3

DESIGN FUNDAMENTALS

$10 - 22$

$32 - 96$

In this chapter three main subjects are discussed: (1) general aspects of reactor design, in preparation for design problems for specific reactors in later chapters, (2) mass and energy balances for the two ideal types of reactors, and (3) an introduction to deviations from these ideal types.

3-1 Reactor Design and Laboratory Rate Data

Designing a reactor entails determining the *size* of vessel needed to obtain the specified amounts of products and determining the temperature, pressure, and composition of the reaction mixture (i.e., the *operating conditions*) in various parts of the equipment. Required information includes the initial, or entrance, conditions of temperature, pressure, and reactants composition and the method of operating the reactor—batch or flow, isothermal, adiabatic, etc. Such information, along with the flow rates of feed and products, provides the *design conditions*. Usually there are many combinations of reactor size and operating conditions which satisfy the design conditions. The optimum design—that which will produce the greatest profit—depends

on raw materials, initial and operating costs, and the market value of the end products.

The ideal approach to design is apparent: the method of designing the reactor should be established, and then an optimization technique should be used to find the most profitable design. Such a procedure should lead to an optimum solution for a set of constant values of the design conditions.

Generally some of the conditions, such as feed composition, will change with time. Such changes may be abrupt, as in switching to feed from another storage tank that contains material of a different composition, or they may be mild cyclical changes. The problem in *reactor control* is determining how to change operating conditions so that the reactor returns to optimum performance as quickly as possible. The first decision is what operating conditions to use as control points; then a policy or strategy is developed for responding to fluctuations in such a way as to maximize profit. The resulting control procedure may be manual; or it may be a semicomputerized procedure, in which a computer is used to determine rapidly the value of the profit function but the indicated changes in operating conditions are made manually; or it may be a direct-digital or closed-loop procedure, in which adjustments to operating conditions are made automatically on signal from the computer. All control procedures, to be successful, require a knowledge of how to design the reactor for a set of constant design conditions.

The optimum design requires iterative numerical work; hence machine computation greatly simplifies the optimization task. In this book we shall limit the problem to answering design questions for a single set of design conditions. Even for such a limited scope we shall find that the numerical integrations often require repetitive calculations well suited for machine solution.

As mentioned in Sec. 1-1, the first step in a logical design procedure is to obtain a suitable expression for the rate of the chemical reaction process, and this requires experimental data. The data can be obtained in several ways:

1. From a bench-scale laboratory reactor designed to operate at nearly constant temperature and composition. Usually operating conditions are chosen to facilitate separating the effects of diffusion and heat transfer (the physical processes) from the observed measurements, so that the rate of the chemical step can be accurately evaluated. This is the most successful of the three methods.
2. From a small-scale reactor (pilot plant) in which the composition, temperature, and pressure may change. Here calculations similar to,

but the reverse of, the design steps are required to evaluate the rate of the chemical reaction. Accurate separation of the diffusion and heat-transfer effects from the chemical step may be difficult.

3. From a commercial-scale reactor which happens to be already available. The problems in obtaining an expression for the chemical rate are similar to those in method 2 but are usually even more severe, because there is less instrumentation, and hence fewer data.

As an illustration of the first two methods of arriving at the data necessary for design calculations, consider the oxidation of sulfur dioxide. Suppose that an air-SO_2 mixture flows over particles of solid catalyst in a tubular-flow reactor. In the bench-scale study the reactants would be passed over a very small amount of catalyst, and the rate of production of sulfur trioxide would be determined by measuring the rates of flow and composition of the inlet and exit streams.[1] This production rate, divided by the mass of catalyst, would represent the rate of reaction,[2] for example, in grams of sulfur trioxide per hour per gram of catalyst. It would approach a point rate rather than an average value, because the amount of catalyst is small enough that the temperature, pressure, and composition changes in passing over the catalyst bed are similarly small.[3] In the second approach the amount of catalyst in the pilot-plant reactor is sufficient to cause considerable conversion, and the temperature and composition may change appreciably as the mixture flows through the reactor. Since the rate of reaction is a function of these variables, it varies from location to location, and the measured production of sulfur trioxide represents an integrated average of all the point rates. To reduce the measured result (called *integral-conversion, or integral-reactor, data*) to the rate of the chemical step requires a procedure that is reverse of the design calculations. A promising rate equation is assumed. Then the point rates are integrated through the catalyst bed, with the effects of diffusion and heat transfer in causing composition and temperature changes taken into account. Finally, the predicted conversions are compared with the experimental results. Repetition of this procedure will result in an equation for the rate of the chemical step. Because of the

[1] In flow systems such small-scale reactors are commonly called *differential reactors*, since the changes in temperature, pressure, and composition in the reactor are small.

[2] For a reaction requiring a solid catalyst the rate is usually based on a unit mass of catalyst rather than a unit volume, as defined in Chap. 2. The two rates are directly related through the bulk density of the bed of catalyst.

[3] Note that the change in composition between the inlet and exit streams must be large enough for precise measurement; otherwise the rate of conversion in the reactor cannot be accurately established. This restriction imposes a limitation on the applicability of the method. If precise analytical methods of determining small composition changes are not available for the particular reaction, a close approach to a point value of the rate cannot be ascertained.

inaccuracy of the calculations, particularly if there are significant tempera-
ture changes, it is generally not possible to arrive at a rate equation that is
wholly satisfactory.

Data obtained in both bench and pilot-plant equipment are valuable,
and it is common practice to carry out investigations with both before
building the commercial-scale reactor. The first yields a better rate equation
and more knowledge about the kinetics of the reaction; i.e., it tells the
engineer more accurately just what variables affect the rate of the chemical
step and how they influence the course of the reaction. This information is
particularly valuable in case it is necessary to predict how the commercial-
scale plant will be affected by a change of operating conditions not specifi-
cally considered in the pilot-plant work.

The bench-scale study alone leaves the engineer largely dependent
on prediction methods for the effects of the physical processes, whereas
data obtained on the scale of a pilot plant can provide a check on the suit-
ability of the prediction methods.[1] As an illustration, consider the extreme
case where the kinetic studies are carried out in a batch-tank reactor with
diffusion resistances, and the commercial unit is to be a tubular-flow reactor.
The diffusion rates will not be the same under batch and flow conditions.
Hence the observed rate in the batch reactor will not be directly applicable
for design calculations in the commercial unit. While the importance of
such effects can be estimated for different types of reactors, as explained in
Chap. 10, the uncertainties in the estimates are sometimes so large that
experimental verification from pilot-plant data is desirable. There are similar
problems with temperature differences arising from heat-transfer consider-
ations. Even where the kinetic studies are carried out in a flow system similar
to that to be employed in the large plant, pilot-plant investigations provide
invaluable information on such important factors as temperature distribution
in the reactor and the effect of specialized designs on improving the process.[2]

3-2 Mass and Energy Balances

Mass and energy balances on the reactor provide the basis for relating the
production rate and composition of the products to the chemical-reaction
rate. If the operation is not steady, changes with time are also involved.
In a single-reaction system one reactant is usually critical because of cost

[1] From this standpoint the objective of the pilot plant is to obtain a model of the reactor,
that is, an understanding of how the physical processes affect the performance of a reactor.
In contrast, the objective of the bench-scale reactor is to obtain a model for the chemical
kinetics, that is, a rate equation.

[2] A more detailed discussion of the functions of bench-scale and pilot-plant reactors is given by
J. M. Smith, Chem. Eng. Progr., 64, 78 (1968).

or limited availability, and the mass balance is applied to this limiting reactant. For example, in the air oxidation of SO_2 the sulfur dioxide is the limiting reactant. Of course, the balance may be written for each component, and for the total mass, but this is not necessary because the composition of the reaction mixture can be expressed in terms of one variable, the conversion, using the composition of the original reactants and the stoichiometry of the reaction (see Example 4-1). For multiple-reaction systems mass balances may need to be written for additional components.

The conversion x is the fraction of a reactant that has been converted into products. When there is only one reaction, there is no uncertainty in this definition. When a reactant can undergo simultaneous or successive reactions to multiple products, both the total conversion of reactant and the conversions to specific products are important. The conversion to a given product was defined in Chap. 2 as the yield of that product. For example, in the air oxidation of ethylene both ethylene oxide and carbon dioxide are products. It is customary to speak of the *yield* of ethylene oxide or *conversion to* ethylene oxide.

Example 3-1 Liquid benzene is chlorinated by bubbling gaseous chlorine into a well-stirred tank reactor containing the benzene. Three reactions can occur:

1. $C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

2. $C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$

3. $C_6H_4Cl_2 + Cl_2 \rightarrow C_6H_3Cl_3 + HCl$

Initially the reactor contains $(N_B)_0$ moles of benzene. Then a total of N_{Cl_2} [$N_{Cl_2} < 3(N_B)_0$] moles of chlorine per mole of benzene is added to the reactor slowly, so that no unreacted chlorine leaves the reactor. Also, the concentrations of dissolved unreacted chlorine and dissolved HCl are small.[1] If the density of the reaction mixture is constant, express the concentrations of mono-, di-, and trichlorobenzene in terms of their corresponding conversions x_M, x_D, and x_T.

Solution Chlorine is the limiting reactant, so the conversions will be based on this component. Let N_B, N_M, N_D, and N_T represent the moles of benzene and mono-, di-, and trichlorobenzene per mole of original benzene. Since 1 mole of chlorine is required for 1 mole of monochlorobenzene,

$$x_M = \frac{N_M}{N_{Cl_2}} \tag{A}$$

However, 2 moles of chlorine are needed to produce 1 mole of dichlorobenzene. Therefore

$$x_D = \frac{2N_D}{N_{Cl_2}} \tag{B}$$

[1] The HCl produced leaves the reactor as a gas.

and similarly,

$$x_T = \frac{3N_T}{N_{Cl_2}}$$ (C)

The number of moles of unreacted benzene will be

$$N_B = 1 - (N_M + N_D + N_T) = 1 - (x_M + \tfrac{1}{2}x_D + \tfrac{1}{3}x_T)N_{Cl_2}$$ (D)

The initial concentration of benzene in the reactor is $[B]_0 = (N_B)_0/V$. Equations (A) to (D) give the number of moles of each component per mole of initial benzene. Therefore the concentrations at any conversion will be

$$[M] = \frac{(N_B)_0 N_M}{V} = [B]_0 N_{Cl_2} x_M$$

$$[D] = \tfrac{1}{2}[B]_0 N_{Cl_2} x_D$$

$$[T] = \tfrac{1}{3}[B]_0 N_{Cl_2} x_T$$

$$[B] = \frac{(N_B)_0 N_B}{V} = [1 - (x_M + \tfrac{1}{2}x_D + \tfrac{1}{3}x_T)N_{Cl_2}][B]_0$$

These four equations give the desired relationships for the concentrations in terms of the conversions for a constant-density system. All three conversions are not independent, because it is supposed that there is no unreacted chlorine; that is, their sum must be unity. This is made clear by writing a mass balance of chlorine,

Total chlorine fed = total chlorine in products

$$N_{Cl_2} = N_M + 2N_D + 3N_T$$ (E)

Introducing the conversions with Eqs. (A) to (C), we have

$$N_{Cl_2} = x_M N_{Cl_2} + x_D N_{Cl_2} + x_T N_{Cl_2}$$

or

$$1 = x_M + x_D + x_T$$

Example 3-2   When ethylene is oxidized with air by means of a silver catalyst at low temperature (200 to 250°C), two reactions occur:

1. $C_2H_4(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_4O(g)$

2. $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

If the conversion of ethylene is x_1 by reaction 1 and x_2 by reaction 2, express the molal composition of the reaction mixture in terms of the conversions and the ratio a, moles of air per mole of ethylene in the feed. What is the yield and selectivity of ethylene oxide?

Solution   If a basis of 1 mole of C_2H_4 is chosen, and $N_{C_2H_4O}$ and N_{CO_2} represent the moles of these components at any conversions, x_1 and x_2, then

$$x_1 = \frac{N_{C_2H_4O}}{1} \qquad \text{or } N_{C_2H_4O} = x_1$$

and

$$x_2 = \frac{\tfrac{1}{2}N_{CO_2}}{1} \qquad \text{or } N_{CO_2} = 2x_2$$

The moles of the other components will be

$$H_2O = 2x_2$$

$$C_2H_4 = 1 - x_1 - x_2$$

$$N_2 = 0.79a$$

$$O_2 = 0.21a - (\tfrac{1}{2}x_1 + 3x_2)$$

$$\text{Total moles} = 1 + a - \tfrac{1}{2}x_1$$

Then the mole fractions of each component are as follows:

$$C_2H_4O = \frac{x_1}{1 + a - \tfrac{1}{2}x_1}$$

$$CO_2 = \frac{2x_2}{1 + a - \tfrac{1}{2}x_1}$$

$$H_2O = \frac{2x_2}{1 + a - \tfrac{1}{2}x_1}$$

$$C_2H_4 = \frac{1 - x_1 - x_2}{1 + a - \tfrac{1}{2}x_1}$$

$$N_2 = \frac{0.79a}{1 + a - \tfrac{1}{2}x_1}$$

$$O_2 = \frac{0.21a - (\tfrac{1}{2}x_1 + 3x_2)}{1 + a - \tfrac{1}{2}x_1}$$

The total conversion of ethylene is $x_1 + x_2$. The yield of ethylene oxide is x_1, and its overall selectivity is x_1/x_2.

Mass Balance The mass balance for a reactant can be written in a general form applicable to any type of reactor. For a time element Δt and a volume element ΔV this general form is

$$\begin{Bmatrix} \text{Mass of reactant} \\ \text{fed to volume} \\ \text{element} \end{Bmatrix} - \begin{Bmatrix} \text{mass of reactant} \\ \text{leaving volume} \\ \text{element} \end{Bmatrix} - \begin{Bmatrix} \text{mass of reactant} \\ \text{converted in the} \\ \text{volume element} \end{Bmatrix}.$$

$$= \begin{Bmatrix} \text{accumulation of reactant} \\ \text{in the volume element} \end{Bmatrix} \quad (3\text{-}1)$$

The first two terms represent the mass of reactant entering and leaving the reactor in the time Δt. The third term depends on the rate of reaction applicable to the volume element ΔV. The fourth term expresses the resultant change in mass of reactant in time Δt caused by the other three terms. The third term will have the form $r \, \Delta V \, \Delta t$, where r is the rate of disappearance of the reactant per unit volume. It is important to note that r is equal to the rate of the chemical step (used exclusively in Chap. 2) only if there are no physical resistances, i.e., no temperature or concentration gradients within ΔV.

Energy Balance Energy balances are needed solely because the rate of the chemical reaction may be a strong function of temperature (Arrhenius equation, Chap. 2). The purpose of the energy balance is to describe the temperature at each point in the reactor (or at each time for a batch reactor), so that the proper rate may be assigned to that point.

For a volume element ΔV and time period Δt conservation of energy requires

$$\begin{Bmatrix} \text{Energy in streams} \\ \text{fed to volume element} \end{Bmatrix} - \begin{Bmatrix} \text{energy in streams} \\ \text{leaving volume element} \end{Bmatrix} + \begin{Bmatrix} \text{energy transferred} \\ \text{from surroundings} \\ \text{to volume element} \end{Bmatrix}$$

$$= \begin{Bmatrix} \text{accumulation of} \\ \text{energy in the volume} \\ \text{element} \end{Bmatrix} \quad (3\text{-}2)$$

To be complete, all forms of energy—internal, potential, and kinetic—should be included in the terms referring to the energy of a fluid.[1] However, in chemical reactors only the internal and, rarely, the mechanical work-forms are quantitatively important. We can evaluate only *changes* in the internal energy of a fluid, so that the first, second, and fourth terms must be referred to the same reference state of zero energy. The difference between the first and second terms reflects temperature differences and differences in energy due to differences in composition of the entering and leaving streams (i.e., the heat of reaction). The third term accounts for possible exchange of energy with the surroundings by heat transfer through the reactor walls. The solution of Eq. (3-2) gives the temperature as a function of position and/or time in the reactor.

The form of Eqs. (3-1) and (3-2) depends on the type of reactor. In most cases one or more of the terms do not exist. More important, the possibility of solving the equations depends on the assumptions made about

[1] For more complete and detailed formulation of macroscopic mass and energy balances see R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," John Wiley & Sons, Inc., New York, 1960.

the conditions of mixing, or diffusion, in the reactor. This explains the signif-
icance of the classification of reactors into stirred tank or tubular flow,
because it is for these ideal types that extreme assumptions about the nature
of mixing are valid. In the following sections Eqs. (3-1) and (3-2) are applied
to these types of reactors.

3-3 The Ideal Stirred-tank Reactor

The *stirred-tank reactor* may be operated as a steady-state flow type (Fig.
3-1a), a batch type (Fig. 3-1b), or as a non-steady-state, or semibatch,
reactor (Fig. 3-1c). The key feature of this reactor is that the mixing is com-
plete, so that the properties of the reaction mixture are uniform in all parts
of the vessel and are the same as those in the exit (or .product) stream.
This means that the volume element chosen for the balances can be taken
as the volume V of the entire reactor. Also, the composition and temperature
at which reaction takes place are the same as the composition and tempera-
ture of any exit stream.

*Fig. 3-1 Ideal stirred-tank reactors classified according to method of
operation: (a) flow (steady-state), (b) batch, (c) semibatch (non-steady-
flow)*
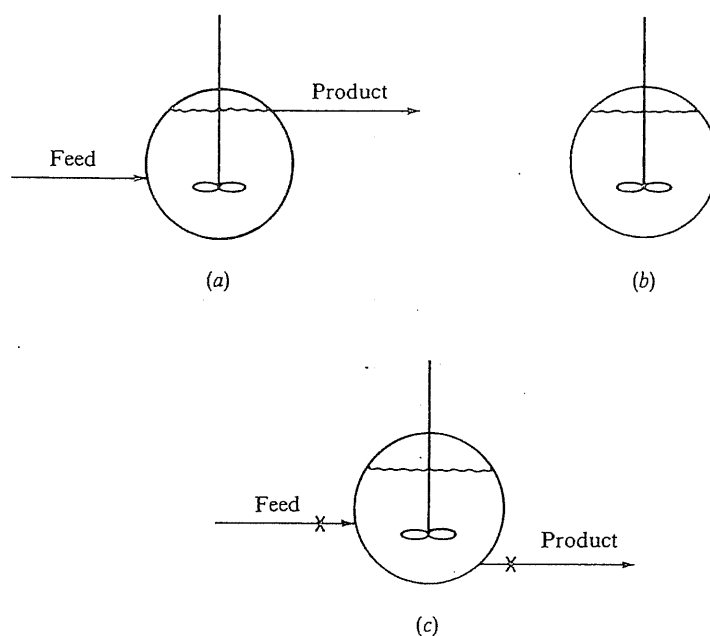
Steady-state Flow   Consider the simple case of a single feed stream and a single product stream, as shown in Fig. 3-1a. The properties of these streams do not change with time. Hence the first and second terms in Eq. (3-1) are constants, equal to the mass-flow rate of limiting reactant multiplied by Δt. Suppose there is only one reaction occurring. If the mass-flow rate[1] of *reactant* corresponding to zero conversion is F, and its conversion in the feed stream is x_F, then $F(1 - x_F) \Delta t$ is the first term and, similarly, $F(1 - x_e) \Delta t$ is the second. Since the reaction mixture in the vessel is at uniform temperature and composition, the rate of reaction is constant and should be evaluated at the temperature and composition of the *product* stream. If the rate of conversion of reactant is r_e, with the subscript e indicating exit or product conditions, the third term in Eq. (3-1) is $r_e V \Delta t$. There can be no accumulation of mass of reactant in the reactor at steady-state conditions, so the fourth term is zero. Then Eq. (3-1) can be written

$$F(1 - x_F) \Delta t - F(1 - x_e) \Delta t - r_e V \Delta t = 0$$

or

$$\frac{V}{F} = \frac{x_e - x_F}{r_e} \tag{3-3}$$

This expression can be used to evaluate the volume of reactor needed to produce a given conversion x_e for known design conditions F and x_F, provided r_e is available. Notice that the exit conversion can be determined from Eq. (3-3) without integration through the volume of the reactor. This is because the rate is constant throughout the vessel—a direct consequence of the assumption of complete mixing.

There are many variations of the simple form of stirred-tank reactor just considered: multiple units in parallel, series, split streams, more than one reaction, etc. Some of these will be discussed in Chap. 4. Deviations from the assumption of complete mixing are mentioned in Sec. 3-5 and discussed in more detail in Chap. 6.

To evaluate r_e it is necessary to know the temperature of the product stream leaving the reactor. This requires an energy balance, which again may be written over the total volume element V. The fourth term in Eq.

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[1] Mass and energy balances may be written either in terms of mass or moles as long as all quantities are on the same basis. For example, if mass units are used, both the rate and the feed rate must be in mass units. For isothermal reactors molal units are more convenient, and the examples in Chap. 4 are solved using these units. Mass units may be more suitable for energy balances so that some examples in Chap. 5 are treated on a mass basis. In this chapter all the equations are written with the supposition that mass units are employed. Also note that the conversion x refers to the fraction of the reactant feed rate F that is converted, not to the fraction of the total feed rate F_t.

(3-2) is zero. Next we choose a base state (temperature, composition, and pressure) from which to evaluate the energy. Suppose the enthalpy[1] (per unit mass) above the base state of the feed stream is H_F and that of the product H_e. If F_t is the total mass feed rate, the first and second terms in Eq. (3-2) are $F_t H_F \Delta t$ and $F_t H_e \Delta t$, and the balance becomes

$$F_t(H_F - H_e) \Delta t + UA_h(T_s - T_e) \Delta t = 0$$

or

$$F_t(H_F - H_e) + UA_h(T_s - T_e) = 0 \tag{3-4}$$

Heat exchange with the surroundings is expressed here in terms of the surroundings temperature T_s, the overall heat-transfer coefficient U, and the effective area for heat transfer A_h. The heat of reaction ΔH and the rate of reaction do not appear directly in Eq. (3-4). However, their effects are reflected in the difference in the enthalpies of the feed and product streams, since these streams will have different compositions. That is, to calculate the enthalpy H_e of the product stream it is necessary to know ΔH and the rate r. Therefore it is more convenient to replace $H_F - H_e$ with the appropriate T, r, and ΔH. This is accomplished by considering the enthalpy change when feed at T_F is first heated to T_e and then changed in composition to that of the product.[2] Expressed mathematically, the first contribution is $c_p(T_e - T_F)$ and the second is $(x_e - x_F)\Delta H/M$. Hence

$$H_e - H_F = c_p(T_e - T_F) + (x_e - x_F)\frac{\Delta H}{M}\frac{F}{F_t} \tag{3-5}$$

where M is the molecular weight of the limiting reactant and ΔH is heat of reaction per mole of limiting reactant. Combining Eqs. (3-5) and (3-4) yields

$$F_t(T_F - T_e)c_p - F(x_e - x_F)\frac{\Delta H}{M} + UA_h(T_s - T_e) = 0 \tag{3-6}$$

This result can also be expressed in terms of the rate of reaction, rather than the conversion, by using the mass balance. Replacing $x_e - x_F$ with its value from Eq. (3-3) gives

$$F_t(T_F - T_e)c_p - r_e V\frac{\Delta H}{M} + UA_h(T_s - T_e) = 0 \tag{3-7}$$

[1] The internal energy plus the pV term, or enthalpy, is the correct form of the energy in the feed and exit streams because the reactor is operated on a steady-flow basis.

[2] Since enthalpy is a state property, $H_e - H_F$ can be evaluated by any conveniently chosen path. Rigorously, for the path described, ΔH applies at the product temperature T_e, and the specific heat c_p is for a mixture of the composition of the feed. Except for simple gaseous systems, the thermodynamic data available are insufficient to take into account variations in ΔH with temperature and c_p with composition. Often these variations are small.

Equations (3-4), (3-6), and (3-7) are equivalent forms of the energy balance. They are useful in homogeneous-reactor design (Chap. 5).

Batch Operation (Non-steady State) In batch operation there are no streams entering and leaving the reactor (see Fig. 3-1b). Suppose again that the limiting reactant undergoes only one reaction. If m is the mass of reactant corresponding to zero conversion and Δx is the conversion in the time Δt, the accumulation of reactant in the vessel in time Δt is $-m\,\Delta x$. Then the mass balance may be written[1]

$$-\mathbf{r}V\Delta t = -m\,\Delta x \tag{3-8}$$

The properties of the reaction mixture will vary with time, so that the mass balance becomes a differential equation. If we divide by Δt and take the limit as $\Delta t \to 0$, Eq. (3-8) becomes

$$\frac{dx}{dt} = \mathbf{r}\frac{V}{m} \tag{3-9}$$

For isothermal operation $\mathbf{r}$ is dependent only on the composition (or conversion, for a single reaction), so that a solution for conversion with respect to time is obtainable from the mass balance alone. We can show the result by solving Eq. (3-9) for dt and integrating formally:

$$t = m \int_{x_1}^{x_2}\frac{dx}{\mathbf{r}V} = \frac{m}{m_t}\int_{x_1}^{x_2}\rho\,\frac{dx}{\mathbf{r}} \tag{3-10}$$

where x_1 is the initial conversion and x_2 the conversion at any time t. The second equality follows by expressing the volume of the reaction mixture in terms of its total mass m_t and density ρ. The importance of arranging the expression in this way is that time, the independent design variable, is separated from the dependent variables characteristic of the chemical reaction. If the rate $\mathbf{r}$ and the density of the reaction mixture are known as a function of conversion, the value of the integral for any desired conversion can be evaluated without reference to reaction equipment. Then the various combinations of time and mass of charge that will give the required production rate of product can be examined separately. Expressed differ-

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[1] Note that this does not require that the conversion be zero initially. If the initial conversion is greater than zero, m will be the actual mass of reactant in the charge plus an amount equivalent to the initial conversion. For example, suppose the initial conversion is 20% and the mass of reactant in the initial charge to the reactor is 1,000 lb. Evidently the 1,000 lb is equivalent to 80% of the reactant that would have been present with no conversion. Hence $m = 1,000 + (0.20/0.80)(1,000) = 1,250$ lb.

ently, Eq. (3-10) relates the time to an integral dependent on the series of intensive states experienced by the reaction mixture.

If the reactor does not operate isothermally, an energy balance is required. In this case the first and second terms of Eq. (3-2) do not exist, but the other two can be finite. The accumulation term should express the energy change with time due to the change in composition and the change in temperature of the mixture. The energy accumulated from the change in composition is due to the heat of reaction and may be written $(\Delta H/M)\mathrm{r}V\Delta t$. If the change in temperature of the reaction mixture in time Δt is ΔT, the accumulated energy due to the temperature change is $m_t c_v \Delta T$.[1] Then Eq. (3-2) may be written

$$UA_h(T_s - T)\Delta t = \frac{\Delta H}{M}\mathrm{r}V\Delta t + m_t c_v \Delta T$$

where T is the temperature and c_v the specific heat of the reaction mixture. Dividing by Δt and taking the limit as $\Delta t \rightarrow 0$ gives

$$m_t c_v \frac{dT}{dt} = \frac{-\Delta H}{M}\mathrm{r}V + UA_h(T_s - T) \qquad (3\text{-}11)$$

Equation (3-11) relates the temperature to the reaction variables and, with Eq. (3-9), establishes the relationships of conversion, temperature, and time for nonisothermal operation.

It is possible to express Eq. (3-10) for isothermal operation in simpler forms when assumptions such as constant density are permissible. These will be considered in Chap. 4. The constant-density form of Eq. (3-10) was used in Chap. 2 to calculate rate constants from measured conversions or concentrations as a function of time (see, for example, Sec. 2-7). It is important to recall that we could determine the rate equation for the chemical step from a form of Eq. (3-10) because the reactor is assumed to be an ideal stirred-tank type, with no physical resistances involved.

Semibatch Operation   In semibatch operation the rates of mass flow into and out of the system are unequal (see Fig. 3-1c). For example, benzene may be chlorinated in a stirred-tank reactor by first adding the charge of liquid benzene and catalyst and then continuously adding chlorine gas until the required ratio of chlorine to benzene has been obtained. Operation of this kind is batch from the standpoint that the composition of the reaction mixture changes with time. However, from a process standpoint the chlorine is added continuously. The system is still an ideal stirred-tank reactor if the

[1] The volume of the reaction mixture should be constant to make the use of c_v rigorously correct.

mixing in the vessel is complete. An advantage of semibatch operation is
that a small concentration of one reactant (the chlorine in this example)
can be maintained at all times. This may be important when it is desired to
obtain a predominant amount of one product from several possible products.
Thus a large concentration of chlorine would favor the formation of di- and
trichlorobenzenes, while the monochlorination of the benzene ring is favored
when a small amount of chlorine is present.

Semibatch operation is also advantageous when a high heat of reaction
would cause excessive temperature changes in normal batch operation. For
example, hexamethylenetetramine is manufactured by reacting ammonia
and formaldehyde. If the reaction is carried out in the liquid phase by
using ammonium hydroxide and formalin solutions, ordinary batch opera-
tion (in which the two reactants are mixed initially) may result in a large
increase in temperature because of the highly exothermic heat of reaction.
The temperature rise can be reduced and controlled by adding the ammon-
ium hydroxide continuously, at a controlled rate, to a reactor containing
formalin. The rate of this chemical step is extremely rapid; the ammonia
reacts just as soon as it is mixed with the formalin. Hence the rate of pro-
duction of product is controlled by the rate at which the ammonia is added
rather than by the rate of the chemical reaction.

These two examples are special cases in which there was no exit
stream and no change in flow rate of the feed stream. In its general form
semibatch operation includes variations with respect to time in both the
rate and state of the inlet and exit streams. The combustion zone in
liquid rockets is an example of such a case; as the fuel and oxidant are
consumed, their state (temperature, pressure, and composition) and flow
rates from the fuel tanks may change.

All the terms in Eqs. (3-1) and (3-2) may be significant in semibatch
operation. However, the exact formulation of terms depends on the specific
case. A few of these are considered in detail in Chaps. 4 and 5.

3-4 The Ideal Tubular-flow (Plug-flow) Reactor

In a *tubular-flow reactor* the feed enters one end of a cylindrical tube and
the product stream leaves at the other end (Fig. 3-2). Such equipment is
normally operated at steady state (except at startup or shutdown), so that
the properties are constant with respect to time. The long tube and lack of
provision for stirring prevents complete mixing of the fluid in the tube.
Hence the properties of the flowing stream will vary from point to point.
In general, variations in properties will occur in both the longitudinal
and radial directions. Under these conditions the volume element ΔV
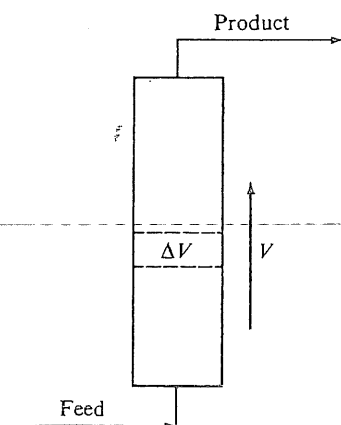chosen in writing Eqs. (3-1) and (3-2) must be small enough that the properties

Fig. 3-2   Ideal tubular-flow reactor

are constant within the element. It is clear that ΔV will have to approach zero for this condition to be satisfied. Then Eqs. (3-1) and (3-2) become partial-differential equations expressing gradients in the longitudinal and radial directions.

The extent of mixing will affect how the properties vary with position; we are particularly interested in the concentrations and temperature, since they determine the rate of reaction. In the *ideal* tubular-flow reactor specific assumptions are made about the extent of mixing: no mixing in the axial direction (the direction of flow), complete mixing in the radial direction, and a uniform velocity across the radius. The absence of longitudinal mixing is the special characteristic of this type of reactor, also called a *plug-flow reactor*. It is an assumption at the opposite extreme from the complete-mixing supposition of the ideal stirred-tank reactor.

The validity of the assumptions will depend on the geometry of the reactor and the flow conditions. Deviations are frequent but not always important. Methods of describing the deviations and their origins are discussed briefly in Sec. 3-5 and considered in more detail in Chap. 6.

Mass Balance   Equations (3-1) and (3-2) can be written for a volume element ΔV extending over the entire cross section of the tube, as shown in Fig. 3-2. This is because there is no variation in properties or velocity in the radial direction. Suppose the mass feed rate of *reactant* to the reactor is F and the conversion of this reactant at the entrance to the volume element is x. In the absence of axial mixing, reactant can enter the element only by bulk flow of the stream. Hence the first term in Eq. (3-1) is $F(1 - x)\Delta t$. If the conversion leaving the element is $x + \Delta x$, the second term is $F(1 - x - \Delta x)$ Δt. Since the operation is at steady state, the fourth term is zero. The third

term is $r \Delta V \Delta t$, where r is the rate of reaction. If there are no physical resistances within ΔV, this rate will be determined solely by the chemical step. If physical resistances are possible, as in a fluid-solid heterogeneous reaction, then r will be determined by the combined resistances of the chemical and physical processes.

Equation (3-1) takes the form

$$F(1 - x)\Delta t - F(1 - x - \Delta x)\Delta t - r\Delta V \Delta t = 0$$

or

$$F\Delta x - r\Delta V = 0$$

Dividing by ΔV and taking the limit as $\Delta V \to 0$ gives

$$\frac{dx}{dV} = \frac{r}{F} \tag{3-12}$$

This is the relationship between conversion and size of reactor for the ideal tubular-flow type. The rate is a variable, as in Eq. (3-9), but now r varies with longitudinal position (volume) in the reactor, rather than with time.

Since F is a constant, the integrated form may be formally written

$$\frac{V}{F} = \int_{x_1}^{x_2} \frac{dx}{r} \tag{3-13}$$

This method of writing the mass balance, like Eq. (3-10) for batch operation of a tank reactor, separates the extensive variables V and F and relates them to an integral dependent on the intensive conditions in the reaction mixture. It is worthwhile to note the similarity between Eq. (3-13) and the more familiar design equation for heat-transfer equipment based on an energy balance. This may be written

$$\frac{A_h}{F_t} = \int_{T_1}^{T_2} \frac{c_p \, dT}{U\Delta T} \tag{3-14}$$

where A_h is the required heat-transfer area [analogous to V in Eq. (3-13)] and F_t is the mass-flow rate of one fluid through the exchanger (analogous to F).

The rate of reaction plays the same role in reactor design that the product of the overall heat-transfer coefficient U and the temperature difference ΔT plays in sizing heat-transfer equipment. Thus the numerical value of the integrals in Eqs. (3-10), (3-13), and (3-14) represents the degree of difficulty of the job to be done—whether it be chemical conversion or heat

transfer. Similarly, the design equation for the absorption of a gas in a packed column through which an absorbent is passed can be written

$$\frac{V}{L} = \int_{C_1}^{C_2} \frac{dC}{K_l a_v (C_{eq} - C)}$$ (3-15)

where V = required volume of the absorption tower
       C = concentration
       L = volumetric rate of flow of liquid absorbent
       $K_l a_v$ = rate of absorption of liquid per unit concentration difference
       $C_{eq} - C$

The similarity to Eq. (3-13) is apparent here as well. Again the integral measures the difficulty of the job.

The design equations for ideal tubular-flow reactors involve no new concepts but simply substitute a rate of reaction for a heat-transfer rate or mass-transfer-rate function. The increased complexity of reactor design in comparison with the design of equipment for the purely physical processes lies in the difficulty in evaluating the rate of reaction. This rate is dependent on more, and less clearly defined, variables than a heat- or mass-transfer coefficient. Accordingly, it has been more difficult to develop correlations of experimental rates, as well as theoretical means of predicting them.

Energy Balance If the enthalpy of the reaction mixture per unit mass above the base state is H at the entrance to the element and $H + \Delta H$ at the exit, the energy balance becomes

$$F_t H \Delta t - F_t (H + \Delta H) \Delta t + U(\Delta A_h)(T_s - T)\Delta t = 0$$

or

$$-F_t \Delta H + U(\Delta A_h)(T_s - T) = 0$$ (3-16)

where F_t is the total mass-flow rate. The change in enthalpy ΔH in the volume element will depend on the heat of reaction and the rate of reaction. As in the development of Eq. (3-5), we add the change in enthalpy due to the temperature change, $c_p \Delta T$, and the change due to the reaction $(\Delta H / M)\Delta x$. Hence

$$\Delta H = c_p \Delta T + \frac{\Delta H}{M} \Delta x \frac{F}{F_t}$$

Using this expression for ΔH in Eq. (3-16) yields

$$-F_t c_p \Delta T - F \frac{\Delta H}{M} \Delta x + U(\Delta A_h)(T_s - T) = 0$$ (3-17)

If we divide each term by ΔV and take the limit as $\Delta V \to 0$, we obtain[1]

$$F_t c_p \frac{dT}{dV} = U(T_s - T)\frac{dA_h}{dV} + F\left(\frac{-\Delta H}{M}\right)\frac{dx}{dV}$$

(3-18)

This result can be written in terms of the rate instead of the conversion if we substitute r/F for dx/dV, according to Eq. (3-12). Note that dA_h/dV is the rate of change of heat-transfer area with reactor volume; for a cylindrical tube this would be

$$\frac{dA_h}{dV} = \frac{d(\pi d_t z)}{d(\pi d_t^2 z/4)} = \frac{4}{d_t}$$

(3-19)

where z is the axial distance along the tube.

Equation (3-18) establishes the temperature at any element of volume in the reactor. It is useful in conjunction with the mass balance, Eq. (3-12), in solving nonisothermal problems.

Example 3-3   The thermal (noncatalytic) decomposition of acetaldehyde,

$$CH_3CHO(g) \to CH_4(g) + CO(g)$$
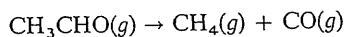
is studied in an ideal tubular-flow reactor at a constant total pressure of p_t atm. Suppose pure acetaldehyde vapor enters the reactor at T_0°K and a steady rate of F g/sec. The heat of reaction and specific heat of the reaction mixture can be assumed constant and equal to ΔH cal/g mole and c_p cal/(g mole)(°C). The rate of reaction is given by the second-order equation

$$r = A(e^{-E/R_g T})\, p_A^2 \qquad \text{g moles/(sec)(cm}^3\text{)}$$

(A)

where E is the activation energy, in calories per gram mole, and p_A is the partial pressure of acetaldehyde, in atmospheres. If the reactor operates adiabatically, express the rate of reaction in terms of the conversion as the sole variable.

Solution   The energy balance relates the temperature to conversion, providing a method of eliminating T from the rate equation. Variables other than x and T are not involved in the energy balance because the operation is adiabatic. In Eq. (3-18) the second term is zero, so that the volume of the reactor does not enter into the problem. Thus

$$Fc_p \frac{dT}{dV} = F\left(\frac{-\Delta H}{M}\right)\frac{dx}{dV}$$

---

[1] The term $F_t c_p$ is the heat capacity of the reaction mixture per unit time. While the total mass-flow rate F_t is constant throughout the reactor, c_p may vary with temperature and composition. Where the specific heats of the various components differ, it may be convenient to evaluate $F_t c_p$ as $\Sigma_i F_i c_{pi}$, where F_i is the mass-flow rate of component i. This quantity varies with location in the reactor. The evaluation of the term is illustrated in Example 5-2.

or

$$dT = \frac{-\Delta H}{c_p M}\, dx \tag{B}$$

Since the coefficient of dx is constant, Eq. (B) may be integrated to give the absolute temperature T at any conversion x,

$$T - T_0 = \frac{-\Delta H}{c_p M}(x - 0) = \frac{-\Delta H(x)}{c_p M} \tag{C}$$

where $x = 0$ at $T = T_0$ (entrance to reactor).

Through Eq. (C) the part of the rate equation involving the temperature can be expressed in terms of x. The partial pressure of CH_3CHO is related to the conversion by the stoichiometry of the reaction. If we choose 1 mole of acetaldehyde as a basis, at any conversion x the number of moles of the constituents will be

Acetaldehyde $= 1 - x$
Methane $= x$
Carbon monoxide $= x$
Total moles $= 1 + x$

Hence the mole fraction and partial pressure of acetaldehyde are

$$y_A = \frac{1 - x}{1 + x}$$

$$p_A = \frac{1 - x}{1 + x} p_t \tag{D}$$

Substituting Eqs. (C) and (D) into Eq. (A) gives the required expression for the rate in terms of x,

$$r = A \exp\left[-\frac{E}{R_g}\left(\frac{1}{T_0 - [\Delta H(x)/c_p M]}\right)\right]\left(\frac{1 - x}{1 + x}\right)^2 p_t^2 \tag{E}$$

This expression could be used in the mass-balance equation (3-12) and integrated (p_t is constant) to obtain the exit conversion in terms of the volume of the reactor. It is possible here to obtain a single equation relating x and V only because the reactor operated adiabatically. Otherwise the volume of the reactor would have been included in the energy balance, and both Eq. (3-18) and Eq. (3-12) would have to be solved simultaneously. Such solutions are illustrated in Chap. 5.

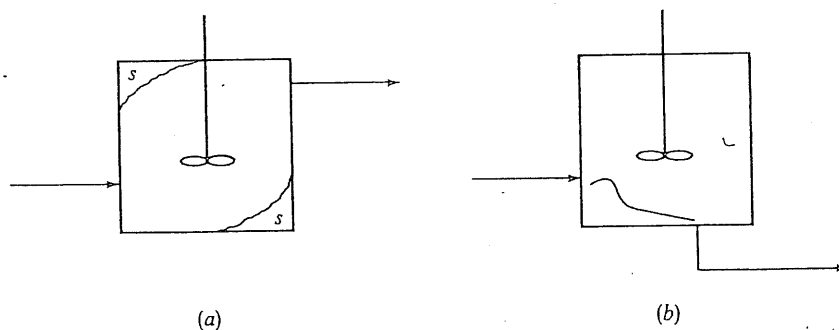## 3-5 *Deviations from Ideal Reactors: Mixing Concepts*

Imagine a tank reactor of poor design such that pockets of stagnant fluid exist, as shown by regions marked S in Fig. 3-3a. The conversion will become very high in the stagnant fluid, but this fluid does not leave the reactor. The remainder of the fluid will spend less time in the reactor than it would if the pockets did not exist, and hence it will have less time to react.

The result will be an average conversion in the exit stream which is less than that for the ideal type. Figure 3-3*b* shows another type of deviation, caused by bypassing or short-circuiting of the fluid. Here a part of the fluid entering the tank takes a shortcut to the exit and maintains its identity (does not mix) while doing so. Again, the conversion in the exit stream is reduced below that of the ideal stirred-tank reactor. While these are extreme cases attributable to poor design, it is clear that actual reactors may deviate to some degree from ideal behavior, and the behavior of a specific reactor will depend on the extent of mixing.

Deviations from ideal tubular-flow behavior are also possible. Two kinds of deviations are: (1) some mixing in the longitudinal direction and (2) incomplete mixing in the radial direction. Figure 3-4*a* and *b* illustrates these two effects. In Fig. 3-4*a* the inlet and exit nozzles are such that vortices and eddies produce mixing in the longitudinal direction. Figure 3-4*b* represents the situation where the fluid is in laminar flow, forming a parabolic velocity profile across the tube. Since the molecular-diffusion process is relatively slow, the annular elements of fluid flow through the reactor only slightly mixed in the radial direction. Also, the fluid near the wall will have a longer residence time in the reactor than for ideal tubular-flow performance, while the fluid near the center will have a shorter residence time. The result again is a decrease in conversion. Bypassing or short-circuiting can also occur in a fixed-bed, fluid-solid catalytic reactor, as shown in Fig. 3-4*c*. The nonuniform packing arrangement results in a higher flow rate about one pellet diameter from the wall. The composition of the fluid will be different at this radius, so that the requirement of complete radial mixing is not satisfied.

All deviations from ideal performance fall into two classifications. The first is a flow arrangement in which elements of fluid do not mix, but

Fig. 3-3 Deviations from ideal stirred-tank performance: (a) stagnant regions, (b) bypassing

(*a*)   (*b*)

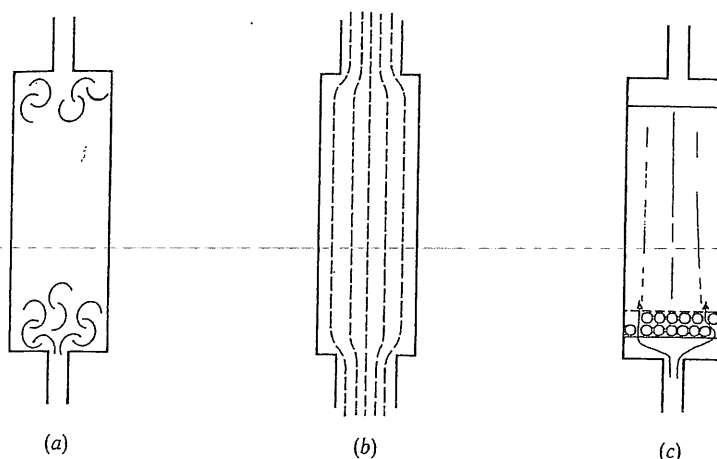(a)   (b)   (c)

Fig. 3-4   Deviations from ideal tubular-flow performance: (a) longitudinal mixing due to vortices and turbulence, (b) laminar-flow (poor radial mixing), (c) bypassing in fixed-bed catalytic reactor

follow separate paths through the reactor (segregated flow). These elements are retained in the reactor for different times; that is, they have different residence times. The second is a flow arrangement whereby adjacent elements of fluid partially mix (micromixing). The effects of these deviations on the conversion can be evaluated, provided we know the distribution of residence times in the fluid leaving the reactor *and* the extent of micromixing. Such complete information is seldom available. However, for well-defined cases of micromixing the effect of a distribution of residence times on the conversion can be evaluated. Procedures for treating these factors quantitatively are considered in Chap. 6. Usually the effects are relatively small, although for special reactors, such as a stirred-tank type with internal coils and a viscous reaction mixture, they may be large. Because of the great influence of temperature on the rate of reaction, unaccounted-for temperature profiles in a reactor are often more significant.[1]

3-6 Space Velocity and Space Time in Tubular-flow Reactors

The term V/F evaluated from Eqs. (3-3) and (3-13) determines the size of the flow reactor necessary to process a given feed rate F. The inconsistency of comparing volume with mass can be overcome by converting the feed rate to a volumetric basis. If ρ_F is the density of the feed, then F_t/ρ_F represents

[1]See K. G. Denbigh, "Chemical Reactor Theory," pp. 44, 63, Cambridge University Press, New York, 1965.

the total feed rate as volume per unit time. The ratio of the feed rate in volumetric units to the volume of reactor is the space velocity,

$$\vartheta_F = \frac{F_t}{V\rho_F}$$

(3-20)

Space velocity, a term commonly used to describe the extensive operating characteristics of a tubular-flow reactor, is the maximum feed rate per unit volume of reactor that will give a stated conversion. Also space velocity is a measure of the ease of the reaction job. A high space velocity means that the reaction can be accomplished with a small reactor or that a given conversion can be obtained with a high feed rate.

The reciprocal of the space velocity is the space time θ_F

$$\theta_F = \frac{V\rho_F}{F_t} = \frac{1}{\vartheta_F}$$

(3-21)

If the feed consists only of reactant, then $F_t = F$ and the mass balance, Eq. (3-13), may be written

$$\theta_F = \frac{1}{\vartheta_F} = \rho_F \int_{x_1}^{x_2} \frac{dx}{r}$$

(3-22)

The space time is usually not equal to the actual time an element of fluid resides in the reactor. Variations in the temperature, pressure, and moles of reaction mixture can all cause the local density to change through the reactor and be unequal to ρ_F. Also, feed rates frequently are measured under conditions grossly different from those in the reactor. For example, the feed may be measured as a liquid and then vaporized before it enters the reactor. Also, as observed in Sec. 3-5, there may well be a distribution of residence times in the fluid leaving, so that we must use the concept of a *mean residence time*. The mean residence time is equal to θ_F only when the following conditions are met:

1. The temperature and pressure are constant throughout the reactor.
2. The feed rate is measured at the temperature and pressure in the reactor.
3. The density of the reaction mixture is constant (for a gaseous reaction this requires, in addition to 1, that there be no change in number of moles).

The effect of temperature and pressure variations on the residence time for an *ideal* tubular-flow (plug-flow) reactor can be evaluated by comparing an actual residence time θ with θ_F. The actual time required for an element of fluid to pass through the volume of reactor dV is

$$d\theta = \frac{\text{distance}}{\text{velocity}} = \frac{\text{volume}}{\text{volumetric flow rate}} = \frac{dV}{F_t/\rho} \qquad (3\text{-}23)$$

where ρ is the local mass density at the point dV in the reactor. For a gaseous reaction it is more appropriate to express $d\theta$ in terms of the total molal flow rate N_t' and the volume per mole v. In this form Eq. (3-23) may be written

$$d\theta = \frac{dV}{N_t'v} \qquad (3\text{-}24)$$

In Eq. (3-24) both N_t' and v can change with position. When ρ, or N_t' and v, are constant, Eqs. (3-23) and (3-21) show that $\theta = \theta_F$. When this is not true, the actual time must be obtained by integration. Since N_t' and v are more easily related to the conversion than to V, it is convenient to substitute for dV the value from Eq. (3-12). Then Eq. (3-24) becomes

$$d\theta = \frac{F\,dx}{N_t'v\mathbf{r}}$$

Integrating formally, we obtain

$$\theta = F \int_{x_1}^{x_2} \frac{dx}{N_t'v\mathbf{r}} \qquad (3\text{-}25)$$

Example 3-4   Acetaldehyde vapor is decomposed in an *ideal* tubular-flow reactor according to the reaction

$$CH_3CHO \rightarrow CH_4 + CO$$
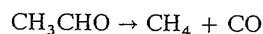
The reactor is 3.3 cm ID and 80 cm long and is maintained at a constant temperature of 518°C. The acetaldehyde vapor is measured at room temperature and slightly above atmospheric pressure. For consistency, the measured flow rate is corrected to standard conditions (0°C and 1 atm) before the space velocity is reported. In one run, at a reported space velocity of 8.0 hr^{-1}, 35% of the acetaldehyde is decomposed in the reactor. The second-order specific-rate constant is 0.33 liter/(sec)(g mole) at 518°C, and the reaction is irreversible. The pressure is essentially atmospheric. Calculate the actual residence time and compare it with the space time determined from Eq. (3-21).

Solution   The rate equation may be written

$$\mathbf{r} = k[CH_3CHO]^2 = \text{g moles/(liter)(sec)}$$

At a point in the reactor where the conversion is x, the molal flow rates are

$$CH_3CHO = F(1 - x)$$

$$CH_4 = Fx$$

$$CO = Fx$$
$$N_t' = F(1 + x)$$

The molal concentration of CH_3CHO is the ratio of $F(1 - x)$ to the total volumetric flow rate Q_t,

$$[CH_3CHO] = \frac{F(1 - x)}{Q_t} = \frac{F(1 - x)p_t}{N_t R_g T} = \frac{1 - x}{1 + x} \frac{p_t}{R_g T}$$

Then the rate in terms of x is

$$r = k\left(\frac{1 - x}{1 + x}\right)^2 \left(\frac{p_t}{R_g T}\right)^2$$

Under perfect-gas conditions the volume per mole of reaction mixture will be

$$v = \frac{1 R_g T}{p_t}$$

and

$$N_t' = F(1 + x)$$

Substituting these values for r, v, and N_t' in Eq. (3-25) gives

$$\theta = F \int_0^{x_2} \frac{p_t(1 + x)^2 \, dx}{F(1 + x)R_g Tk(1 - x)^2 (p_t/R_g T)^2}$$

$$= \frac{R_g T}{p_t k} \int_0^{x_2} \frac{(1 + x) \, dx}{(1 - x)^2} = \frac{R_g T}{p_t k} \left[\frac{2}{1 - x} + \ln(1 - x)\right]_0^{x_2 = 0.35}$$

$$= \frac{0.082(518 + 273)}{1(0.33)} \left[\frac{2}{1 - 0.35} + \ln(1 - 0.35) - 2\right] = 127 \text{ sec}$$

The space time, from Eq. (3-21), is

$$\theta_F = \frac{1}{\vartheta_F} = \frac{1}{8.0} = 0.125 \text{ hr} \qquad \text{or } 450 \text{ sec}$$

The major difference between θ and θ_F arises because the space velocity was based on a flow rate at a standard temperature of 273°C. If the density of feed ρ_F were based on the actual reaction temperature of 518°C (791°K), the residence time would be much lower. Thus if the space velocity were corrected to the reactor temperature, it would be

$$\vartheta_F \text{ (at 791°K)} = 8.0 \frac{\rho_F \text{(at 273°K)}}{\rho_F \text{(at 791°K)}} = 8.0\left(\frac{791}{273}\right) = 23.2 \text{ hr}^{-1}$$

and the space time would be

$$\theta_F = \frac{1}{23.2}(3{,}600) = 155 \text{ sec}$$

The difference between this value and the actual θ (127 sec) is due to the increase in the number of moles occurring as a result of reaction.

3-7 Temperature Effects

In a few cases the heat of reaction is so low that heat exchange with the surroundings is sufficient to eliminate temperature changes. The design problem for such isothermal reactors is greatly simplified because the variation in rate of reaction with temperature need not be considered. The isomerization of n-butane (ΔH at 25°C = -1600 cal/g mole) is an example of this class of reactions. Even when the heat of reaction is moderate, it may be possible to approach isothermal operation by adding or removing heat from the reactor. In the sulfuric acid alkylation process for producing iso-octane from isobutane and butenes the heat of reaction is about $-17,000$ cal/g mole at 25°C. However, by cooling the liquid mixture in the reactor with external cooling jackets it is possible to reduce the temperature variation to 20 to 40°F.

When the heat of reaction is large, sizable temperature variations may be present even though heat transfer between the reactor and surroundings is facilitated. In such cases it is necessary to consider the effect of temperature on the rate of reaction. Reactors operating in this fashion are termed *nonisothermal* or *nonadiabatic*.

Reactors (both flow and batch) may also be insulated from the surroundings so that their operation approaches adiabatic conditions. If the heat of reaction is significant, there will be a change in temperature with time (batch reactor) or position (flow reactor). In the flow reactor this temperature variation will be limited to the direction of flow; i.e., there will be no radial variation in a tubular-flow reactor. We shall see in Chap. 13 that the design procedures are considerably simpler for adiabatic operation.

In addition to heat exchange with the surroundings, there are other methods of approaching isothermal operating conditions. For example, in the dehydrogenation of butylenes to butadiene the temperature must be maintained at a rather high level (1200 to 1400°F) for a favorable equilibrium conversion. However, the endothermic nature of the reaction means that the reaction mixture will cool as it flows through the reactor bed. It is both difficult and expensive to transfer heat to the reaction mixture at this high temperature level by external heating. Instead, high-temperature steam is added directly to the butenes entering the reactor. The large quantity of steam serves to maintain the reaction mixture at a high temperature level.[1] Another device frequently employed for tank reactors is internal cooling

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[1] Steam has other advantages; in particular, it reduces polymerization.

or heating coils. A modification of the same principle is illustrated by the Downs[1] reactor for the oxidation of naphthalene to phthalic anhydride. The flow reactor is divided into a large number of small tubes rather than a single large-diameter tube. Each small tube is surrounded with cooling fluid which absorbs the heat of reaction. In this particular operation boiling mercury is employed as the cooling medium. Under actual operating conditions some naphthalene is oxidized completely to carbon dioxide and water vapor, so that the heat of reaction per gram mole of naphthalene is as high as $-570,000$ cal.

In summary, the operation of commercial reactors falls into three categories: isothermal, adiabatic, and the broad division of nonadiabatic, where attempts are made to approach isothermal conditions, but the magnitude of the heat of reaction or the temperature level prevents attaining this objective. Quantitative calculations for isothermal and nonisothermal homogeneous reactors are given in Chaps. 4 and 5.

3-8 Mechanical Features

Batch Reactors   The batch reactor is a kettle or tank, or it may be a closed loop of tubing provided with a circulating pump. It should have a number of accessories to be operated satisfactorily. It generally must be closed, except for a vent, to prevent loss of material and danger to the operating personnel. For reactions carried out under pressure the vent is replaced by a safety valve.

High-pressure conditions frequently introduce complications in the design and greatly increase the initial cost. For tanks the top closure must be able to withstand the same maximum pressure as the rest of the autoclave. At medium pressures a satisfactory closure can be assembled by using bolts or studs and suitable flanges and gaskets. The seal is obtained by tightening the six or more bolts holding the flange to the head. Such a closure is illustrated in the batch reactor shown in Fig. 3-5. For higher pressure (above approximately 5,000 psia) this type of construction is not desirable because of the very high stresses that the bolts must withstand. The preferred design is one in which the pressure itself seals the vessel, and increases in pressure do not cause a corresponding increase in stress in the bolts. An example of this self-sealing closure is shown in Fig. 3-6. The pressure acting on the head is transmitted to the gasket, which is confined by the reactor wall, the head, and a retaining ring. The internal pressure pushes the head against the gasket, augmenting the force exerted by the bolts through the lifting collar. The problems encountered in designing batch

[1] C. R. Downs, *Ind. Eng. Chem.*, 32, 1294 (1940); U.S. Patent 1.604,739, 1926.

Top cover
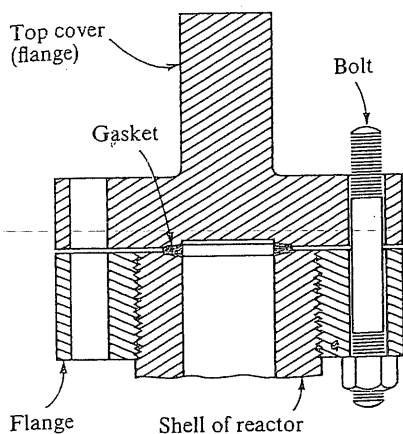(flange)

Bolt

Gasket

Flange   Shell of reactor

Fig. 3-5   Conventional flange-and-bolt closure for batch reactor

reactors for medium- and high-pressure operation have been studied in some detail.[1] Loop reactors are well suited for high pressure, because the tubing has a smaller diameter than a tank.

It is necessary to agitate the reaction mixture in tank reactors. This can be done mechanically with stirrers operated by a shaft extending through the reactor wall. In high-pressure reactors rather complicated packing glands are needed around the shaft to prevent leakage. A typical design is illustrated in Fig. 3-7, where the mechanical details of a reactor, which is also jacketed, are shown.

[1] D. B. Gooch, *Ind. Eng. Chem.*, 35, 927 (1943); E. L. Clark, P. L. Golber, A. M. Whitehouse, and H. H. Storch, *Ind. Eng. Chem.*, 39, 1955 (1947); F. D. Moss, *Ind. Eng. Chem.*, 45, 2135 (1945).
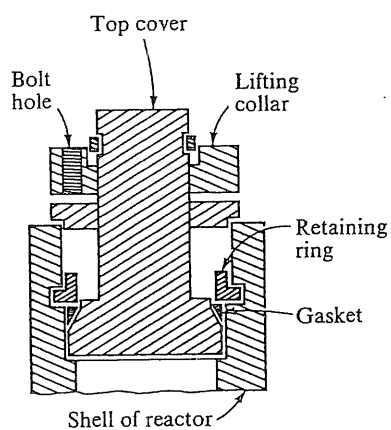
Top cover

Bolt
hole

Lifting
collar

Retaining
ring

Gasket

Shell of reactor

Fig. 3-6   Closure for high-pressure batch reactor

Motor reducer

Flexible coupling

Timken bearings

Water cooled stuffing box

Internal bearing

High pressure packing

High tensile steel bolts

Forged steel cover

Connection for gauges

Charging opening

Lubricant sealing gland

Vent connection

Steam inlet connection

Thermometer well

2'–6" I.D.

Blow pipe

Forged steel body

Support lugs

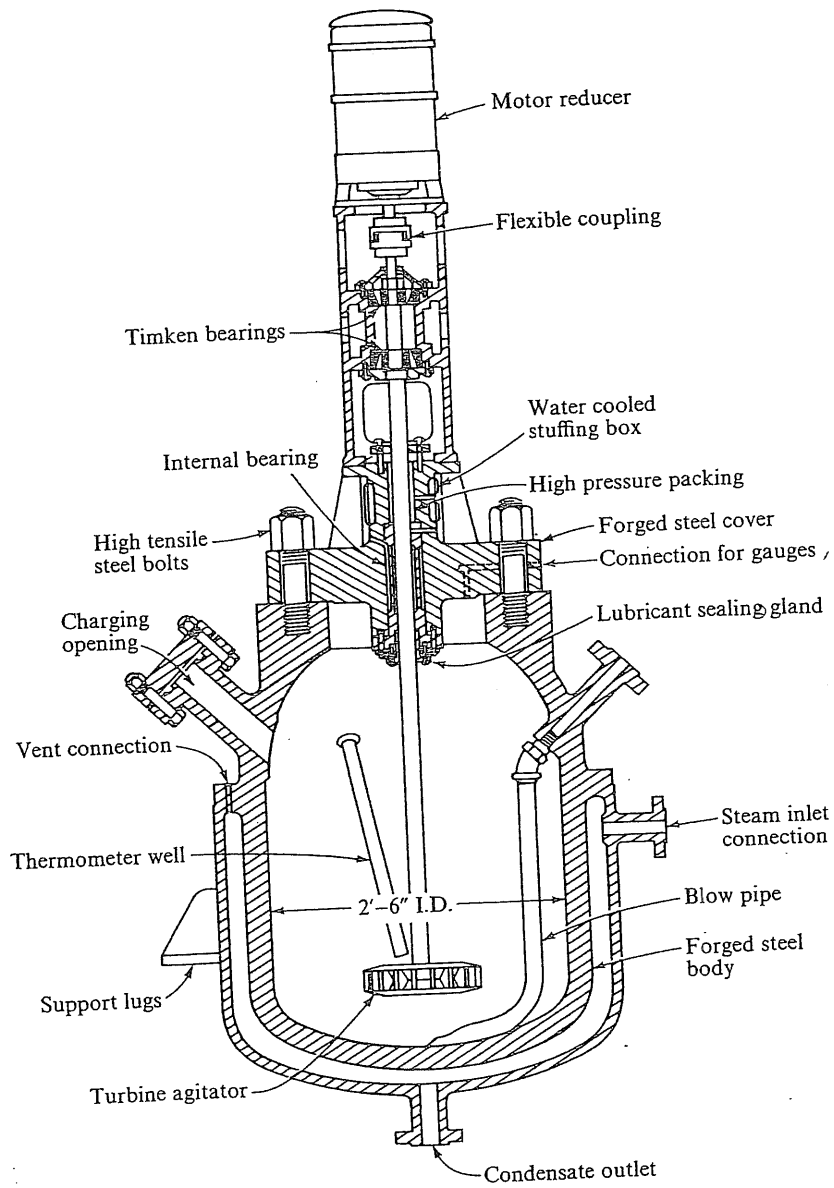Turbine agitator

Condensate outlet

Fig. 3-7   Jacketed batch reactor [*by permission from D. B. Gooch*, Ind. Eng. Chem., *35, 927 (1943)*]

Batch reactors vary in construction from ordinary steel tanks to glass-lined equipment, depending on the properties of the reaction mixture for which they are to be used. In pilot-plant operations either stainless-steel or glass-lined reactors are ordinarily used because of their corrosion resistance, and hence their general applicability to a variety of systems. In commercial-scale equipment it may be more economical to use ordinary steel even though corrosion is significant. In the food and pharmaceutical industries it is frequently necessary to use glass-lined or stainless-steel equipment to ensure purity of the product.[1]

Flow Reactors Flow reactors may be constructed in a number of ways. The conventional thermal cracking units in the petroleum industry are examples of a noncatalytic type. The petroleum fraction is passed through a number of lengths of alloy-steel tubes placed in series on the walls and roof of a furnace. Heat is transferred by convection and radiation to the tube surface in order to raise the temperature of the fluid to the reaction level (600 to 1300°F) and to supply the endothermic heat of reaction. Flow reactors may consist of a tank or kettle, much like a batch reactor, with provision for continuously adding reactants and withdrawing product. The tank type is not suitable for reactions such as thermal cracking, where large quantities of thermal energy must be supplied, because of the low-heat-transfer surface per unit volume of reactor. Tank-type flow reactors are advantageous for conversions that require a long reaction time. In such reactors it is possible to obtain essentially complete mixing by mechanical agitation. Under these conditions the composition, temperature, and pressure are uniform through the vessel. In the tubular type, where the length is generally large with respect to the tube diameter, the forced velocity in the direction of flow is sufficient to retard mixing in the axial direction; that is, it is possible to approach plug-flow performance.

A large number of commercially important reactions are of the fluid-solid catalytic class. Examples are the catalytic cracking of petroleum, oxidation of sulfur dioxide, ammonia synthesis, dehydrogenation of butenes to butadiene, and oxidation of naphthalene to phthalic anhydride. In this group of reactions the solid catalyst may be held in a fixed position while the fluid moves through it (fixed-bed reactors), or much smaller catalyst particles may be suspended in the fluid phase by the motion of the fluid (fluidized-bed reactor), or the solid particles may be in point-to-point contact and fall slowly by gravity through the fluid (moving-bed reactor).

[1]See J. H. Perry, "Chemical Engineers' Handbook," McGraw-Hill Book Company, New York, 1950.

A fixed-bed reactor built as a single large-diameter tube is less costly than a multitubular design. However, the latter arrangement may be required when large quantities of heat must be transferred to the surroundings, as in the case of a highly exothermic reaction. The smaller the tube diameter, the larger the ratio of heat-transfer surface to mass of reaction mixture in the tube, and the easier it is to limit temperature changes between inlet and exit. Of course, the low capacity of small tubes means that a larger total number of tubes must be built into the reactor in parallel to achieve a given production rate. Other means of preventing large temperature variations in fixed-bed reactors may be used. In addition to the devices suggested earlier, the catalyst bed may be divided into sections, with heating or cooling coils placed between each section.

All these devices to reduce temperature gradients in the fixed-bed reactor are corrective rather than preventive. In solid catalytic reactors the potentially large temperature variations in the direction of flow are due to the fact that the solid catalyst is unable to mix and reach a more uniform temperature. Near the entrance to the bed the rate of reaction is high and large quantities of heat are evolved (for an exothermic reaction), while near the exit, where the rate is low, there is a relatively small evolution of heat. Because the heat-transfer rate from pellet to pellet and between pellet and gas is small, each layer of catalyst in the bed is, in effect, partially insulated from adjacent layers. This effectively prevents the flow of heat from the entrance to the exit of the catalyst bed, which in turn causes significant temperature gradients. The fluidized-bed reactor does away with the source of this difficulty, the stationary condition of the bed. The rapid movement of the small catalyst particles goes a long way toward eliminating temperature variations within the solid phase. Any one particle may be near the entrance of the reactor at one instant and near the exit at the next. This rapid mixing tends to equalize both fluid- and solid-phase temperatures, so that the entire reactor system approaches a uniform temperature. The small size (generally 5 to 100 microns) of the fluidized particles provides a large heat-transfer area per unit mass and in this way increases the heat-transfer rates between solid and gas phases. Although the resultant motion of the gas is upward through the reactor, usually neither plug-flow nor complete mixing describes the flow pattern (see Chap. 13).

An important advantage of the fluidized-bed reactor over the fixed-bed type is that the catalyst can be regenerated without disturbing the operation of the reactor. In fluidized-bed catalytic cracking units a portion of the solid particles is continuously removed from the reactor and regenerated in a separate unit. The regeneration is accomplished by burning off the carbon with air, and the reactivated catalyst is continuously returned to the reactor proper. In the fixed-bed reactor the closest approach to

continuous operation obtainable with a catalyst of limited life is to construct two or more identical reactors and switch streams from one to the other when the catalyst needs to be regenerated.

A disadvantage of fluidized-bed reactors is that the equipment is large. So that the solid particles will not be blown out the top of the reactor, the gas velocity must be low. This in turn necessitates large-diameter vessels and increases the initial cost. There are also losses of catalyst fines from the reactor, necessitating expensive dust-collection equipment in the exit streams.

Moving-bed systems do not permit the uniformity of temperature achieved in fluidized-bed reactors, but they do allow continuous handling of the solid phase. This is advantageous in some operations, such as catalyst or adsorbent regeneration. For example, the regeneration of the charcoal adsorbent for the hypersorption process[1] of separating hydrocarbons has been accomplished in a moving-bed reactor. The deactivated charcoal is added to the top of the regenerator, and steam is passed upward through the slowly moving bed of solid to strip out and react with the adsorbed hydrocarbons. Moving-bed systems are also employed for fluid-solid noncatalytic reactions; e.g., blast furnaces, lime kilns, and smelters (see Chap. 14).
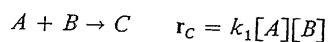
Problems

3-1. A pellet of uranium dioxide actually consists of a mixture of UO_2 and UO_3 with a composite formula $UO_{2.14}$. The pellet is reacted with HF gas, and the extent of reaction is followed by weighing the pellet at successive time increments. The reactions are

1. $UO_2(s) + 4HF(g) \rightarrow UF_4(s) + 2H_2O(g)$

2. $UO_3(s) + 2HF(g) \rightarrow UO_2F_2(s) + H_2O(g)$
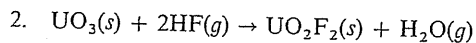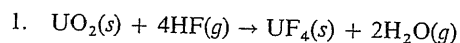
Derive a relationship between the initial weight of the pellet, m_0, its weight at any time, m, and a composite conversion expressed as the fraction of $UO_{2.14}$ reacted.

3-2.† Desired product C is produced in an ideal tubular-flow reactor by the second-order reaction

$$A + B \rightarrow C \qquad r_C = k_1[A][B]$$

Unwanted product A_2 is also produced by a second-order reaction

$$A + A \rightarrow A_2 \qquad r_{A_2} = k_2[A]^2$$

For the maximum selectivity of C to A_2 it is necessary to keep the concentration

[1] Clyde Berg, *Trans. AIChE*, 42, 685 (1946).
† This problem was supplied by Professor J. B. Butt.

of A as low as possible. To approach this ideal, only B is added to the inlet to the reactor, and A is added uniformly along the length, as indicated in the figure. The molal flow rate of B is $Q_B[B]_0$, where Q_B is the volumetric flow rate entering the reactor and $[B]_0$ is the concentration of B in the feed. Reactant A is added

Continuous, uniform addition of A
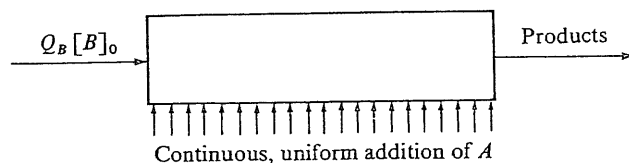
through the reactor wall in a stream whose concentration is $[A]_0$. The uniform rate of addition of this stream is dQ_A/dV, as volumetric flow rate per unit volume of reactor. Assuming that the density is constant, write mass balances for reactants A and B for this reactor operating at steady state.

3-3. (a) An endothermic gaseous reaction is carried out in an ideal tubular-flow reactor operated adiabatically. If the heat capacity of the reaction mixture is constant, develop an integrated relationship [starting with Eq. (3-18)] between the conversion and temperature at any axial position in the reactor. The feed temperature is T_0 and the conversion in the feed is zero. (b) To reduce the temperature drop along the reactor it is proposed to add inert nitrogen at temperature T_0 to the feed. If sufficient nitrogen is added to double the heat capacity of the reaction mixture, how much will the temperature drop be reduced?

3-4. In an otherwise ideal stirred-tank reactor it is estimated that 10% of the reactor volume is occupied by stagnant fluid (Fig. 3-3a). If the reactor had no stagnant regions, the conversion in the effluent stream would be 60%. What conversion is expected in the actual reactor?

3-5. In studying the kinetics of the homogeneous gas-phase reaction between sulfur vapor and methane, Fisher[1] reported conversions for various space velocities. These space velocities were defined as the volumetric flow rate in milliters per hour divided by the total volume of empty reactor in cubic centimeters. The flow rate is based on all the sulfur being considered S_2 and is referred to 0°C and 1 atm pressure.

From the fact that the operating pressure was 1.0 atm and the temperature 600°C, compute the values of V/F corresponding to the space velocities given in the reference for runs 55, 58, 57, 78, and 79. V/F is the ratio of the volume of reactor to the molal feed rate, in gram moles per hour. Also determine the true contact time for a slug of reaction mixture for each of the runs; i.e., the time it takes for a slug of gas to pass through the reactor.[2]

3-6. The production of toluene from benzene and xylenes was studied by Johanson and Watson[3] in a standard 1-in.-pipe reactor, with a silica-alumina catalyst. At the reactor temperature of 932°F the reaction mixture is in the vapor phase.

[1] R. A. Fisher, *Ind. Eng. Chem.*, 42, 704 (1950).

[2] See Fisher's work (or Table 4-5) for the conversion values for the runs.

[3] L. N. Johanson and K. M. Watson, *Natl. Petrol. News*, Aug. 7, 1946.

However, the benzene and xylenes were measured and pumped separately into the system as liquids by means of a proportioning pump. Hence the space velocity was reported on a liquid-hourly basis; that is, as the ratio of the feed rate, in cubic centimeters of liquid per hour, to the total volume of the reactor, in cubic centimeters. The feed consisted of an equimolal mixture of reactants, and the liquid rates were corrected to 60°F before reporting the following information:

Liquid-hourly space velocity, hr^{-1}	0.5	0.25	1.0	2.0	2.0	4.0
Reactor pressure, psia	20	20	65	65	115	115

The reactor contained 85 g of catalyst packed in a volume of 135 cm³, and the densities of benzene and xylenes at 60°F may be taken as 0.879 and 0.870 g/cm³, respectively.

From the data determine corresponding ratios of mass of catalyst to feed rate, expressed in units of g catalyst/[(g mole)/(hr)].

3-7. Convert the liquid-hourly space velocities in Prob. 3-6 to a gas basis, that is, to space velocities defined as the ratio of the gas-flow rate at reaction conditions to the total reactor volume. Then calculate the actual contact time for each run. The gases may be assumed to obey the perfect-gas law. The reaction does not result in a change in number of total moles,

$$C_6H_6 + C_6H_4(CH_3)_2 = 2C_6H_5CH_3$$