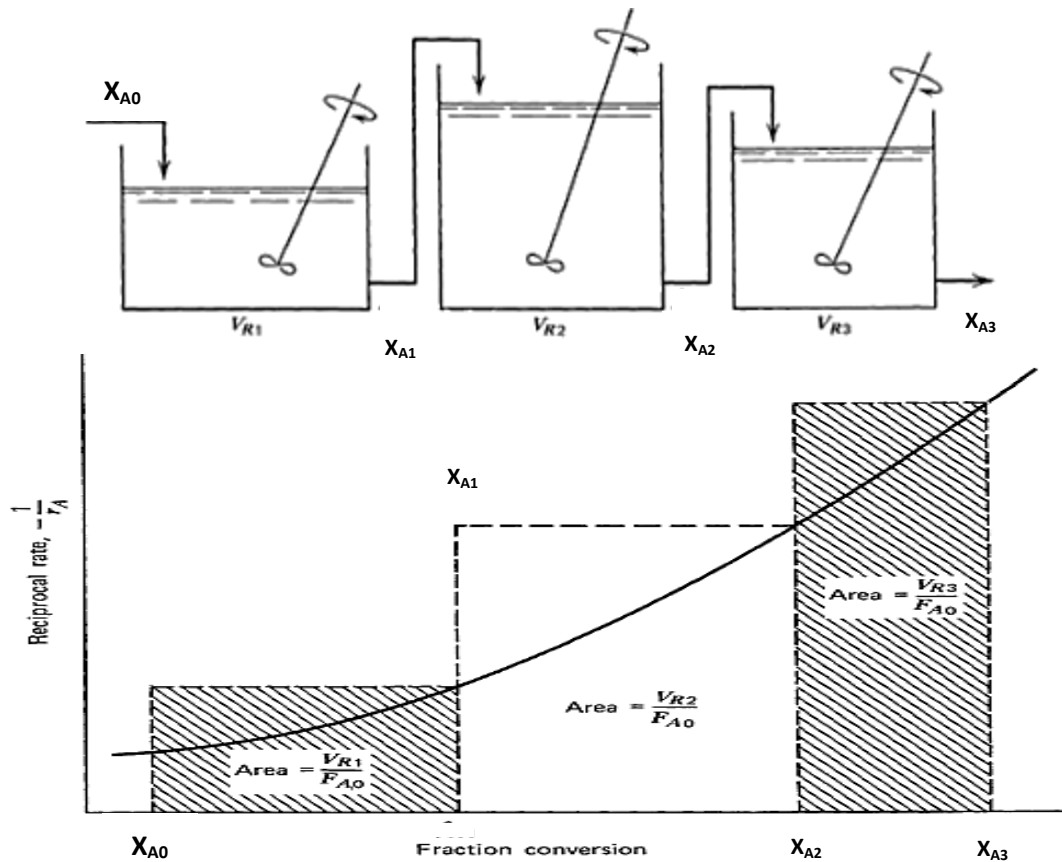


Figure 11.1. Schematic representation of reciprocal rate curve for cascade of three arbitrary size CSTR's.

In the general non-isothermal case one will also encounter stepwise variations in temperature as one moves from one reactor to another in the cascade. Each of the individual CSTR's that make up the cascade can be analyzed using the techniques and concepts developed in previous lectures. Consider the cascade of ideal CSTR's shown in Figure 11.2.
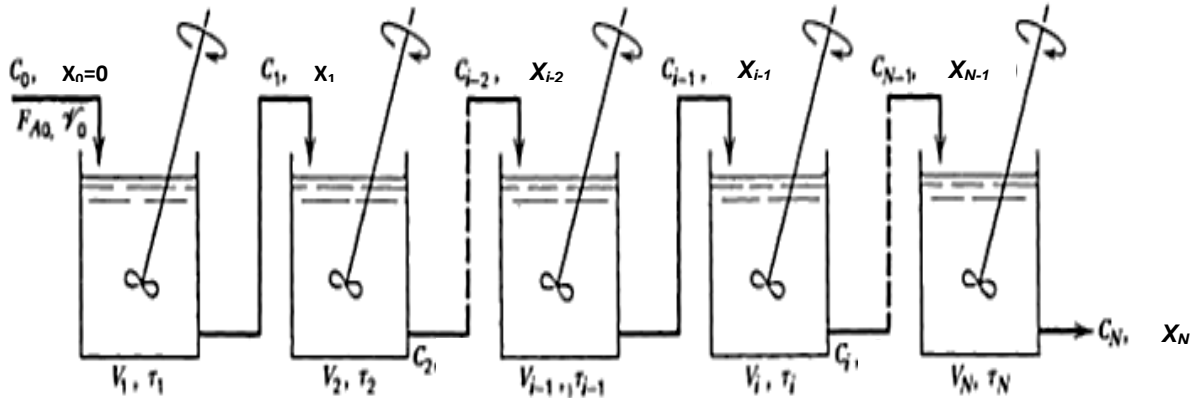


**Fig. 11.2**. A cascade of N CSTR's in series

For any individual reactor denoted by the subscript $i$ the basic design equation developed earlier is appropriate:

$$\frac{V_{Ri}}{F_{A0}} = \frac{X_{A\,out} - X_{A\,in}}{-r_{AF}} = \frac{X_{A\,i} - X_{A\,i-1}}{-r_{A\,i}} \qquad (11.1)$$

where the subscripts used are as indicated in the figure and ($-r_{Ai}$) is the rate of disappearance of species $A$ in reactor $i$. We should also note that the conditions within any individual reactor are not influenced by what happens in reactors downstream. The conditions of the inlet stream and those prevailing within the reactor itself are the only variables that influence reactor performance under either steady-state or transient conditions. Equation (11.1) could be rewritten in terms of the reactor space time as follows where both equations 11.1 and 11.2 are generally applicable to all types of CSTR cascades

$$\tau_i = \frac{V_{Ri}}{v_0} = C_{A0} \frac{X_{A\,i} - X_{A(\,i-1)}}{-r_{A\,i}} \qquad (11.2)$$

Or equation 11.2 could be in the following most appropriate form:

$$\tau_i = \frac{V_{Ri}}{v_0} = \frac{C_{A(i-1)} - C_{Ai}}{-r_{Ai}} \qquad (11.3)$$

Or,

$$-r_{Ai} = \frac{C_{A(i-1)} - C_{Ai}}{\tau_i} \qquad (11.4)$$

Where:

$$X_{Ai} = \frac{C_{A0} - C_{Ai}}{C_{A0}} \qquad and \qquad X_{A(i-1)} = \frac{C_{A0} - C_{A(i-1)}}{C_{A0}}$$

As an example for an aqueous first-order reaction, equation 11.3 could be as

$$\tau_i = \frac{C_{A(i-1)} - C_{Ai}}{kC_{Ai}} \qquad (11.5)$$

Or

$$\frac{C_{A(i-1)}}{C_{Ai}} = 1 + k\tau_i \qquad (11.6)$$

Where the space time is identical for all equal-size CSTRs connected in series. Therefore,

$$\frac{C_{A0}}{C_{AN}} = \frac{1}{1 - X_{AN}} = (1 + k\tau_i)^N \qquad (11.7)$$

Or,

$$\frac{C_{AN}}{C_{A0}} = 1 - X_{AN} = \frac{1}{(1 + k\tau_i)^N} \qquad (11.8)$$

Or,

$$\tau_N = N\tau_i = \frac{N}{k}\left[\left(\frac{C_{A0}}{C_{AN}}\right)^{1/N} - 1\right] \qquad (11.9)$$

For infinity numbers of CSTR, i.e. $N \to \infty$, they seem to be as a single PFR then

$$\tau_p = \frac{1}{k} \ln \frac{C_{A0}}{C_A} \qquad\qquad (11.10)$$

The number of CSTRs and the intermediate concentration could be estimated using graphical approach. In graphical terms this equation indicates that a plot of $(- r_{Ai})$ versus $C_{Ai}$ is a straight line with a slope $(-1/\tau_i)$ that cuts the abscissa at $C_{A(i-1)}$.

Consider the three ideal CSTR's shown in Figure 11.3. The characteristic space times of these reactors may differ widely. Note that the direction of flow is from right to left. The first step in the analysis requires the preparation of a plot of reaction rate versus reactant concentration based on experimental data (i.e., the generation of a graphical representation of the rate equation). It is presented as curve **I** in Figure 11.3.
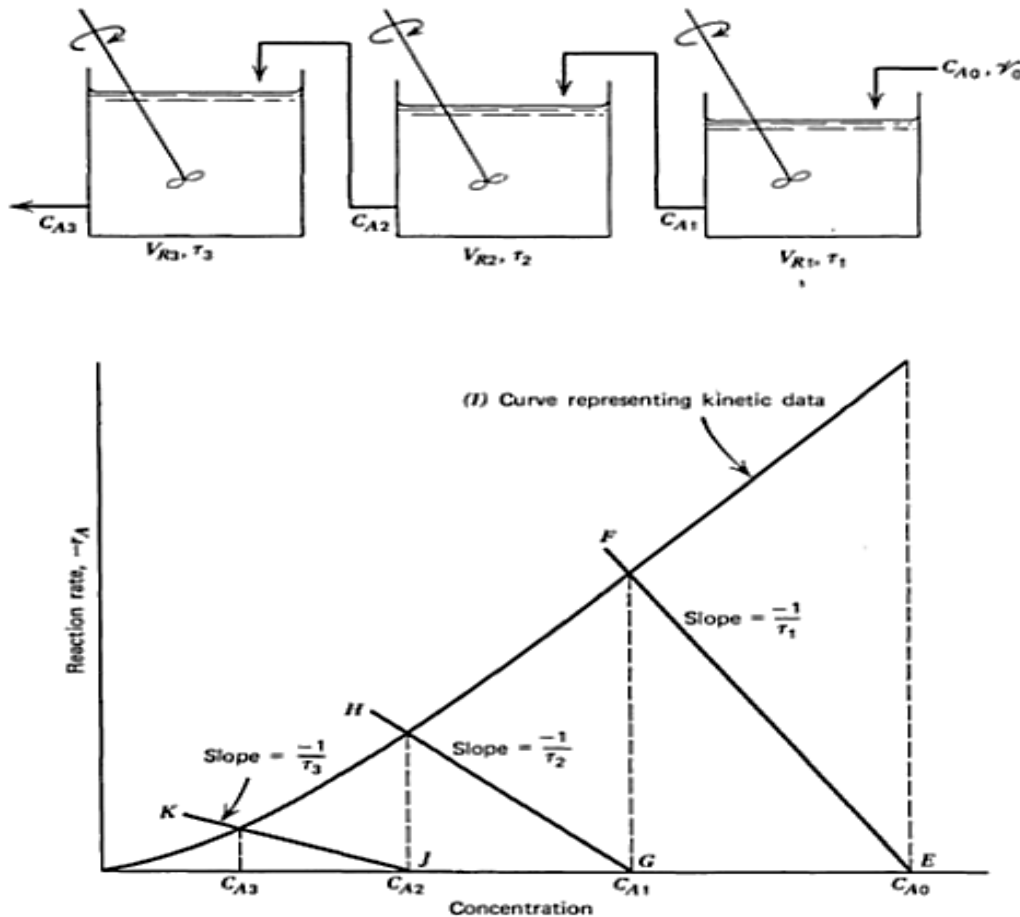


**Fig. 11.3**. Plots used in the graphical analysis of cascades of ideal CSTR's.

Now, for the first reactor, equation 11.4 becomes

$$-r_{A1} = \frac{C_{A0} - C_{A1}}{\tau_1} \qquad (\mathbf{11.11})$$

For a specified inlet concentration this equation indicates that a plot of $-r_1$ versus $C_{A1}$ is a straight line with slope $(\mathbf{-1/\tau_1})$ that passes through the point where the ordinate is zero and the abscissa is $C_{A0}$. However, only the point of intersection of the straight line with the curve representing the rate equation has physical meaning. It represents the conditions that must prevail in the first reactor. Hence the solution to the first part of our problem consists of drawing straight line $\textbf{\textit{EF}}$ through point $\textbf{\textit{E}}$ with slope $(\mathbf{-1/\tau_1})$. $C_{A1}$ is the point of intersection of this straight line with curve I, as shown in Figure 11.3.

Now that $C_{A1}$ is known, it is evident that a similar process can be used to find $C_{A2}$ because, in this case, equation 11.4 becomes

$$-r_{A2} = \frac{C_{A1} - C_{A2}}{\tau_2} \qquad (\mathbf{11.12})$$

Thus we may construct straight line $\textbf{\textit{GH}}$ in Figure 11.3, by drawing a line of slope $(\mathbf{-1/\tau_2})$ through the point with an ordinate of zero and an abscissa of $C_{A1}$. The intersection of this line with curve $\textbf{\textit{I}}$ gives us the effluent concentration from the second reactor. This same procedure can be repeated for any other reactors that may be part of the cascade. The straight line $\textbf{\textit{JK}}$ was constructed in this fashion for the present case.

The similar CSTRs in size having the same slope of $(\mathbf{1/\tau})$, which means that

$$-\frac{1}{\tau_1} = -\frac{1}{\tau_2} = -\frac{1}{\tau_3} = \cdots = -\frac{1}{\tau_N}$$

But, for different size of CSTRS this relation is inapplicable because each reactor has its own space time,

$$-\frac{1}{\tau_1} \neq -\frac{1}{\tau_2} \neq -\frac{1}{\tau_3} \neq \cdots \neq -\frac{1}{\tau_N}$$

## Chemical Reactor Design:

## Design for single reaction

## Stirred Tank Reactors in Series

Now, for second order reactions, the procedure is similar to that to that of a first-order reaction:

*Case 1:*

$$-r_A = k \, C_A^2 \qquad where \quad C_{A0} = C_{B0}$$

$$\frac{C_{A(i-1)}}{C_{Ai}} = 1 + k \, \tau \, C_{Ai} \qquad (12.1)$$

*Case 2:*

$$-r_A = k \, C_A C_B \qquad where \quad C_{A0} \neq C_{B0}$$

$$\frac{C_{A(i-1)}}{C_{Ai}} = 1 + k \, (E + C_{Ai})\tau \qquad where \quad E = C_{B0} - C_{A0} \qquad (12.2)$$

## Mixed flow reactors of different sizes in series

The following issues should be taken into consideration when different sizes of CSTRs are connected in series:

- If the order of reaction (**n=1**) (either irreversible or reversible with first-order kinetics in both directions), any way of the arrangement of CSTRs is acceptable regardless the difference of their sizes. But the optimum arrangement of CSTRs is that when equal-sized CSTRs should be used, i.e. $\tau_1 = \tau_2 = \cdots = \tau_N$.
- If the order of reaction (**n>1**), the smaller CSTR should precede the larger. (*a concave curve of (1/r$_i$) vs. X$_i$*)
- If the order of reaction (**n<1**), the larger CSTR should precede the smaller. (*a convex curve of (1/r$_i$) vs. X$_i$*)

- If the order of reaction (**n=2**) and whether the CSTRs sizes are similar or different, the number of these reactors and the intermediate concentrations of materials could be obtained using analytical and/or graphical methods. The analytical method proceeds depending on the material balance for any compound around each reactor. While the graphical method could be achieved depending on data given such as the rate of reaction and the conversion.

- If the sizes of CSTRs are known then the final concentration could be obtained graphically.

   - If the sizes of CSTRs are given and the optimum design of these reactors are required, the lowest total size of these reactors is preferred. For example, for a simple second-order reaction where 99% conversion is desired, the minimum total volume required is only about 3% less than if equal volume tanks had been used. For 99.9% conversion the difference is only about 4%. Generally, the savings associated with this small reduction in total volume requirements would scarcely be adequate to cover the extra costs of engineering, installing, and maintaining two tanks of different sizes. The argument for uniformity in tank sizes becomes even stronger when cascades composed of more than two reactors are considered. Consequently, except in those rare cases where there are compelling reasons to the contrary, the reactor designer tends to employ multiple identically sized CSTR's in working up design specifications. However, it may be advantageous to run the various CSTR's at different temperatures

Consider the two cascade configurations shown in Figure 12.1. For the first reactor, the performance equation becomes

$$\frac{V_{R1}}{F_{A0}} = \frac{X_{A1} - X_{A0}}{-r_{A1}} \qquad (12.3)$$

while, for the second, it becomes

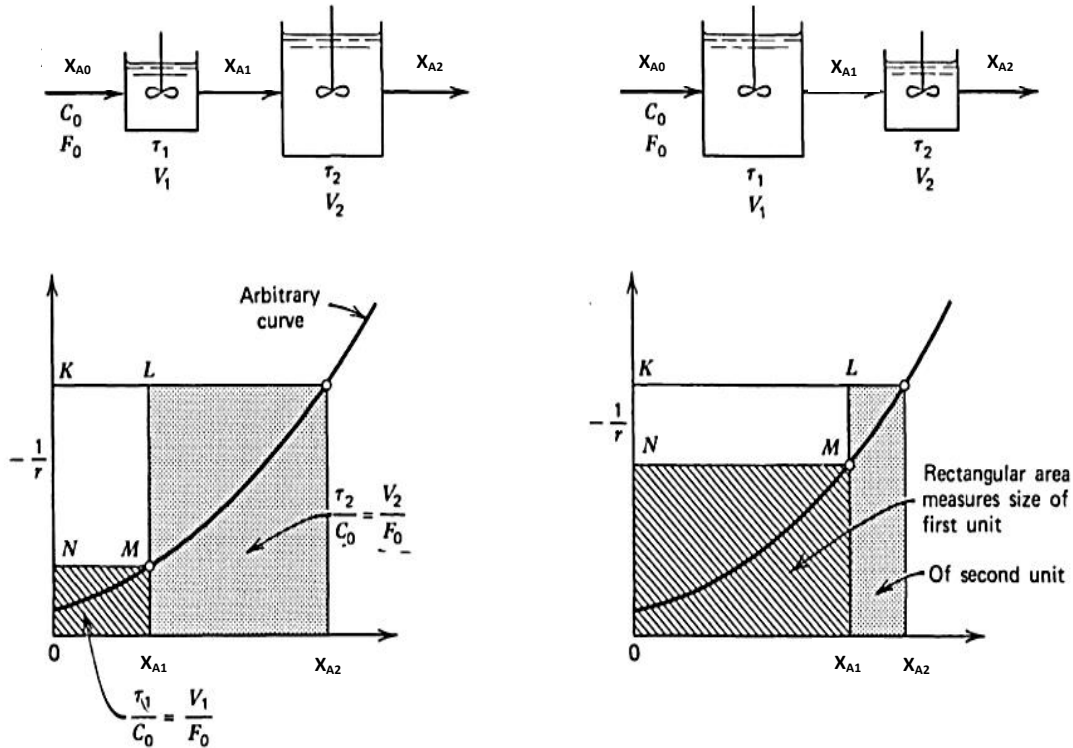$$\frac{V_{R2}}{F_{A0}} = \frac{X_{A2} - X_{A1}}{-r_{A2}} \qquad (12.4)$$

**Fig. 12.1.** Graphical representation of variables for two CSTR's.

The relations indicated by these two equations are shown graphically in Figure 12.1 for two alternative configurations. In both cases the cascade operates between the same initial and final conversion levels. The same arbitrary reaction rate expression is appropriate in both instances. As the composition of the effluent from the first reactor is changed, the relative size requirements for the two individual reactors also change, as does the total volume required. The size ratio is determined by the ratio of the two shaded areas and the total volume by the sum of these areas. The total reactor volume is minimized when rectangle **KLMN** is made as large as possible so the problem of selecting the optimum sizes of the two reactor components in this sense reduces to that of selecting point $X_i$ so that the area of rectangle **KLMN** is maximized (Fig. 12.2).
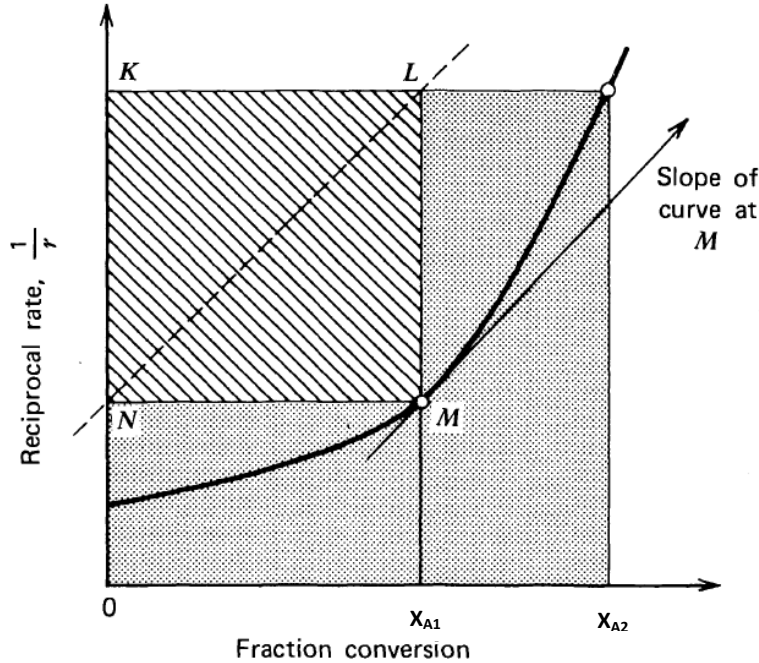
**Fig. 12.2.** Maximization of rectangles applied to find the optimum intermediate conversion and optimum sizes of two CSTR's in series.

For reaction rate expressions of the *n*th-order form it can be shown that there is always one and only one point that minimizes the total volume when *n > 0*. This situation is obtained when the intermediate fraction conversion $X_{A1}$ is selected so that the slope of the curve representing the reaction rate expression at this conversion level is equal to the slope of the diagonal of rectangle *KLMN*, as shown in Figure 12.2.

When CSTRs are connected in a parallel manner, the conversion obtained and, consequently, the space time will be identical of all branches as proved in the following example.

*Example 12.1.* A CSTR having a volume of 100 liter had been connected to a 400 liter CSTR where the initial volumetric flow rate is 1000 lit./min. Find the individual values of the volumetric flow rates and the space time of each branch.

*Ans.*:

$$\frac{v_i}{v_0} = \frac{V_i}{V_t} \quad \rightarrow \quad v_i = v_0 \frac{V_i}{V_t}$$

$$v_1 = (1000)\frac{100}{(100+400)} = 200\frac{lit}{min}$$

$$v_2 = (1000)\frac{400}{(100+400)} = 800\frac{lit}{min}$$

$$\tau_i = \frac{V_i}{v_i}$$

$$\tau_1 = \frac{V_1}{v_1} = \frac{100}{200} = 0.5\ min$$

$$\tau_2 = \frac{V_2}{v_2} = \frac{400}{800} = 0.5\ min$$

As found that the space time was identical for both tanks.

**H.W. 12.1**. *Repeat Example 12.1 but the size of these reactors is equal as 100 liter for each one.*

## Chemical Reactor Design:

## Design for single reaction

## Reactors of different types in Series

To this point it has been shown, mainly by illustration, that the performance of a reactor depends on three factors:

(1) The kinetics of reaction, as described by the rate law; thus, the fractional conversion depends on the order of reaction.

(2) The characteristics of flow through the vessel as described by the residence time; thus, for given kinetics, the fractional conversion in a PFR is different from that in a CSTR.

(3) The nature of mixing of fluid elements during flow through the vessel. In the CSTR, mixing of fluid elements of all ages takes place "early''-at the point of entry. While in the PFR, mixing takes place "late''-in fact, not at all (in the axial direction).

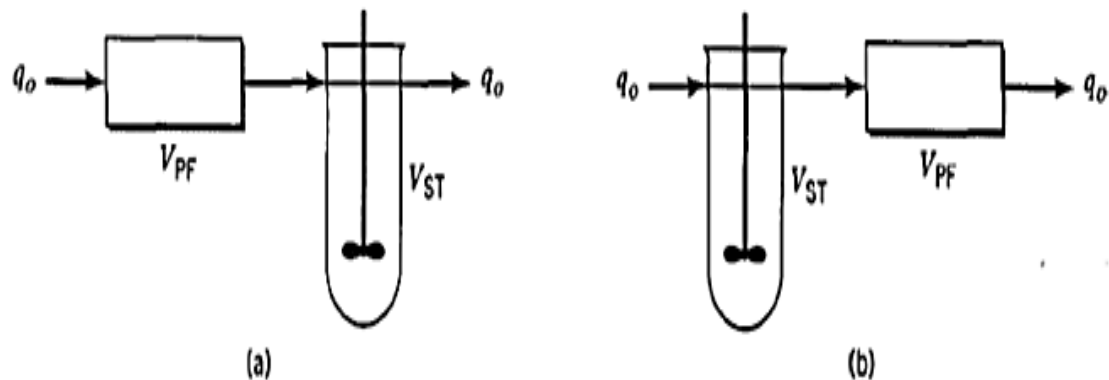The following figure (13.1) explore the consequences of such series arrangements:
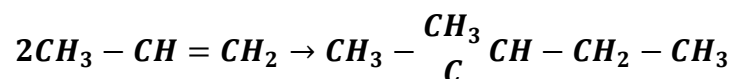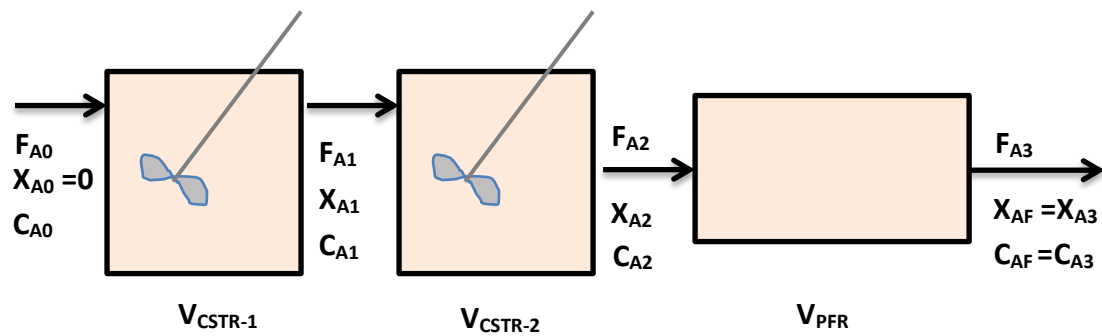


**Fig. 13.1.** Flow diagrams for Example 17-5: (a) PFR followed by CSTR; (b) CSTR followed by PFR

An example of this application in industries is  the dimerization of propylene into isohexanes as follows:

$$2CH_3 - CH = CH_2 \rightarrow CH_3 - \overset{CH_3}{\underset{C}{}} CH - CH_2 - CH_3$$
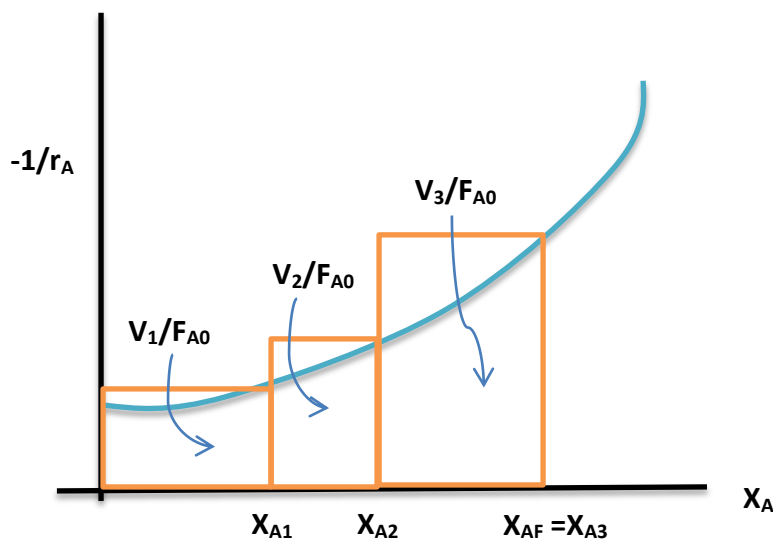
$$V_{CSTR-1} = \frac{F_{A0}X_1}{-r_{A1}}$$

$$V_{CSTR-2} = \frac{F_{A0}(X_2 - X_1)}{-r_{A2}}$$

$$V_{PFR} = \int_{X_2}^{X_3} \frac{F_{A0}}{-r_{A3}} dx$$

The corresponding reactors volumes for each of the three reactors can be found from the selected areas. Therefore, the overall and the intermediate conversions could be obtained.



***Example 13.1***. A compound (*A*) has a density of 1082 kg/m$^3$ is to be treated in a cascade of identical CSTRs of 2.65 m$^3$ size of each one. The initial concentration of (*A*) is 0.795 mol/lit with a flow rate of 1970 kg/hr. The order of this reaction was a

first-order with a rate constant of $0.158$ hr$^{-1}$. Estimate the number of CSTRs required to achieve a conversion of 85%.

*Ans.*:

$$\frac{C_{AN}}{C_{A0}} = 1 - X_{AN} = \frac{1}{(1 + k\tau_i)^N} \qquad (11.8)$$

$$\tau_i = \frac{V_i}{v_0} = \frac{V_i\,\rho_A}{F_{A0}} = \frac{2.65 \times 1082}{1970} = 1.46\ hr$$

$$1 - 0.85 = \frac{1}{(1 + 0.158 \times 1.46)^N}$$

$$N = 9.17 \approx 10\ CSTRs$$

*Example 13.2*. The isomerization of butane ($n\text{-}C_4H_{10} \leftrightarrows i\text{-}C_4H_{10}$) was carried out adiabatically in the liquid phase using three different reactors in series where the first and the last reactors are CSTR-type and the intermediate one is a PFR as shown in the figure and the table attached. Calculate the volume of each reactor for an entering molar flow rate of n-butane of 50 kmol/hr.
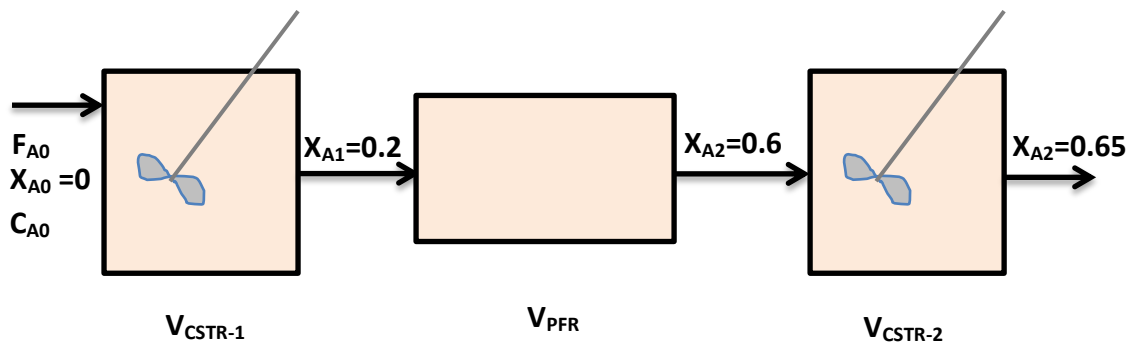


| $X_A$ | 0.0 | 0.2 | 0.4 | 0.6 | 0.65 |
|---|---|---|---|---|---|
| $-r_A$ (kmol/m$^3$.h) | 39 | 53 | 59 | 38 | 25 |

*Ans*.:

Calculate ($F_{A0}$/-$r_A$) for each value of the fractional conversion as follows:

| $X_A$ | 0.0 | 0.2 | 0.4 | 0.6 | 0.65 |
|---|---|---|---|---|---|
| -$r_A$ (kmol/m$^3$.h) | 39 | 53 | 59 | 38 | 25 |
| ($F_{A0}$/-$r_A$) (m$^3$) | 1.28 | 0.94 | 0.85 | 1.32 | 2.0 |

For the first CSTR in the case of $X_{A1} = 0.2$

$$V_{CSTR-1} = \frac{F_{A0}X_{A1}}{-r_A} = 0.94 \times 0.2 = 0.188 \ m^3$$

For the PFR, Simpson's rule could be used (three points formula)

$$V_{PFR} = \int_{0.2}^{0.6} \frac{F_{A0}}{-r_A} dx$$

$$\Delta x = \frac{0.6 - 0.2}{2} = 0.2 \ ; \ X_{A1} = 0.2; \ X_{A2} = 0.4; \ X_{A3} = 0.6$$

$$V_{PFR} = \frac{\Delta x}{3}\left[\left(\frac{F_{A0}}{-r_A}\right)_{0.2} + 4\left(\frac{F_{A0}}{-r_A}\right)_{0.4} + \left(\frac{F_{A0}}{-r_A}\right)_{0.6}\right]$$

$$V_{PFR} = \frac{0.2}{3}[0.94 + 4(0.85) + 1.32] = 0.38 \ m^3$$

For the second CSTR,

$$In - Out + Generation = 0$$

$$F_{A2} - F_{A3} + r_A V_{CSTR-3} = 0$$

$$V_{CSTR-3} = \frac{F_{A2} - F_{A3}}{-r_A} = \frac{F_{A0}(1 - X_2) - F_{A0}(1 - X_3)}{-r_A}$$

$$V_{CSTR-3} = \frac{F_{A0}}{-r_A}(X_3 - X_2) = 2 \times (0.65 - 0.6) = 0.10 \ m^3$$

---

**H.W. 13.1.** Draw ($\frac{F_{A0}}{-r_A}$) vs. the fractional conversion to find the volume of each reactor.

---

***Example 13.3***. Which reactor should go first to give the highest overall conversion? Should it be a PFR followed by a CSTR, or two CSTRs, the PFR, or …?

***Ans*.:**

It depends on the shape of [(1/-r$_A$) vs. X$_A$] and on the relative reactor sizes. Temperature, pressure and initial reactant concentration are extremely important in this object. If the relation of the rate of reaction as a function of the fractional conversion is known, one can design a variety of reactors or a combination of reactors.

***Example 13.4***. A chain of four equal CSTR in series is used to carry out the isothermal first-order decomposition of *A* in solution. Under normal operating conditions, the concentration of *A* in the stream leaving the plant is 5% of that entering the plant. Due to a mal function of the first reactor, it is removed from the chain and the feed had been entered to the second reactor. What will be the conversion if the feed rate is not changed.

***Ans*.:**

Since we have equal-size CSTRs, Eq. (11.8) could be used:

$$\frac{C_{AN}}{C_{A0}} = 1 - X_{AN} = \frac{1}{(1 + k\tau_i)^N} \qquad (\mathbf{11.8})$$

As given that the concentration of A in the stream leaving the plant is 5% of the initial concentration, so:

$$C_{AN} = 0.05\, C_{A0}$$

$$\frac{C_{AN}}{C_{A0}} = 0.05$$

For **N=4**,

$$0.05 = \frac{1}{(1 + k\tau)^4}$$

$$4 \log (1 + k\tau) = \log 20$$

$$k\tau = 1.11$$

When the first CSTR is removed, **N=3**:

$$\frac{C_{AN}}{C_{A0}} = \frac{1}{(1 + k\tau_i)^N} \qquad (11.8)$$

$$\frac{C_{AN}}{C_{A0}} = \frac{1}{(1 + 1.11)^3}$$

$$\frac{C_{AN}}{C_{A0}} = 0.106 = 1 - X_{A3}$$

$$X_{A3} = 1 - 0.106 = 0.894$$

*Example 13.5*. Acetic anhydride is hydrolyzed using three CSTRs having the volumes of 1, 2, and 1.5 liter which are operated in series at $25^0$C. The volumetric feed flows through this system is 400 cm$^3$/min. The rate constant of this reaction is 0.158 min$^{-1}$. Estimate the final conversion of this battery of CSTRs.

*Ans*.:

Since this system consisting of different sizes of CSTRs, therefore, material balance around each reactor should be proceeded as follows:
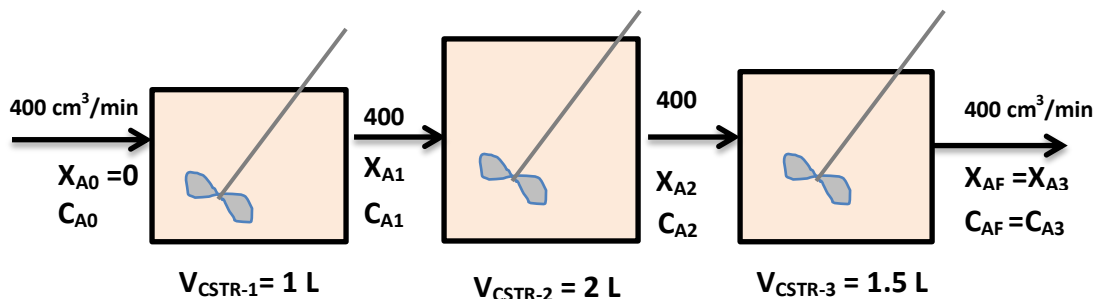


$$v_0 = 400 \frac{cm^3}{min} = 0.4 \frac{lit}{min}$$

$$\tau_i = \frac{V_{Ri}}{v_0} = \frac{V_{Ri}}{0.4}$$

$$\tau_1 = \frac{1}{0.4} = 2.5 \; min \;\; ; \; \tau_2 = \frac{2}{0.4} = 5 \; min \;\; ; \; \tau_3 = \frac{1.5}{0.4} = 3.75 \; min$$

For CSTR No. 1:

$$\tau_1 = \frac{C_{A0} - C_{A1}}{-r_{A1}}$$

$$\tau_1 = \frac{C_{A0} - C_{A1}}{k \, C_{A1}}$$

$$2.5 = \frac{C_{A0} - C_{A1}}{0.158 \, C_{A1}}$$

$$0.395 \, C_{A1} = C_{A0} - C_{A1}$$

$$C_{A1} = 0.717 \, C_{A0}$$

$$0.717 \, C_{A0} = C_{A0}(1 - X_{A1})$$

$$X_{A1} = 0.283$$

For CSTR No. 2:

$$\tau_2 = \frac{C_{A1} - C_{A2}}{-r_{A2}}$$

$$5 = \frac{0.717 \, C_{A0} - C_{A2}}{0.158 \, C_{A2}}$$

$$0.790 \, C_{A2} = 0.717 \, C_{A0} - C_{A2}$$

$$C_{A2} = 0.40 \, C_{A0}$$

$$0.40 \, C_{A0} = C_{A0}(1 - X_{A2})$$

$$X_{A2} = 0.60$$

7

For CSTR No. 3:

$$\tau_3 = \frac{C_{A2} - C_{A3}}{-r_{A3}}$$

$$3.75 = \frac{0.40\ C_{A0} - C_{A3}}{0.158\ C_{A3}}$$

$$0.593\ C_{A3} = 0.40\ C_{A0} - C_{A3}$$

$$C_{A3} = 0.251\ C_{A0}$$

$$0.251\ C_{A0} = C_{A0}(1 - X_{A3})$$

$$X_{A3} = 0.749$$

Now, we could summarized the results obtained in a table for a comparison as follows:

| No. of CSTR | $V_{CSTR\text{-}i}$ (liter) | $\tau_i$ (min) | $X_{Ai}$ (%) |
|:---:|:---:|:---:|:---:|
| 1 | 1 | 2.5 | 28.3 |
| 2 | 2 | 5 | 60.0 |
| 3 | 1.5 | 3.75 | 74.9 |

**H.W. 13.2.** *For Example 13.5, change the third CSTR using another size (1, 2, 2.5, 3 liter) to find the space time of the third CSTR and the final conversion.*

**H.W. 13.3.** Repeat Example 13.5 but the arrangement of CSTRs will be as 2, 1.5, 1 liter then 2, 1, 1.5 liter. Tabulate the obtained results.
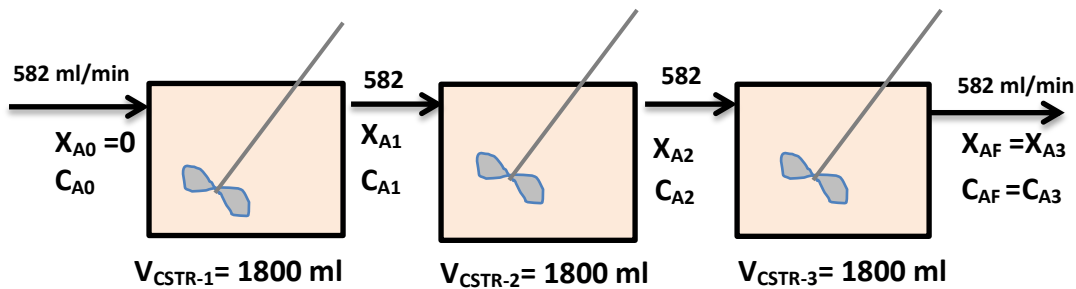
## Chemical Reactor Design:

## Design for single reaction

***Example 15.1***. Acetic anhydride is to be hydrolyzed using three equal-sizes CSTRs (*$V_{Ri}$= 1800 ml*) operating in series where the volumetric flow rate is *582 ml/min* and the rate of reaction is expressed as *(-$r_A$=0.1558 $C_A$)*. Estimate the conversion in each reactor of the CSTRs battery.

***Ans*.**:

This system having equal-size of CSTRs as shown in the following figure:



$$V_{Ri} = V_{R1} = V_{R2} = V_{R3} = 1800\ ml$$

$$v_0 = 582\ \frac{ml}{min}$$

$$\tau_i = \frac{V_{Ri}}{v_0} = \frac{1800}{582} = 3.092\ min$$

$$\tau_i = \tau_1 = \tau_2 = \tau_3 = 3.092\ min$$

$$\frac{C_{A\,N}}{C_{A0}} = 1 - X_{A\,N} = \frac{1}{(1 + k\tau_i)^N} \qquad (11.8)$$

For CSTR No. 1 (*N=1*):

$$\frac{C_{A1}}{C_{A0}} = 1 - X_{A1} = \frac{1}{(1 + 0.1558 \times 3.092)^1}$$

$$X_{A1} = 1 - \frac{C_{A1}}{C_{A0}} = 1 - 0.675 = 0.325$$

For CSTR No. 2 (*N=2*):

$$\frac{C_{A2}}{C_{A0}} = 1 - X_{A2} = \frac{1}{(1 + 0.1558 \times 3.092)^2}$$

$$X_{A2} = 1 - \frac{C_{A2}}{C_{A0}} = 1 - 0.455 = 0.544$$

For CSTR No. 3 (*N=3*):

$$\frac{C_{A3}}{C_{A0}} = 1 - X_{A3} = \frac{1}{(1 + 0.1558 \times 3.092)^3}$$

$$X_{A3} = 1 - \frac{C_{A3}}{C_{A0}} = 1 - 0.307 = 0.693$$

Now, we could summarized the results obtained in a table for a comparison as follows:

| No. of CSTR | $V_{\text{CSTR-i}}$ (ml) | $\tau_i$ (*min*) | $X_{Ai}$ (%) |
|:---:|:---:|:---:|:---:|
| 1 | 1800 | 3.092 | 32.50 |
| 2 | 1800 | 3.092 | 54.40 |
| 3 | 1800 | 3.092 | 69.30 |

*Example 15.2*. A first-order reaction is proceeds in CSTR. This reactor of a volume of *27 m³* had been performed to obtain **90%** conversion of the limiting reactant. Find the volumetric flow rate flowing through this reactor and for the following cases when (*N= 2, 3, 4, and 5*) are connected in series assuming that the rate constant is equal for all these cases (*k=1 min⁻¹*).

**Ans.:**

$$\tau_N = N\tau_i = \frac{N}{k}\left[\left(\frac{C_{A0}}{C_{AN}}\right)^{1/N} - 1\right] \qquad (11.9)$$

$$C_{AN} = C_{A0}(1 - X_{AN})$$

$$\frac{C_{A0}}{C_{AN}} = \frac{1}{1 - X_{AN}} = \frac{1}{1 - 0.9} = 10$$

$$\tau_N = \frac{N}{1}\left[(10)^{1/N} - 1\right]$$

2

| N | $\tau_i$ $(min)$ | $v_0 = \dfrac{V_{Ri}}{\tau_i} = \dfrac{m^3}{min}$ |
|---|---|---|
| 1 | 9 | 3 |
| 2 | 4.325 | 6.24 |
| 3 | | |
| 4 | | |
| 5 | | |

***Example 15.3***. A series of CSTRs each of volume ($26.5 \ m^3$) have been employed to polymerized Styrene (A) and Butadiene (B) with initial concentrations of **0.795** and **3.55 mol/lit**, respectively, in a second order reaction ($-r_A = kC_A C_B$) with a rate constant of ($k = 10^{-5} \ lit. \ mol^{-1}.sec^{-1}$). If the volumetric flow rate is **22.6 $m^3$/hr**, find the total number of reactors required to achieve **85%** conversion of the limiting reactant.

*Ans.*:

$$\tau_i = \frac{V_{Ri}}{v_0} = \frac{26.5}{22.6} = 1.172 \ hr = 4222 \ sec$$

$$\frac{C_{A(i-1)}}{C_{A i}} = 1 + k \ (E + C_{A i}) \tau_i \qquad where \ \ E = C_{B0} - C_{A0} \qquad (12.2)$$

Or,

$$\frac{C_{Ai}}{C_{A(i-1)}} = \frac{1}{1 + k \ \tau_i (E + C_{A i})}$$

$$E = C_{B0} - C_{A0} = 3.550 - 0.795 = 2.755$$

$$C_{Ai}[1 + k \ \tau_i (E + C_{A i})] = C_{A(i-1)}$$

$$C_{Ai}^2 + \left(\frac{1 + k \ \tau_i E}{k \ \tau_i}\right) C_{Ai} - \frac{C_{A(i-1)}}{k \ \tau_i} = 0$$

$$C_{Ai}^2 + \left(\frac{1 + 4222 \times 10^{-5} \times 2.755}{4222 \times 10^{-5}}\right) C_{Ai} - \frac{C_{A(i-1)}}{4222 \times 10^{-5}} = 0$$

$$C_{Ai}^2 + 26.44 \ C_{Ai} - 23.68 \ C_{A(i-1)} = 0$$

$$C_{Ai} = \frac{-26.44 \mp \sqrt{(26.44)^2 + 4(23.68)C_{A(i-1)}}}{2}$$

For CSTR No. 1 (*N=1*):

$$C_{A1} = \frac{-26.44 \mp \sqrt{(26.44)^2 + 4(23.68)(0.795)}}{2} = 0.693$$

$$X_{A1} = 1 - \frac{C_{A1}}{C_{A0}} = 1 - \frac{0.693}{0.795} = 0.128 \ < 0.85$$

For CSTR No. 2 (*N=2*):

$$C_{A2} = \frac{-26.44 \mp \sqrt{(26.44)^2 + 4(23.68)(0.693)}}{2} = 0.666$$

$$X_{A2} = 1 - \frac{C_{A2}}{C_{A0}} = 1 - \frac{0.666}{0.795} = 0.236 \ < 0.85$$

This procedure is continued until the conversion reaches 85%. Listing the results obtained in a table as follows:

| N | $X_{Ai}$ | N | $X_{Ai}$ |
|---|---|---|---|
| 1 | 0.128 | | |
| 2 | 0.236 | | |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |
| 7 | | | |
| | | | |
| | | | |
| | | | |
| | | | |

*Example 15.4*. Two CSTRS are connected in series where the second reactor having a *double size* of the first reactor. The space time in the first reactor is *96 sec* and the initial concentration entering to it is *1 mol/lit* which decreased by *50%* and *75%* in the second reactor. Find the rate equation proceeded in this battery.

Ans.:

$$\tau_i = \frac{V_{Ri}}{v_0}$$

$$\tau_1 = \frac{V_{R1}}{v_0}$$

$$\tau_2 = \frac{V_{R2}}{v_0} = \frac{2\,V_{R1}}{v_0} = 2\,\tau_1 = 2 \times 96 = 192\ sec$$

$$-r_{A1} = \frac{C_{A0} - C_{A1}}{\tau_1} = \frac{1 - 0.5}{96} = 5.2 \times 10^{-3}\ \frac{mol}{lit.sec}$$

$$-r_{A2} = \frac{C_{A1} - C_{A2}}{\tau_2} = \frac{0.5 - 0.25}{192} = 1.3 \times 10^{-3}\ \frac{mol}{lit.sec}$$

$$-r_A = kC_A^n$$

$$ln(-r_A) = ln\,k + n\,ln\,C_A$$

$$ln(-r_{A1}) = ln\,k + n\,ln\,C_{A1}$$

$$ln(-r_{A2}) = ln\,k + n\,ln\,C_{A2}$$

$$n = \frac{ln\frac{-r_{A1}}{-r_{A2}}}{ln\frac{C_{A1}}{C_{A2}}} = \frac{ln\frac{5.2 \times 10^{-3}}{1.3 \times 10^{-3}}}{ln\frac{0.5}{0.25}} = 2$$

$$k = \frac{-r_{A1}}{C_{A1}^2} = \frac{5.2 \times 10^{-3}}{0.5^2} = 0.0208$$

So, the rate equation is
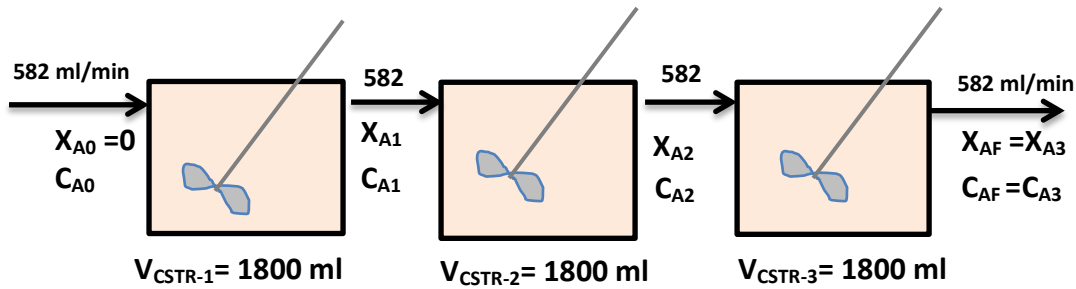
$$-r_A = 0.0208\ C_A^2$$

## Chemical Reactor Design:

## Design for single reaction

***Example 15.1***. Acetic anhydride is to be hydrolyzed using three equal-sizes CSTRs (*$V_{Ri}$= 1800 ml*) operating in series where the volumetric flow rate is *582 ml/min* and the rate of reaction is expressed as *($-r_A$=0.1558 $C_A$)*. Estimate the conversion in each reactor of the CSTRs battery.

***Ans*.:**

This system having equal-size of CSTRs as shown in the following figure:



$$V_{Ri} = V_{R1} = V_{R2} = V_{R3} = 1800 \; ml$$

$$v_0 = 582 \frac{ml}{min}$$

$$\tau_i = \frac{V_{Ri}}{v_0} = \frac{1800}{582} = 3.092 \; min$$

$$\tau_i = \tau_1 = \tau_2 = \tau_3 = 3.092 \; min$$

$$\frac{C_{AN}}{C_{A0}} = 1 - X_{AN} = \frac{1}{(1 + k\tau_i)^N} \qquad (11.8)$$

For CSTR No. 1 (*N=1*):

$$\frac{C_{A1}}{C_{A0}} = 1 - X_{A1} = \frac{1}{(1 + 0.1558 \times 3.092)^1}$$

$$X_{A1} = 1 - \frac{C_{A1}}{C_{A0}} = 1 - 0.675 = 0.325$$

For CSTR No. 2 (*N=2*):

$$\frac{C_{A2}}{C_{A0}} = 1 - X_{A2} = \frac{1}{(1 + 0.1558 \times 3.092)^2}$$

$$X_{A2} = 1 - \frac{C_{A2}}{C_{A0}} = 1 - 0.455 = 0.544$$

For CSTR No. 3 (*N=3*):

$$\frac{C_{A3}}{C_{A0}} = 1 - X_{A3} = \frac{1}{(1 + 0.1558 \times 3.092)^3}$$

$$X_{A3} = 1 - \frac{C_{A3}}{C_{A0}} = 1 - 0.307 = 0.693$$

Now, we could summarized the results obtained in a table for a comparison as follows:

| No. of CSTR | $V_{CSTR-i}$ (ml) | $\tau_i$  (*min*) | $X_{Ai}$  (%) |
|:---:|:---:|:---:|:---:|
| 1 | 1800 | 3.092 | 32.50 |
| 2 | 1800 | 3.092 | 54.40 |
| 3 | 1800 | 3.092 | 69.30 |

***Example 15.2***. A first-order reaction is proceeds in CSTR. This reactor of a volume of *27 m³* had been performed to obtain **90%** conversion of the limiting reactant. Find the volumetric flow rate flowing through this reactor and for the following cases when (*N= 2, 3, 4, and 5*) are connected in series assuming that the rate constant is equal for all these cases (*k=1 min⁻¹*).

**Ans.:**

$$\tau_N = N\tau_i = \frac{N}{k}\left[\left(\frac{C_{A0}}{C_{AN}}\right)^{1/N} - 1\right] \qquad (11.9)$$

$$C_{AN} = C_{A0}(1 - X_{AN})$$

$$\frac{C_{A0}}{C_{AN}} = \frac{1}{1 - X_{AN}} = \frac{1}{1 - 0.9} = 10$$

$$\tau_N = \frac{N}{1}\left[(10)^{1/N} - 1\right]$$

2

| N | $\tau_i$ (min) | $v_0 = \dfrac{V_{Ri}}{\tau_i} = \dfrac{m^3}{min}$ |
|:---:|:---:|:---:|
| 1 | 9 | 3 |
| 2 | 4.325 | 6.24 |
| 3 | | |
| 4 | | |
| 5 | | |

***Example 15.3***. A series of CSTRs each of volume (**26.5 $m^3$**) have been employed to polymerized Styrene (A) and Butadiene (B) with initial concentrations of **0.795** and **3.55 mol/lit**, respectively, in a second order reaction (**$-r_A = kC_AC_B$**) with a rate constant of (**$k=10^{-5}$ lit. $mol^{-1}.sec^{-1}$**). If the volumetric flow rate is **22.6 $m^3$/hr**, find the total number of reactors required to achieve **85%** conversion of the limiting reactant.

*Ans*.:

$$\tau_i = \frac{V_{Ri}}{v_0} = \frac{26.5}{22.6} = 1.172 \, hr = 4222 \, sec$$

$$\frac{C_{A(i-1)}}{C_{Ai}} = 1 + k \, (E + C_{Ai})\tau_i \qquad where \;\; E = C_{B0} - C_{A0} \qquad (12.2)$$

Or,

$$\frac{C_{Ai}}{C_{A(i-1)}} = \frac{1}{1 + k \, \tau_i(E + C_{Ai})}$$

$$E = C_{B0} - C_{A0} = 3.550 - 0.795 = 2.755$$

$$C_{Ai}[1 + k \, \tau_i(E + C_{Ai})] = C_{A(i-1)}$$

$$C_{Ai}^2 + \left(\frac{1 + k \, \tau_i E}{k \, \tau_i}\right)C_{Ai} - \frac{C_{A(i-1)}}{k \, \tau_i} = 0$$

$$C_{Ai}^2 + \left(\frac{1 + 4222 \times 10^{-5} \times 2.755}{4222 \times 10^{-5}}\right)C_{Ai} - \frac{C_{A(i-1)}}{4222 \times 10^{-5}} = 0$$

$$C_{Ai}^2 + 26.44 \, C_{Ai} - 23.68 \, C_{A(i-1)} = 0$$

$$C_{Ai} = \frac{-26.44 \mp \sqrt{(26.44)^2 + 4(23.68)C_{A(i-1)}}}{2}$$

For CSTR No. 1 ($N=1$):

$$C_{A1} = \frac{-26.44 \mp \sqrt{(26.44)^2 + 4(23.68)(0.795)}}{2} = 0.693$$

$$X_{A1} = 1 - \frac{C_{A1}}{C_{A0}} = 1 - \frac{0.693}{0.795} = 0.128 \ < 0.85$$

For CSTR No. 2 ($N=2$):

$$C_{A2} = \frac{-26.44 \mp \sqrt{(26.44)^2 + 4(23.68)(0.693)}}{2} = 0.666$$

$$X_{A2} = 1 - \frac{C_{A2}}{C_{A0}} = 1 - \frac{0.666}{0.795} = 0.236 \ < 0.85$$

This procedure is continued until the conversion reaches 85%. Listing the results obtained in a table as follows:

| N | $X_{Ai}$ | N | $X_{Ai}$ |
|---|---|---|---|
| 1 | 0.128 | | |
| 2 | 0.236 | | |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |
| 7 | | | |
| | | | |
| | | | |
| | | | |
| | | | |

*Example 15.4.* Two CSTRS are connected in series where the second reactor having a *double size* of the first reactor. The space time in the first reactor is *96 sec* and the initial concentration entering to it is *1 mol/lit* which decreased by *50%* and *75%* in the second reactor. Find the rate equation proceeded in this battery.

Ans.:

$$\tau_i = \frac{V_{Ri}}{v_0}$$

$$\tau_1 = \frac{V_{R1}}{v_0}$$

$$\tau_2 = \frac{V_{R2}}{v_0} = \frac{2\,V_{R1}}{v_0} = 2\,\tau_1 = 2 \times 96 = 192\ sec$$

$$-r_{A1} = \frac{C_{A0} - C_{A1}}{\tau_1} = \frac{1 - 0.5}{96} = 5.2 \times 10^{-3}\,\frac{mol}{lit.sec}$$

$$-r_{A2} = \frac{C_{A1} - C_{A2}}{\tau_2} = \frac{0.5 - 0.25}{192} = 1.3 \times 10^{-3}\,\frac{mol}{lit.sec}$$

$$-r_A = kC_A^n$$

$$ln(-r_A) = ln\,k + n\,ln\,C_A$$

$$ln(-r_{A1}) = ln\,k + n\,ln\,C_{A1}$$

$$ln(-r_{A2}) = ln\,k + n\,ln\,C_{A2}$$

$$n = \frac{ln\dfrac{-r_{A1}}{-r_{A2}}}{ln\dfrac{C_{A1}}{C_{A2}}} = \frac{ln\dfrac{5.2 \times 10^{-3}}{1.3 \times 10^{-3}}}{ln\dfrac{0.5}{0.25}} = 2$$

$$k = \frac{-r_{A1}}{C_{A1}^2} = \frac{5.2 \times 10^{-3}}{0.5^2} = 0.0208$$

So, the rate equation is

$$-r_A = 0.0208\,C_A^2$$