4

HOMOGENEOUS REACTOR DESIGN: ISOTHERMAL CONDITIONS

The conservation principles applied to mass and energy were used in Chap. 3 to develop equations for *ideal* forms of batch and flow reactors. Now that we have some knowledge of kinetics of homogeneous reactions (Chap. 2), we can design ideal batch, tubular-flow, and tank reactors. Isothermal behavior is considered here; nonisothermal operation is in Chap. 5. Non-ideal flow complications are taken up in Chap. 6 for homogeneous reactions. Physical resistances are usually most significant for heterogeneous reactions (for example, fluid-solid catalytic reactions) carried out in tubular-flow reactors. Hence a more general approach to tubular-flow reactors, which includes the effect of mass- and energy-transfer resistances, is given in Chap. 13.

There are *homogeneous* reactions of commercial importance of both the catalytic and the noncatalytic type. For example, one process for the production of ethylene dichloride consists of the reaction between ethylene

and chlorine in the presence of bromine, with all three materials in the vapor phase. The bromine reacts with chlorine to form the unstable bromine chloride, which behaves as a catalyst in accordance with the following reactions:

1. $C_2H_4 + BrCl \rightarrow C_2H_4BrCl$

2. $C_2H_4BrCl + Cl_2 \rightarrow C_2H_4Cl_2 + BrCl$

Illustrations of noncatalytic homogeneous reactions are numerous and include the thermal cracking of hydrocarbons, the combustion of gaseous fuels such as natural gas, and various inorganic reactions in aqueous solutions.

IDEAL BATCH REACTORS

Batch reactors are seldom employed on a commercial scale for gas-phase reactions because the quantity of product that can be produced in a reasonably sized reactor is small. The chief use of batch systems for gaseous reactions is in kinetic studies. Batch reactors are often used, however, for liquid-phase reactions, particularly when the required production is small. Batch reactors are generally more expensive to operate than continuous units for the same production rate. However, the initial cost of a continuous system may be higher owing to the instrumentation required. Therefore, for relatively high-priced products (such as pharmaceuticals) where operating expense is not a predominant factor in the total cost, batch reactors are commonly employed.

4-1 Simplified Design Equation for Constant Volume

In Chap. 3 Eq. (3-10) was developed to relate conversion and time in a batch reactor. If the volume of the reaction mixture (i.e., the density) is constant, this expression can be written in a simpler way in terms of concentration. At constant volume the conversion and concentration of *reactant* are related by

$$x = \frac{C_0 - C}{C_0} \tag{4-1}$$

where C_0 is the initial concentration and is equal to m/V. Equation (3-10) then becomes

$$t = C_0 \int_0^x \frac{dx}{r} = -\int_{C_0}^C \frac{dC}{r} \tag{4-2}$$

Note that the differential form of Eq. (4-2),

$$r = -\frac{dC}{dt}$$

is identical to Eq. (2-4), which was used throughout Chap. 2 to interpret laboratory kinetic data.

4-2 Design Procedure

The difficulty in integrating Eqs. (3-10) and (4-2) depends on the number of variables influencing the rate of reaction. For example, if the rate of formation of the desired product depends on only one irreversible reaction, the expression for r will be simpler than if reversible or multiple reactions are involved. The integration of Eq. (4-2) for various reaction networks under constant-temperature conditions was considered in Chap. 2. At that point the objective was determination of the rate constant k. In reactor design the situation is reversed: k, and hence r, is known, and it is the time necessary to obtain a given conversion that is required.

    The following example concerning the rate of esterification of butanol and acetic acid in the liquid phase illustrates the design problem of predicting the time-conversion relationship for an isothermal, single-reaction, batch reactor.

Example 4-1   Leyes and Othmer[1] studied the formation of butyl acetate in a batch-operated reactor at 100°C, with sulfuric acid as catalyst. The original feed contained 4.97 moles butanol/mole acetic acid, and the catalyst concentration was 0.032% by weight H_2SO_4. The following rate equation was found to correlate the data when an excess of butanol was used:

$$r = k[A]^2$$

where $[A]$ is concentration of acetic acid, in gram moles per milliliter, and r is the rate of reaction, in gram moles of acid disappearing per milliliter per minute. For a ratio of butanol to acid of 4.97 and a sulfuric acid concentration of 0.032% by weight, the reaction-velocity constant was

$$k = 17.4 \text{ ml/(g mole)(min)}$$

    Densities of mixtures of acetic acid, butanol, and butyl acetate are not known. Reported densities for each of the three compounds at 100°C were

Acetic acid $= 0.958$ g/ml
Butanol $= 0.742$
Butyl acetate $= 0.796$

Although the density of the reaction mixture varies with conversion, the excess of

[1] C. E. Leyes and D. F. Othmer, *Ind. Eng. Chem.*, 36, 968 (1945).

butanol reduces the magnitude of the change. Therefore, as an approximation, the density of the mixture was assumed constant and equal to 0.75 g/ml.

(a) Calculate the time required to obtain a conversion of 50%. (b) Determine the size of reactor and the original mass of reactants that must be charged to the reactor in order to produce ester at the average rate of 100 lb/hr. Only one reactor will be used, and this unit will be shut down 30 min between batches for removal of product, cleaning, and startup. Assume that the reaction mixture is well mixed.

Solution The molecular weights are

Ester = 116
Butanol = 74
Acetic acid = 60

(a) The concentration of acetic acid, $[A]$, is related to the conversion by

$$[A] = [A]_0(1 - x)$$

where $[A]_0$ is the initial acid concentration. Substituting this expression in the rate equation gives

$$r = k[A]_0^2(1 - x)^2$$

The design expression [Eq. (4-2)], which is applicable at constant volume or density, can be written in terms of the variables t and x as

$$t = [A]_0 \int_0^{x_1} \frac{dx}{k[A]_0^2(1 - x)^2} = \frac{1}{k[A]_0} \int_0^{x_1} \frac{dx}{(1 - x)^2} \tag{A}$$

Integrating and substituting a final value of $x_1 = 0.50$ lead to the result

$$t = \frac{1}{k[A]_0} \left(\frac{1}{1 - x_1} - \frac{1}{1 - 0} \right) = \frac{1}{k[A]_0}(2 - 1) = \frac{1}{k[A]_0} \tag{B}$$

The initial concentration of acetic acid is[1]

$$[A]_0 = \frac{1(0.75)}{4.97(74) + 1(60)} = 0.0018 \text{ g mole/ml}$$

From Eq. (B), the time required for a conversion of 50% is

$$t = \frac{1}{17.4(0.0018)} = 32 \text{ min} \qquad \text{or } 0.53 \text{ hr}$$

(b) The production rate of the reactor, in pounds of ester per hour, in terms of the pounds of acid charged, m_A, will be

$$100 = \frac{(m_A/60)(116)(0.5)}{0.53 + 0.50}$$

[1] Note that in this example r and x and the concentration are expressed in molar units rather than mass units. Design equations can be used with either molar or mass units as long as r and x are consistent.

This expression allows 30 min for shutdown time per charge and takes into account that the conversion is 50%. Thus

$m_A = 106$ lb acetic acid/charge
Total charge $= 106 + 4.97(\frac{74}{60})(106) = 756$ lb

The volume occupied by the charge will be

$$V = \frac{756}{0.75(62.4)(0.1337)} = 121 \text{ gal}$$

The reactor must be large enough to handle 121 gal of reaction mixture. The charge would consist of 106 lb of acid and 650 lb of butanol.

When the rate of the reverse reaction is significant (i.e., when equilibrium is approached in the reactor) or when more than one reaction is involved, the mechanics of solving the design equation may become more complex, but the principles are the same. Equation (4-2) is applicable, but the more complicated nature of the rate function may make the mathematical integration difficult.

The calculations for a reversible reaction are illustrated in Example 4-2 for the esterification of ethyl alcohol.

Example 4-2   In the presence of water and hydrochloric acid (as a catalyst) the rate of esterification, in g moles/(liter)(min), of acetic acid and ethyl alcohol at 100°C is given by

$$r_2 = k[H][OH] \qquad k = 4.76 \times 10^{-4} \text{ liter/(min)(g mole)}$$

The rate of the reverse reaction, the hydrolysis of the ester in the same concentration of catalyst, is

$$r_2' = k'[E][W] \qquad k' = 1.63 \times 10^{-4} \text{ liter/(min)(g mole)}$$

$$CH_3COOH + C_2H_5OH \underset{k'}{\overset{k}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$
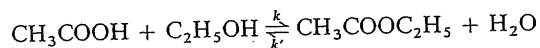
(a) A reactor is charged with 100 gal of an aqueous solution containing 200 lb of acetic acid, 400 lb of ethyl alcohol, and the same concentration of HCl as used to obtain the reaction-velocity constants. What will be the conversion of acetic acid to ester after 120 min of reaction time? The density may be assumed constant and equal to 8.7 lb/gal; neglect the water vaporized in the reactor. (b) What is the equilibrium conversion?

Solution   (a) The net rate of formation of acid is obtained by combining the rate expressions for the forward and reverse reactions,

$$r = k[H][OH] - k'[E][W]$$

The initial concentrations of acid H, alcohol OH, and water W are as follows:

$$[H]_0 = \frac{200}{100(60)} \frac{454(1,000)}{0.1337(30.5)^3} = 4.00 \text{ g moles/liter}$$

$$[OH]_0 = \frac{400}{100(46)} \frac{454(1,000)}{0.1337(30.5)^3} = 10.8 \text{ g moles/liter}$$

$$[W]_0 = \frac{8.7(100) - (200 + 400)}{100(18)} \frac{454(1,000)}{0.1337(30.5)^3} = 18.0 \text{ g moles/liter}$$

With the conversion based on the acid, as required by the statement of the problem, the concentrations at any time are

$$[H] = 4.0(1 - x)$$

$$[OH] = 10.8 - 4x$$

$$[E] = 4.0x$$

$$[W] = 18 + 4x$$

These relationships between concentrations and conversion rest on the assumption of a constant density during the reaction. The problem could still be solved without this assumption, provided data on the variation in density with conversion were available. Substituting the expressions for concentration in the rate equation, we have

$$r = k[4(1 - x)(10.8 - 4x)] - k'[4x(18 + 4x)]$$

The numerical values for k and k' result in the following equation for r, in g moles/(liter) (min):

$$r = (0.257 - 0.499x + 0.062x^2)(8 \times 10^{-2})$$

Substituting this in the design equation for constant volume [Eq. (4-2)] yields

$$t = \frac{[H]_0}{8 \times 10^{-2}} \int_0^{x_1} \frac{dx}{0.257 - 0.499x + 0.062x^2}$$

$$= 50 \int_0^{x_1} \frac{dx}{0.257 - 0.499x + 0.062x^2}$$

This expression can be integrated to give

$$t = \frac{50}{0.430} \left[\ln \frac{0.125x - 0.499 - 0.430}{0.125x - 0.499 + 0.430} \right]_0^{x_1}$$

$$= \frac{50}{0.430} \ln \frac{(0.125x_1 - 0.929)(0.069)}{(0.125x_1 - 0.069)(0.929)}$$

The conversion is desired for a time of 120 min. Hence

$$\frac{120(0.430)}{50} = 1.03 = \ln \frac{0.125x_1 - 0.929}{0.125x_1 - 0.069} \frac{0.069}{0.929}$$

Thus $x_1 = 0.365$, or 36.5% of the acid is converted to ester. It is interesting to compare this result with that based on neglecting the reverse reaction. Under this condition the rate equation is

$$r = k[H][OH] = k[H]_0(1 - x)([OH]_0 - [H]_0x)$$

The design equation becomes

$$t = [H]_0 \int_0^{x_1} \frac{dx}{k[H]_0(1 - x)([OH]_0 - [H]_0x)}$$

$$= \frac{1}{k[OH]_0 - [H]_0} \int_0^{x_1} \left(\frac{1}{1 - x} - \frac{[H]_0}{[OH]_0 - [H]_0x} \right) dx$$

$$= \frac{1}{k([OH]_0 - [H]_0)} \left[-\ln (1 - x_1) + \ln \frac{[OH]_0 - [H]_0x_1}{[OH]_0} \right]$$

Simplifying, we have

$$\frac{[OH]_0 - [H]_0x_1}{[OH]_0(1 - x_1)} = e^{tk([OH]_0 - [H]_0)} = e^{120(4.76 \times 10^{-4})(10.8 - 4.0)} = 1.474$$

Solving for x_1, we find

$$x_1 = \frac{0.474[OH]_0}{1.474[OH]_0 - [H]_0} = \frac{0.474(10.8)}{1.474(10.8) - 4.0} = 0.43$$

If the reverse reaction is neglected, the conversion is in error by

$$[(43 - 36.5)/36.5]100 \quad \text{or } 18\%$$

This deviation would increase as equilibrium is approached.

(b) The conventional method of evaluating the equilibrium conversion is first to calculate the equilibrium constant from the forward- and reverse-reaction rates ($K = k/k'$), and then to use this value of K for the equilibrium ratio of the concentrations. However, it is easier in this case to utilize the expression already available for the net rate of reaction,

$$r = (0.257 - 0.499x + 0.0626x^2)(8 \times 10^{-2})$$

At equilibrium the net rate must be zero. Hence the equilibrium conversion is determined by the expression

$$0.257 - 0.499x_e + 0.0626x_e^2 = 0$$

Solving, we obtain

$$x_e = 0.55 \quad \text{or } 55\%$$

In these examples it has been assumed that a negligible amount of reaction occurs during heating and cooling periods. If only one reaction

is involved, the time computed on the assumption that reaction takes place only at the operating temperature will be a conservative value. However, in reactions of industrial interest it is more likely that byproducts will be created. Then the yield of desired product will be reduced during heating and cooling cycles in a batch operation, provided an undesired reaction is favored at temperatures below the operating temperature. The magnitude of this effect will depend on the time spent for heating and cooling in relation to reaction time. In serious cases the problem may be solved by preheating the reactants separately prior to mixing, or by feeding one reactant continuously to a batch charge of the coreactant (semibatch operation). Rapid quenching after reaction may be realized by rapid discharge of the mass (blowdown) or by rapid coolant injection (directly or indirectly contacted with the product mass).

IDEAL TUBULAR-FLOW (PLUG-FLOW) REACTORS

Tubular-flow reactors are used both as laboratory units, where the purpose is to obtain a rate equation, and for commercial-scale production. In fact, it is a desirable and common practice to develop a rate equation for data obtained in a laboratory-sized reactor of the same form as the proposed large-scale unit.

4-3 Interpretation of Data from Laboratory Tubular-flow Reactors

Interpretation of data to obtain a rate equation requires calculations which are the reverse of those for design. The two procedures differ because in the laboratory it may be feasible to operate at nearly constant temperature, and possibly nearly constant composition; in the commercial unit it may be possible to approach isothermal conditions, but constant composition in a tubular-flow reactor is impossible. These differences simplify the analysis of laboratory results, as illustrated in Example 4-3.

The starting point for evaluating the rate of reaction in a *flow reactor* is Eq. (2-2),

$$r = \frac{dN'}{dV}$$

where dN' is the molal rate of production of product in a reactor volume dV. If the reactor is small enough, the change in composition of the fluid as it flows through the volume will be slight. In addition, suppose that heat-transfer conditions are such that the temperature change is also slight. Since composition and temperature determine the rate, r will also

be nearly constant throughout the reactor. In other words, a *point rate* is measured, corresponding to the average composition and temperature in the reactor. An apparatus of this type is called a *differential reactor*. Since r is a constant, integration of Eq. (2-2) is simple and gives

$$\mathbf{r} = \frac{N'}{V} \tag{4-3}$$

where V is the volume of the differential reactor. The following example illustrates how the rate is calculated and the error that is involved in assuming that it is constant.

Example 4-3   The homogeneous reaction between sulfur vapor and methane has been studied in a small silica-tube reactor of 35.2 ml volume.[1] In a particular run at 600°C and 1 atm pressure the measured quantity of carbon disulfide produced in a 10-min run was 0.10 g. Assume that all the sulfur present is the molecular species S_2. The sulfur-vapor (considered as S_2) flow rate was 0.238 g mole/hr in this steady-state run.

(a) What is the rate of reaction, expressed in g moles of carbon disulfide produced/(hr)(ml of reactor volume)? (b) The rate at 600°C may be expressed by the second-order equation

$$\mathbf{r} = k p_{CH_4} p_{S_2}$$

where p is partial pressure, in atmospheres. Use the rate determined in (a) and this form of the rate equation to calculate the specific reaction rate in units of g moles/(ml) (atm²)(hr). The methane flow rate was 0.119 g mole/hr, and the H_2S and CS_2 concentrations in the reactants were zero. (c) Also compute the value of k without making the assumption that the rate is constant and that average values of the partial pressures may be used; that is, consider the equipment to operate as an integral, rather than a differential, reactor. Compare the results and comment on the suitability of the apparatus as a differential reactor.

Solution   Consider the reaction

$$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$$
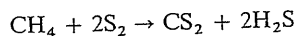
(a) The carbon disulfide formation, in gram moles per hour, is

$$N' = \frac{0.10}{76} \left(\frac{60}{10} \right) = 0.0079$$

Then the rate of reaction, according to Eq. (4-3), will be

$$\mathbf{r} = 0.0079 \left(\frac{1}{35.2} \right) = 2.2 \times 10^{-4} \text{ g mole/(hr)(ml)}$$

(b) With the assumption that at 600°C and 1 atm pressure the components

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

behave as perfect gases, the partial pressure is related to the mole fraction by the expression

$$p_{CH_4} = p_t y_{CH_4} = 1 y_{CH_4}$$

where y_{CH_4} represents the mole fraction of methane. The average composition in the reactor will be that corresponding to a carbon disulfide rate of $(0 + 0.0079)/2 = 0.0040$ g mole/hr. At this point the molal rates of the other components will be

$$CS_2 = 0.0040 \text{ g mole/hr}$$

$$S_2 = 0.238 - 2(0.0040) = 0.230$$

$$CH_4 = 0.119 - 0.0040 = 0.1150$$

$$H_2S = 2(0.0040) = 0.0079$$

$$\text{Total} = 0.357 \text{ g mole/hr}$$

The partial pressures will be

$$p_{CH_4} = \frac{0.1150}{0.357} = 0.322 \text{ atm}$$

$$p_{S_2} = \frac{0.230}{0.357} = 0.645 \text{ atm}$$

From the rate equation, using the value of r obtained in (a), we have

$$k = \frac{r}{p_{CH_4} p_{S_2}} = \frac{2.2 \times 10^{-4}}{0.322(0.645)}$$

$$= 1.08 \times 10^{-3} \text{ g mole/(ml)(atm}^2\text{)(hr)}$$

(c) If the variations in rate through the reactor are taken into account, the integral design expression developed in Chap. 3 for a tubular-flow reactor should be used; this is Eq. (3-13),

$$\frac{V}{F} = \int_0^{x_1} \frac{dx}{r} \qquad\qquad \text{(A) or (3-13)}$$

where the conversion x is based upon methane and F is the methane feed rate. At a point in the reactor where the conversion of methane is x, the molal flow rate of each component will be

$$CS_2 = 0.119x$$

$$S_2 = 0.238(1 - x)$$

$$CH_4 = 0.119(1 - x)$$

$$H_2S = 0.238x$$

$$\text{Total} = 0.357 \text{ g mole/hr}$$

With this information, the rate equation may be written in terms of x as

$$\mathbf{r} = ky_{CH_4}y_{S_2} = k\,\frac{0.119(0.238)(1 - x)^2}{0.357^2} \tag{B}$$

Equation (A) may be integrated from the entrance to the exit of the reactor by means of Eq. (B). Thus

$$\frac{V}{F} = \frac{4.5}{k}\int_0^{x_1}\frac{dx}{(1 - x)^2} = \frac{4.5}{k}\,\frac{x_1}{1 - x_1}$$

Solving for k, we have

$$k = \frac{4.5}{V/F}\,\frac{x_1}{1 - x_1}$$

The conversion of methane at the exit of the reactor, in moles of methane reacted per mole of methane in the feed, is

$$x_1 = \frac{0.0079}{0.119} = 0.0664$$

Hence the specific reaction rate is

$$k = \frac{4.5}{35.2/0.119}\left(\frac{0.0664}{1 - 0.0664}\right) = 1.08 \times 10^{-3}\ \text{g mole/(ml)(atm}^2\text{)(hr)}$$

in good agreement with the result in (b).

In the foregoing example the change in composition in the reactor is sufficiently small that a rate corresponding to the average composition may be used to evaluate the rate. In other words, the concept of a differential reactor is satisfactory. If the conversion had been considerably larger than $x = 0.066$, this would not have been true. By the type of calculation illustrated in part (c) the error in the use of the differential-reactor assumption can be evaluated for any conversion level and for any chosen reaction order. It is surprising how large the conversion may be and still introduce only a small error by the assumption of differential-reactor operation.

While the differential-reactor system was satisfactory in Example 4-3, in many cases there are difficulties with this approach. If the small differences in concentration between entering and exit streams cannot be determined accurately, the method is not satisfactory. Also, when the heat of reaction or the rate, or both, is particularly high, it may not be possible to operate even a small reactor at conditions approaching constant temperature and constant composition. It is interesting that the limitation to *ideal* flow is not significant in a differential reactor. This is because for low conversion (small composition changes) the effects of deviations from ideal flow are negligible, regardless of the cause (axial dispersion, radial velocity, or

composition gradients). When the conversion is large, this is not true; these effects are evaluated in Chap. 6.

When the conditions of approximately constant rate cannot be met, the measured conversion data will represent the integrated value of the rates in all parts of the reactor. A reactor operated in this way is termed an *integral reactor*. The problem of obtaining a rate equation is essentially one of either *differentiating* the measured conversion data to give point values of the rate, or *integrating* an assumed form for the rate equation and comparing the results with the observed conversion data. To give either process a reasonable chance of success, as many variables as possible should remain constant. The ideal situation is one in which the only variable is composition, i.e., where the temperature and pressure are the same in all parts of the reactor. This type of integral operation is just one step removed from that of a differential reactor. If both the temperature and the composition change significantly, the process of differentiating the experimental data to obtain a rate equation is of doubtful accuracy and, indeed, is seldom successful.

These conclusions concerning the ease of interpretation of laboratory data in terms of a rate equation are summarized in Table 4-1.

Table 4-1   Experimental methods of obtaining rate data for tubular-flow systems

| Type of reactor	Characteristics	Interpretation of data
Differential	Constant temperature, composition, and pressure (i.e., constant rate)	Rate data obtained directly, interpretation simple.
Integral (A)	Constant temperature and pressure (rate depends upon composition only)	Interpretation of integral data usually satisfactory by graphical differentiation or fitting of integral-conversion curves.
Integral (B)	Constant pressure only	Interpretation complicated by temperature variation; if effect of temperature on rate is known from independent measurements, interpretation possible in principle.

A complete set of integral-reactor data consists of measurements of the conversion for different flow rates through the reactor, with each run made at constant reactants ratio, pressure, and temperature (if possible). Then an additional set of conversion-vs-flow runs is made at a different reactants ratio but the same pressure and temperature. This procedure is continued until data are obtained over the entire range of reactants

ratio, temperature, and pressure that may be employed in the commercial reactor. A useful means of summarizing the results is to prepare graphs of V/F vs conversion at constant values of reactants ratio and p. Such graphs for representing the experimental data are suggested by the form of the design equation for flow reactors [Eq. (3-13)]. The shape of these curves is determined by the nature of the rate, and they provide some qualitative information about the rate equation.

The two procedures for treating integral-reactor data are equivalent to the integration and differential methods first described in Chap. 2 for batch systems. In the integration approach, a rate equation is assumed and then the design expression is integrated. This integration gives a relationship between V/F and x which may be compared with the experimental data. The final step is the choice of the rate equation that gives the best agreement with the experimental V/F-vs-x curves for all conditions of reactants ratio, temperature, and pressure. The differential method entails differentiating the V/F-vs-x curves graphically to obtain the rate of reaction as a function of composition. Various assumed rate equations can then be tested for agreement with the rate-vs-composition data.

Perhaps the clearest way of explaining these methods of interpreting laboratory data is to carry out specific examples in some detail, pointing out the features of the method which are general and applicable to any reaction. In Example 4-4 the integration and differential methods are applied to a single-reaction system. Example 4-5, which is concerned with the homogeneous reaction of sulfur vapor and methane to produce carbon disulfide, involves multiple reactions.

Example 4-4   A kinetic study is made of the decomposition of acetaldehyde at 518°C and 1 atm pressure in a flow apparatus. The reaction is

$$CH_3CHO \rightarrow CH_4 + CO$$
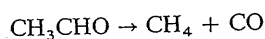
Acetaldehyde is boiled in a flask and passed through a reaction tube maintained by a surrounding furnace at 518°C. The reaction tube is 3.3 cm ID and 80 cm long. The flow rate through the tube is varied by changing the boiling rate. Analysis of the products from the end of the tube gives the results in Table 4-2.

Table 4-2

Rate of flow, g/hr	130	50	21	10.8
Fraction of acetaldehyde decomposed	0.05	0.13	0.24	0.35

What is a satisfactory rate equation for these data?

Solution A second-order rate equation, $\mathbf{r} = k_2[A]^2$, will be tested by both the integral and the differential methods. To utilize either, it is necessary to express the rate in terms of the conversion of acetaldehyde. This may be accomplished by applying material balances and the ideal-gas law.

The molal flow rate of acetaldehyde entering the reaction tube is F. At a point where the conversion is x it will be

$$N_A' = F - Fx$$

The molal rates of the other components will be

$$N_{CH_4}' = xF$$

$$N_{CO}' = xF$$

Total flow rate $N_t' = F(1 + x)$

From the ideal-gas law,

$$[A] = \frac{N_A'}{Q} = \frac{N_A'}{N_t' R_g T/p_t} = \frac{N_A'}{N_t'} \frac{p_t}{R_g T} = \frac{1-x}{1+x} \frac{p_t}{R_g T}$$

The second-order rate expression in terms of conversion is

$$\mathbf{r} = k_2[A]^2 = k_2 \left(\frac{p_t}{R_g T}\right)^2 \left(\frac{1-x}{1+x}\right)^2 \tag{A}$$

INTEGRATION METHOD   Equation (A) may be substituted in the design expression, Eq. (3-13), to evaluate the second-order assumption:

$$\frac{V}{F} = \frac{1}{k_2(p_t/R_g T)^2} \int_0^{x_1} \frac{dx}{[(1-x)/(1+x)]^2}$$

Integration yields

$$k_2 \left(\frac{p_t}{R_g T}\right)^2 \frac{V}{F} = \frac{4}{1-x} + 4\ln(1-x) + x - 4 \tag{B}$$

which provides the relationship between V/F and x to be tested with the experimental data. Since

$$V = \pi \frac{3.3^2}{4}(80) = 684 \text{ cm}^3$$

the experimental data may be expressed in terms of V/F, as shown in Table 4-3. Equation (B) may be used to compute a value of k for each of the sets of x and V/F values given in the table. For example, at $x = 0.13$, substituting in Eq. (B), we obtain

$$k_2 \left[\frac{1}{0.082(518 + 273)}\right]^2 (2,160) = \frac{4}{1 - 0.13} + 4\ln(1 - 0.13) + 0.13 - 4$$

$$k_2 = 0.33 \text{ liter/(g mole)(sec)}$$

Table 4-3

Conversion	Feed rate		V/F, (liters)(sec)/g mole	k_2, liters/(g mole)(sec)
	g/hr	$g\,moles/sec$		
0.05	130	0.000825	828	0.32
0.13	50	0.000316	2,160	0.33
0.24	21	0.000131	5,210	0.32
0.35	10.8	0.0000680	10,000	0.33

Values of k_2 for the other three sets, shown in the last column of the table, are in good agreement with each other.

DIFFERENTIAL METHOD   The experimental V/F data are plotted against conversion in Fig. 4-1. According to Eq. (3-13), the slope of this curve at any conversion gives the rate of reaction at that point. The slopes of the curve at the experimental conversions are given in the second column of Table 4-4. These slopes may be compared with the assumed rate equation either by plotting ln r vs ln $[(1 - x)/(1 + x)]$ according to Eq. (A) and noting whether or not a straight line of slope 2 is obtained, or by computing values of k_2 directly from Eq. (A). Following this second procedure, at $x = 0.13$ we have

$$r = 4.9 \times 10^{-5} = k_2 \left[\frac{1}{0.082(791)} \right]^2 \left(\frac{1 - 0.13}{1 + 0.13} \right)^2$$

$$k_2 = 0.35 \ \text{liter/(g mole)(sec)}$$

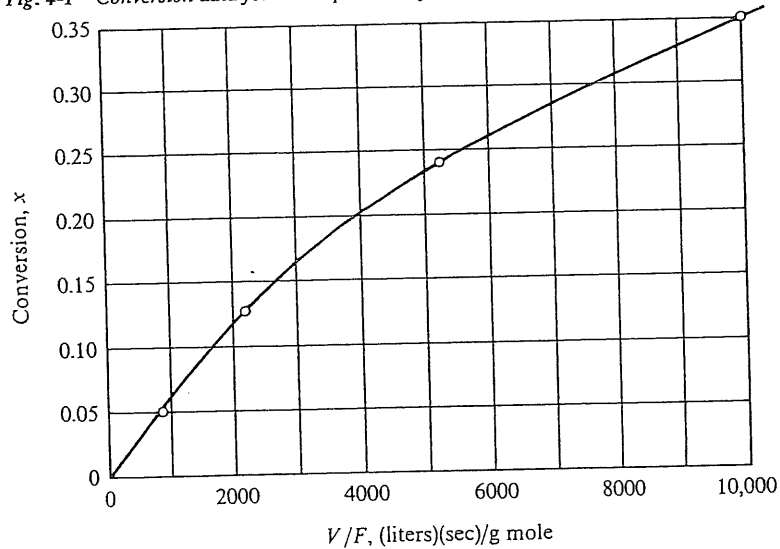*Fig. 4-1*   *Conversion data for decomposition of acetaldehyde*

V/F, (liters)(sec)/g mole

Table 4-4

Conversion	Slope from Fig. 4-1, g moles/(liter)(sec)	k_2, liters/(sec)(g mole)	k_1, sec^{-1}
0.05	6.2×10^{-5}	0.32	0.0045
0.13	4.9×10^{-5}	0.35	0.0041
0.24	2.8×10^{-5}	0.33	0.0030
0.35	2.0×10^{-5}	0.35	0.0027

The results at other conversions are shown in the third column of Table 4-4. Although there is some variation from point to point, there is no significant trend. Hence the differential method also confirms the validity of a second-order rate equation. The variation is due to errors associated with the measurement of slopes of the curve in Fig. 4-1.

FIRST-ORDER RATE EQUATION   For comparison, the differential method will be applied to a first-order mechanism. The rate expression replacing Eq. (A) is

$$\mathbf{r} = k_1[A] = k_1 \frac{p_t}{R_g T} \frac{1 - x}{1 + x} \tag{C}$$

This mechanism may be tested by computing k_1 values from the experimental rates of reaction according to Eq. (C). For example, at $x = 0.13$

$$\mathbf{r} = \text{slope} = 4.9 \times 10^{-5} = k_1 \frac{1}{0.082(791)} \frac{1 - 0.13}{1 + 0.13}$$

$$k_1 = 0.0041 \text{ sec}^{-1}$$

The k_1 values for other conversions (fourth column of Table 4-4) show a distinct trend toward lower values at higher conversions. This indicates that the first-order rate is not a likely one.

Example 4-5   A flow reactor consisting of a 1-in. stainless-steel pipe 6 in. long and packed with inert rock salt is used to study the noncatalytic homogeneous reaction

$$\frac{4}{b} S_b + CH_4 \rightarrow 2H_2S + CS_2$$
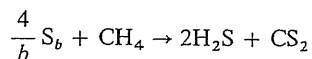
The measurements are carried out at atmospheric pressure in the vapor phase at 600°C. From available data on the rate of dissociation of the sulfur species, it is reasonable to assume that the reactions

$$S_8 \rightleftharpoons 4S_2$$

$$S_6 \rightleftharpoons 3S_2$$
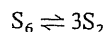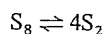
are very fast with respect to the combination of sulfur vapor with methane. Accordingly, assume that S_8, S_6, and S_2 are in equilibrium. The void volume, measured by benzene

Table 4-5

Run	Flow rate, g moles/hr			Reactants ratio, moles (S_2)/moles CH_4	Conversion
	$(CH_4)_f$	$(S_2)_f$	$(CS_2)_p$		
55	0.02975	0.0595	0.0079	2	0.268
58	0.0595	0.119	0.0086	2	0.144
57	0.119	0.238	0.0078	2	0.066
59	0.119	0.238	0.0072	2	0.060
56	0.238	0.476	0.0059	2	0.025
75	0.0595	0.119	0.0079	2	0.133
76	0.02975	0.0595	0.0080	2	0.269
77	0.119	0.238	0.0069	2	0.058
78	0.0893	0.0893	0.0087	1	0.0975
79	0.119	0.0595	0.0096	0.5	0.0807

displacement, was 35.2 ml. The conversion x of methane to carbon disulfide was measured for various flow rates and initial reactants ratios, and the results are shown in Table 4-5. (S_2) represents the total amount of sulfur vapor present, expressed as S_2. Hence

$$(S_2) = N_{S_2} + 3N_{S_6} + 4N_{S_8}$$

where the N values are the number of moles of each sulfur species.

(a) Assuming, first, that the only species of sulfur that exists is S_2, test the assumptions of first- and second-order rate equations with the experimental data. (b) Repeat part (a) with the assumption that S_2, S_6, and S_8 are in equilibrium but that only S_2 reacts with CH_4. (c) Using a second-order rate expression, determine which assumption regarding the reactive sulfur species best fits the experimental data.

Solution   It is convenient to convert the data to a conversion x_t based on the total feed. For example, for run 55

$$F_t = 0.02975 + 0.0595 = 0.0892 \text{ g mole/hr}$$

$$\frac{V}{F_t} = \frac{35.2}{0.0892} = 395$$

$$x_t = \frac{0.0079}{0.0892} = 0.0890$$

where F_t is the molal feed rate. Table 4-6 shows the corresponding values of x_t and V/F_t. These results are also plotted in Fig. 4-2. Note that

$$x_t = \frac{\text{moles product}}{\text{moles total feed}} = x\frac{\text{moles } CH_4 \text{ in feed}}{\text{moles total feed}} = x\frac{1}{1 + a}$$

or

$$x = (a + 1)x_t$$

where a is the moles of sulfur in the feed per mole of methane.

Table 4-6

| Run	Conversion		V/F_t, (ml)(hr)/g mole	$-\log[1 - (a + 1)(x_t)_1]$ or $-\log(1 - x_1)$	$k_1 \times 10^4$	$(k_1)_s \times 10^4$
	x_1	$(x_t)_1$				
55	0.268	0.0890	395	0.135	7.87	3.93
58	0.144	0.0480	197	0.0675	7.90	3.95
57	0.066	0.022	98.6	0.0297	6.93	3.46
59	0.060	0.020	98.6	0.0269	6.29	3.15
56	0.025	0.00833	49.3	0.0110	5.14	2.57
75	0.133	0.0443	197	0.0620	7.25	3.62
76	0.269	0.0895	395	0.136	7.95	3.97
77	0.058	0.0193	98.6	0.0269	6.05	3.02
78	0.0975	0.0487	197	0.045	5.30	5.45
79	0.0807	0.0538	197	0.0368	4.31	9.90

(*a*) Two first-order mechanisms may be assumed, one with respect to methane and one with respect to sulfur vapor (S_2). Starting with the first-order assumption for methane and applying Eq. (3-13), we have

$$\frac{V}{F_t} = \int_0^{(x_t)_1} \frac{dx_t}{r} = \int_0^{(x_t)_1} \frac{dx_t}{k_1 p_{CH_4}} = \int_0^{(x_t)_1} \frac{dx_t}{k_1 y_{CH_4}} \tag{A}$$

$$p_{CH_4} = y_{CH_4} p_t = y_{CH_4}$$

The mole fraction of methane varies with the conversion. Hence to relate y_{CH_4} to x_t we must know the number of moles of each component as a function of conversion. Since we are assuming here that all the sulfur present is S_2, the number of moles of S_2

Fig. 4-2 Experimental conversion data for the sulfurization of methane
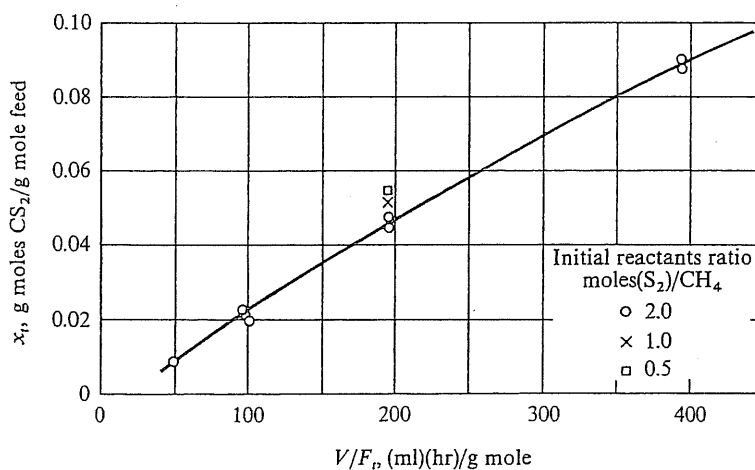
and CH_4 are simple to ascertain. For a mole ratio of S_2 to CH_4 of 2, the mole fraction entering the reactor is

$$y_{CH_4} = \frac{1}{2 + 1} = 0.333$$

If a basis of 1 mole of CH_4 and 2 moles of S_2 is chosen, at a point in the reactor where the conversion is x_t, the number of moles of each component will be

$CS_2 = x = 3x_t$

$H_2S = 2x = 6x_t$

$CH_4 = 1 - x = 1 - 3x_t$

$S_2 = 2 - 6x_t$

Total moles $= 3$

Thus the mole fractions are

$$y_{CH_4} = \frac{1 - 3x_t}{3} = 0.333 - x_t$$

$$y_{S_2} = \frac{2 - 6x_t}{3} = 0.667 - 2x_t$$

More generally, if the initial mole ratio of sulfur to CH_4 is a, then

$$\left. \begin{array}{l} y_{CH_4} = \dfrac{1 - (1 + a)x_t}{1 + a} = \dfrac{1}{1 + a} - x_t \\[4mm] y_{S_2} = \dfrac{a - 2(1 + a)x_t}{1 + a} = \dfrac{a}{1 + a} - 2x_t \end{array} \right\} \quad \text{(B)}$$

By the integral method, Eq. (A) can now be integrated with Eq. (B) to yield

$$\frac{V}{F_t} = \frac{1}{k_1} \int_0^{(x_t)_1} \frac{dx_t}{1/(1 + a) - x_t} = \frac{1}{k_1} \ln \frac{1/(1 + a) - (x_t)_1}{1/(1 + a)}$$

$$= -\frac{1}{k_1} \ln \left[1 - (a + 1)(x_t)_1 \right] = -\frac{1}{k_1} \ln (1 - x_1) \qquad \text{(C)}$$

where $(x_t)_1$ is the conversion leaving the reactor. The V/F_t-vs-$(x_t)_1$ data shown in Table 4-6 can now be used to test Eq. (C). Instead of plotting curves obtained from Eq. (C) with different k values for comparison with the experimental curve (Fig. 4-2), it is more effective to use one of two other approaches:

1. Plot the experimental V/F_t-vs-x data given in Table 4-6 as V/F_t vs $-\ln (1 - x_1)$. This method of plotting should result in a straight line if the assumed rate expression is correct. Figure 4-3 shows that this is not true if the rate is first order with respect to methane. At a constant reactants ratio of $a = 2.0$ the points fall on a straight line, but the data for other ratios deviate widely from the line.
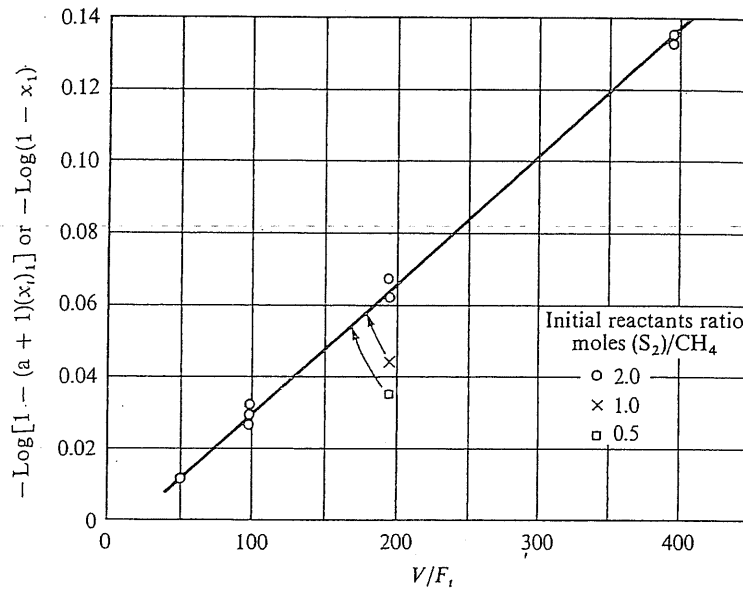
Fig. 4-3 Test of first-order mechanism with respect to CH_4

2. From the data in Table 4-6, compute values of k_1 required by Eq. (C) for each of the runs. If these values are essentially constant, the assumed mechanism fits the data. For this case the resulting k_1 values are given in column 6 of Table 4-6. Again, the runs for different reactants ratios show that the assumed rate equation does not fit the data.

As we shall see later, the assumed rate equation may be complex enough to prevent analytical integration of the design equation (A). However, in such cases it is still possible to evaluate the integral $\int dx_t/r$ graphically and then apply either method 1 or method 2 to determine the suitability of the rate assumption. Both methods are general and hence applicable to any reaction.

The design equation for an assumed mechanism which is first order with respect to sulfur vapor S_2 will be similar to Eq. (C); for example,

$$\frac{V}{F_t} = \int_0^{(x_t)_1} \frac{dx_t}{(k_1)_S y_{S_2}} = \frac{1}{(k_1)_S} \int_0^{(x_t)_1} \frac{dx_t}{a/(1+a) - 2x_t}$$

$$= -\frac{1}{2(k_1)_S} \ln \frac{a - 2(a+1)(x_t)_1}{a} = \frac{-1}{2(k_1)_s} \ln\left(1 - \frac{2x_1}{a}\right) \qquad (D)$$

For $a = 2$, Eq. (D) becomes the same as Eq. (C) if $(k_1)_S = \frac{1}{2}k_1$. Hence the test of this mechanism is whether or not the two runs for $a = 1.0$ and $a = 0.5$ are either brought in line with the other data on a plot similar to Fig. 4-3 or else give the same value of

$(k_1)_S$. The values of $(k_1)_S$ are given in the last column of Table 4-6. It is clear that the results for the runs with $a = 1.0$ and 0.5 are far removed from the rest of the data. Hence neither first-order mechanism is satisfactory.

If a second-order mechanism is tried, again with the assumption that all the sulfur vapor is present as S_2, the design equation is
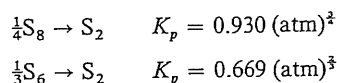
$$\frac{V}{F_t} = \int \frac{dx_t}{k_2 p_{CH_4} p_{S_2}} = \frac{1}{k_2} \int \frac{dx_t}{y_{CH_4} y_{S_2}}$$

$$= \frac{1}{k_2} \int \frac{dx_t}{\{[1/(1 + a)] - x_t\}\{[a/(1 + a)] - 2x_t\}}$$

This expression can be simplified and integrated to[1]

$$\frac{V}{F_t} = \frac{a + 1}{k_2} \int_0^{x_1} \frac{dx}{(1 - x)(a - 2x)}$$

$$= \frac{a + 1}{a - 2} \frac{1}{k_2} \left[\ln \left(1 - \frac{2}{a} x_1 \right) - \ln (1 - x_1) \right] \tag{E}$$

$$= \frac{3}{2k_2} \frac{x_1}{1 - x_1} \quad \text{for } a = 2$$

Figure 4-4 shows a plot of V/F_t vs $[(a + 1)/(a - 2)] \{\ln [1 - (2/a)x_1] - \ln (1 - x_1)\}$, or $\frac{3}{2} x_1/(1 - x_1)$, for $a = 2$ for the experimental data. It is apparent that this correlation is an improvement over the previous ones, since the point for $a = 1.0$ is close to the straight line. However, the data point for $a = 0.5$ is still not satisfactorily correlated. From this preliminary investigation, neglecting the S_6 and S_8 species, we conclude that a second-order rate is more appropriate than a first-order one.

(b) The next step is to refine the analysis by considering the distribution of sulfur vapor between S_2 and S_6 and S_8. To take into account the presence of the S_6 and S_8 species we shall assume equilibrium among S_2, S_6, and S_8, utilizing the following equilibrium constants at 600°C:

$$\tfrac{1}{4}S_8 \rightarrow S_2 \qquad K_p = 0.930 \text{ (atm)}^{\frac{1}{2}}$$

$$\tfrac{1}{3}S_6 \rightarrow S_2 \qquad K_p = 0.669 \text{ (atm)}^{\frac{1}{3}}$$

This information, along with the stoichiometry of the reaction, can be used to develop expressions analogous to Eqs. (B) for the relation between y_{S_2}, or y_{CH_4}, and the conversion. As in part (a), suppose that there are a moles of sulfur vapor per mole of CH_4 entering the reactor. However, let a refer to the total moles of sulfur considered as S_2, not to the sum of the moles of S_2, S_6, and S_8. If α_0, β_0, and γ_0 represent the moles of S_2, S_6, and S_8 entering the reactor, the total moles of sulfur, considered as S_2, will be

$$a = \alpha_0 + 3\beta_0 + 4\gamma_0$$

[1] Equation (E) becomes indeterminate when $a = 2$. Hence it is necessary to substitute $a = 2$ prior to integration and obtain the particular solution.
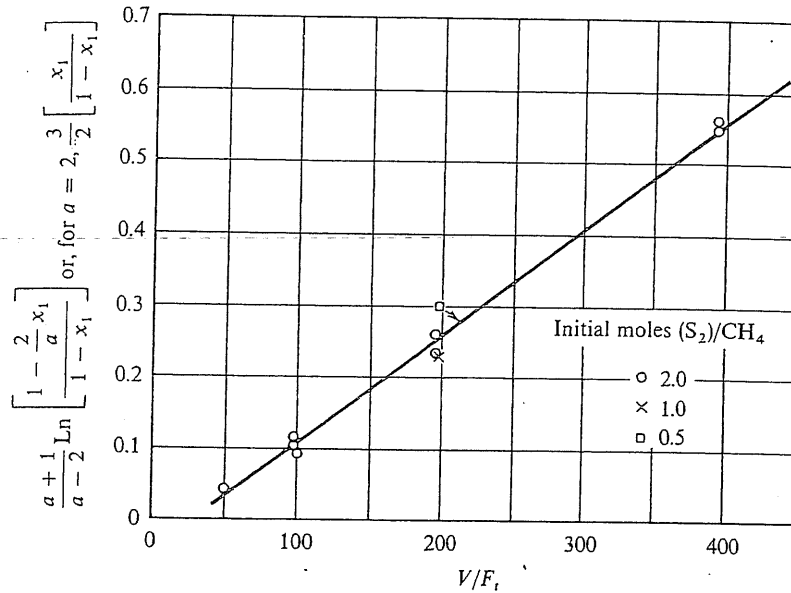
Fig. 4-4 Test of second-order reaction mechanism

At a point in the reactor where the conversion is x, the moles of each component will be

$$CS_2 = x$$

$$H_2S = 2x$$

$$CH_4 = 1 - x$$

$$S_2 = \alpha$$

$$S_6 = \beta$$

$$S_8 = \gamma$$

Total moles $= \alpha + \beta + \gamma + 2x + 1$

The conversion has been defined in terms of the methane reacted. It can also be written in terms of the sulfur used, providing a relationship between x, α, β, and γ. If (S_2) represents the total moles of sulfur (considered as S_2) present at any point in the reactor, then

$$x = \tfrac{1}{2}[a - (S_2)]$$

but $S_2 = \alpha + 3\beta + 4\gamma$

so that

$$x = \frac{a - \alpha - 3\beta - 4\gamma}{2}$$

(F)

Two additional relationships among x, α, β, and γ must exist because of the dissociation equilibria:

$$0.930 = \frac{p_{S_2}}{p_{S_8}^{\frac{1}{4}}} = \frac{y_{S_2}}{y_{S_8}^{\frac{1}{4}}} = \frac{\alpha}{\gamma^{\frac{1}{4}}(\alpha + \beta + \gamma + 2x + 1)^{\frac{3}{4}}} \tag{G}$$

$$0.669 = \frac{p_{S_2}}{p_{S_6}^{\frac{1}{3}}} = \frac{y_{S_2}}{y_{S_6}^{\frac{1}{3}}} = \frac{\alpha}{\beta^{\frac{1}{3}}(\alpha + \beta + \gamma + 2x + 1)^{\frac{2}{3}}} \tag{H}$$

Equations (F) to (H) permit the evaluation of α, β, and γ at any conversion and reactants ratio a. Then the mole fractions are immediately obtainable from the expressions

$$y_{S_2} = \frac{\alpha}{\alpha + \beta + \gamma + 2x + 1}$$

$$y_{CH_4} = \frac{1 - x}{\alpha + \beta + \gamma + 2x + 1}$$

To see the method of calculation let us take $a = 2$. Entering the reactor, $x = 0.0$, and Eqs. (F) to (H) become

$$2 = \alpha + 3\beta + 4\gamma$$

$$\gamma^{\frac{1}{4}}(\alpha + \beta + \gamma + 1)^{\frac{3}{4}} = \frac{\alpha}{0.93}$$

$$\beta^{\frac{1}{3}}(\alpha + \beta + \gamma + 1)^{\frac{2}{3}} = \frac{\alpha}{0.669}$$

Solving these by trial gives

$$\alpha = 0.782 \qquad y_{S_2} = \frac{0.782}{2.171} = 0.360$$

$$\beta = 0.340 \qquad y_{S_6} = \frac{0.340}{2.171} = 0.156$$

$$\gamma = 0.049 \qquad y_{S_8} = \frac{0.049}{2.171} = 0.023$$

$$CH_4 = 1.000 \qquad y_{CH_4} = \frac{1.000}{2.171} = 0.461$$

$$\text{Total} = 2.171 \qquad \Sigma y = 1.000$$

The mole fractions corresponding to any conversion can be evaluated in a similar manner. The results of such calculations are shown in Fig. 4-5, where composition of the reaction mixture is plotted against x. Information for other values of a are obtained in an analogous fashion.

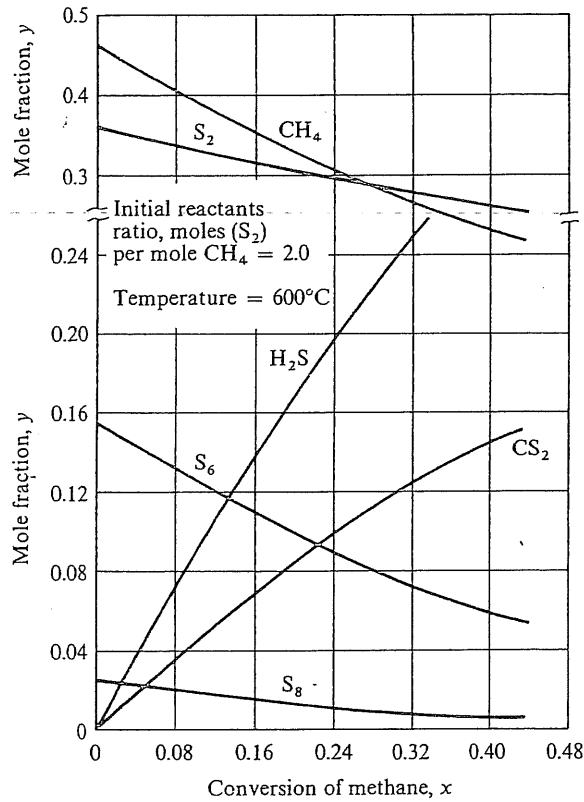The necessary data are now at hand for testing the second-order rate expression.

Fig. 4-5   Composition of reaction mixture vs conversion for the sulfurization of methane

However, the calculational procedure used in part (a) is not applicable because the design equation

$$\frac{V}{F_t} = \frac{1}{k_2'} \int_0^{(x_t)_1} \frac{dx_t}{y_{CH_4} y_{S_2}}$$ (I)

cannot be integrated analytically. Two alternatives are possible. The integral method entails graphical evaluation of the integral in Eq. (I) for each experimental point, with the measured value of the conversion as the upper limit in each case. This procedure leads to values of $\int_0^{(x_t)_1} dx_t / y_{CH_4} y_{S_2}$ for each value of V/F_t shown in Table 4-6. The results are given in the fourth column of Table 4-7 and are plotted in Fig. 4-6, with V/F_t as the abscissa and $\int_0^{(x_t)_1} dx_t / y_{CH_4} y_{S_2}$ as the ordinate. If the assumed mechanism is a satisfactory

*Table 4-7   Test of reaction mechanisms for sulfurization of methane*

Run	Reactants ratio	V/F_t	$\int_0^{(x_t)_1} dx_t/y_{CH_4}y_{S_b}$		
			$b = 2$	$b = 6$	$b = 8$
55	2	395	0.762	2.11	17.0
58	2	197	0.347	0.890	6.64
57	2	98.6	0.144	0.350	2.48
59	2	98.6	0.130	0.315	2.23
56	2	49.3	0.052	0.123	0.855
75	2	197·	0.316	0.800	5.88
76	2	395	0.765	2.17	17.1
77	2	98.6	0.126	0.303	2.15
78	1	197	0.315	1.27	12.1
79	0.5	197	0.388	2.97	36.8

interpretation of the data, Fig. 4-6 should be a straight line with a slope equal to k_2'. This is apparent if Eq. (I) is rearranged as

$$\int_0^{(x_t)_1} \frac{dx_t}{y_{CH_4}y_{S_2}} = k_2' \frac{V}{F_t}$$

It is evident from the plot that this condition is satisfied.

The other approach, the differential method, entails graphical differentiation of the data for comparison with the differential form of Eq. (I). If the data are plotted

Fig. 4-6   Test of rate equation $r = k_2' p_{CH_4} p_{S_2}$

V/F_t (ml)(hr)/g mole
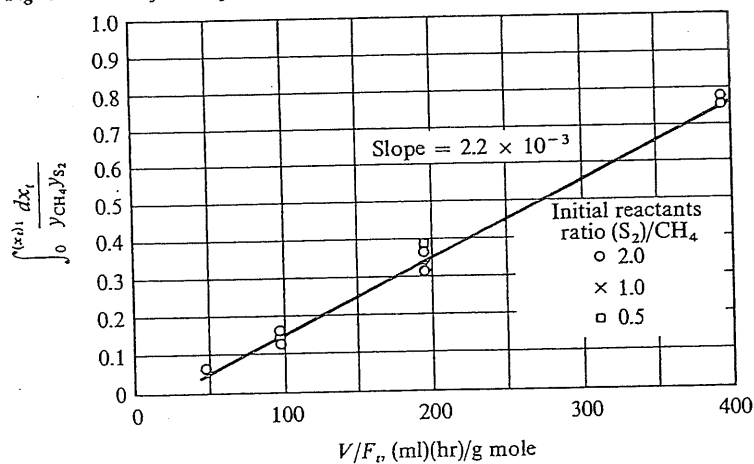
as x_t vs V/F_t, as in Fig. 4-2, the slope of the curve is equal to the rate of reaction. Thus, from Eq. (I),

$$d\left(\frac{V}{F_t}\right) = \frac{dx_t}{k_2' y_{CH_4} y_{S_2}}$$

or

$$\frac{dx_t}{d(V/F_t)} = \text{slope} = k_2' y_{CH_4} y_{S_2}$$

If the slope is taken at various values of the conversion from Fig. 4-2 and the corresponding values of y_{CH_4} and y_{S_2} are read from Fig. 4-5, and this is done for each reactants ratio, complete information on the effect of composition on the rate is available. The equation $r = k_2' y_{CH_4} y_{S_2}$ can then be tested by observing the constancy in computed values of k_2'.

(c) The results of part (b) indicate that the assumption of S_2 as the active sulfur-vapor species in the second-order mechanism gives a satisfactory interpretation of the conversion data. However, it is important to know whether equally good correlations would be obtained by assuming that S_6 or S_8 is the reactive form. To do this, the design equations corresponding to (I) may be written for the other species

$$\frac{V}{F_t} = \frac{1}{k_6'} \int_0^{(x_t)_1} \frac{dx_t}{y_{CH_4} y_{S_6}}$$ (J)

$$\frac{V}{F_t} = \frac{1}{k_8'} \int_0^{(x_t)_1} \frac{dx_t}{y_{CH_4} y_{S_8}}$$ (K)

Figures 4-7 and 4-8, which show V/F_t plotted against the integrals in (J) and (K), were prepared by graphical integration, with Fig. 4-5 used for the relations of x_t to y_{S_6} and y_{S_8}. The values of the integrals are given in the last two columns of Table 4-7. We see that in contrast to Fig. 4-6, based on S_2, the data do not fall on a straight line as required by Eqs. (J) and (K). Also, the points for various reactants ratios are not in agreement. We conclude that a second-order mechanism based on either S_6 or S_8 as the reactive sulfur species does not agree with the experimental data.

The preferred equation for the rate of reaction is

$$r = k_2' p_{CH_4} p_{S_2}$$

From Fig. 4-6, the slope of the straight line is 2.2×10^{-3} g mole/(hr)(ml)(atm^2). Since this number is equal to k_2', the final expression for the rate of reaction at 600°C is[1]

$$r = 2.2 \times 10^{-3} p_{CH_4} p_{S_2}$$

It is not advisable to make a firm statement regarding the mechanism of a reaction from data as limited as that in Example 4-5. It is perhaps best

[1] By evaluating the specific-reaction rate k_2' at other temperatures an activation energy can be determined. For this aspect of the problem see R. A. Fisher and J. M. Smith, *Ind. Eng. Chem.*, 42, 704 (1950).

to consider that the final rate equation is a satisfactory interpretation of the kinetic data. The problem of interpreting laboratory kinetic data in terms of a rate equation for catalytic reactions will be considered in Chap. 10.

4-4 Design Procedure

Once a satisfactory expression has been established for the rate of reaction, the size of reactor as a function of operating variables can be found by combining and solving the rate and mass-balance (design) equations. The design equation assumes a simpler form when the volume of the reaction mixture (or density) is constant. If QC_0, where Q is the constant volumetric flow rate and C_0 is the feed concentration, is substituted for the reactant feed rate F and the conversion is expressed in terms of concentration according to Eq. (4-1), Eq. (3-13) may be written

$$\frac{V}{QC_0} = \int_0^x \frac{dx}{r} = -\frac{1}{C_0} \int_{C_0}^C \frac{dC}{r}$$

(4-4)

or, since V/Q is the residence or contact time,

$$\frac{V}{Q} = \theta = -\int_{C_0}^C \frac{dC}{r}$$

(4-5)

Fig. 4-7   *Test of rate equation* $r = k'_6 p_{CH_4} p_{S_6}$

V/F_t, (ml)(hr)/g mole
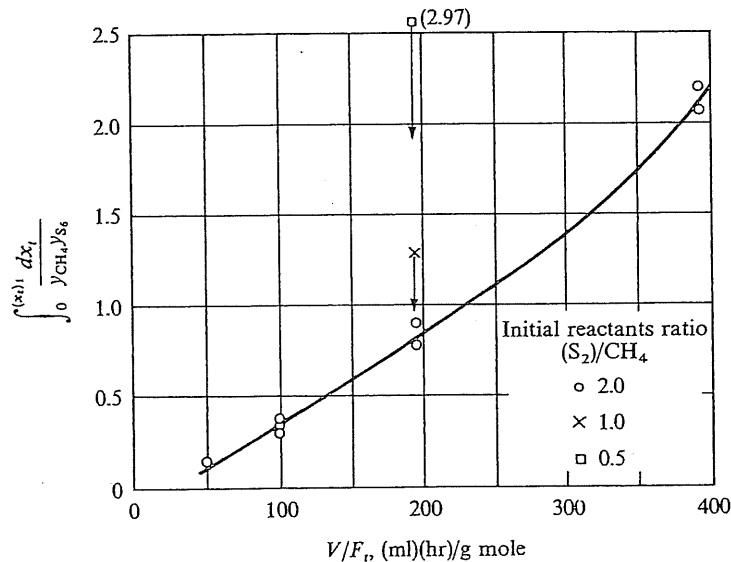
Comparison of Eqs. (4-2) and (4-5) shows that the form of the design equations for ideal batch and tubular-flow reactors are identical if the real-time variable in the batch reactor is considered as the residence time in the flow case. The important point is that the integral $\int dC/r$ is the same in both reactors. If this integral is evaluated for a given rate equation for an *ideal* batch reactor, the result is applicable for an *ideal* tubular-flow reactor; this conclusion will be utilized in Example 4-10.

When multiple reactions are involved, the yield and selectivity are important as well as the conversion. The following example illustrates the method of solving Eq. (4-4) for both single and consecutive reaction systems. The procedure is essentially the reverse of that for interpreting laboratory data on integral reactors (see Sec. 4-3).

Example 4-6 Hougen and Watson,[1] in an analysis of Kassell's data for the vapor-phase dehydrogenation of benzene in a homogeneous flow reactor, reported the reactions

1. $2C_6H_6(g) \rightarrow C_{12}H_{10}(g) + H_2(g)$

2. $C_6H_6(g) + C_{12}H_{10}(g) \rightarrow C_{18}H_{14}(g) + H_2(g)$

[1]O. A. Hougen and K. M. Watson, "Chemical Process Principles," vol. 3, p. 846, John Wiley & Sons, Inc., New York, 1947.

Fig. 4-8 *Test of rate equation* $r = k'_8 p_{CH_4} p_{S_8}$

V/F_t, (ml)(hr)/g mole
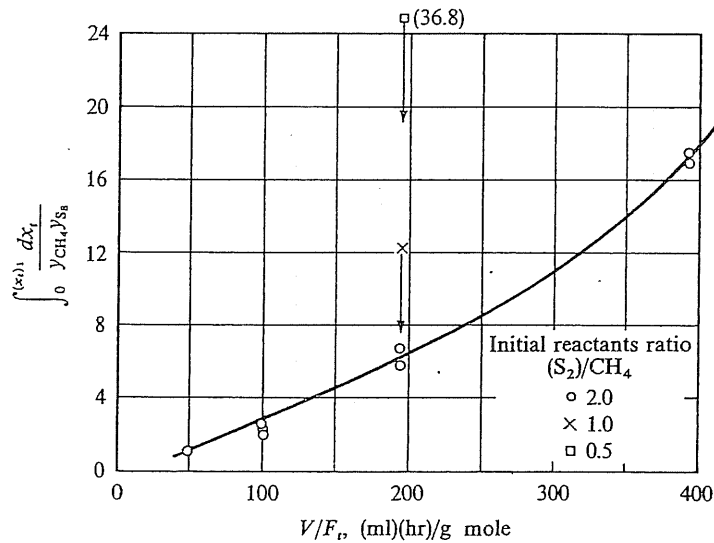
and the following rate equations:

$$r_1 = 14.96 \times 10^6 e^{-15,200/T} \left(p_B^2 - \frac{p_D p_H}{K_1} \right) \quad \text{lb moles benzene reacted/(hr)(ft}^3)$$

$$r_2 = 8.67 \times 10^6 e^{-15,200/T} \left(p_B p_D - \frac{p_T p_H}{K_2} \right)$$

$$\text{lb moles triphenyl produced or diphenyl reacted/(hr)(ft}^3)$$

where p_B = partial pressure of benzene, atm
p_D = partial pressure of diphenyl, atm
p_T = partial pressure of triphenyl, atm
p_H = partial pressure of hydrogen, atm
T = temperature, °K
K_1, K_2 = equilibrium constants for the two reactions in terms of partial pressures

The data on which the rate equations are based were obtained at a total pressure of 1 atm and temperatures of 1265° and 1400°F in a 0.5-in. tube 3 ft long.

It is now proposed to design a tubular reactor which will operate at 1 atm pressure and 1400°F. (a) Determine the total conversion of benzene to di- and triphenyl as a function of space velocity. (b) Determine the reactor volume required to process 10,000 lb/hr of benzene as a function of the total conversion. First carry out the solution with the assumption that only reaction 1 occurs, and then proceed to the solution for the two consecutive reactions. Assume that the reactor will be operated isothermally and that no other reactions are significant.

Solution (a) Since the reactor is isothermal, the equilibrium constants K_1 and K_2 will have fixed values. They may be estimated at 1400°F from equations developed by Hougen and Watson, by methods analogous to those described in Chap. 1. The results are

$$K_1 = 0.312$$

$$K_2 = 0.480$$

As these values are not large, the reverse reactions may be important. At 1400°F (1033°K), in terms of the rate of disappearance of benzene, the two rates are

$$r_1 = (14.96 \times 10^6) e^{-14.7} \left(p_B^2 - \frac{p_D p_H}{0.312} \right) = 6.23 \left(p_B^2 - \frac{p_D p_H}{0.312} \right) \quad (A)$$

$$r_2 = (8.67 \times 10^6) e^{-14.7} \left(p_B p_D - \frac{p_T p_H}{0.480} \right) = 3.61 \left(p_B p_D - \frac{p_T p_H}{0.480} \right) \quad (B)$$

An equation of the form of Eq. (3-13) may be written for each reaction:

$$\frac{V}{F} = \int \frac{dx_1}{r_1} \quad (C)$$

$$\frac{V}{F} = \int \frac{dx_2}{r_2} \quad (D)$$

where the conversion x_1 is the pound moles of benzene disappearing by reaction 1 per pound mole of feed, and the conversion x_2 is the pound moles of benzene disappearing by reaction 2 per pound mole of feed.

If we take as a basis 1.0 mole of entering benzene, the moles of each component are

$H_2 = \frac{1}{2}x_1 + x_2$

$C_{12}H_{10} = \frac{1}{2}x_1 - x_2$

$C_6H_6 = 1 - x_1 - x_2$

$C_{18}H_{14} = x_2$

Total moles = 1.0

Since the total moles equals 1.0 regardless of x_1 and x_2, the mole fractions of each component are also given by these quantities. If the components are assumed to behave as ideal gases, the partial pressures are

$p_H = 1.0(\frac{1}{2}x_1 + x_2) = \frac{1}{2}x_1 + x_2$

$p_D = \frac{1}{2}x_1 - x_2$

$p_B = 1 - x_1 - x_2$

$p_T = x_2$

With these relationships the rate equations (A) and (B) can be expressed in terms of x_1 and x_2 as

$$r_1 = 6.23\left[(1 - x_1 - x_2)^2 - \frac{(\frac{1}{2}x_1 - x_2)(\frac{1}{2}x_1 + x_2)}{0.312}\right] \tag{E}$$

$$r_2 = 3.61\left[(1 - x_1 - x_2)(\frac{1}{2}x_1 - x_2) - \frac{x_2(\frac{1}{2}x_1 + x_2)}{0.480}\right] \tag{F}$$

In principle, Eqs. (E) and (F) can be substituted in the design equations (C) and (D) and values of exit conversions x_1 and x_2 computed for various values of V/F. If only the first reaction is considered, then only x_1 is involved and direct integration is possible. Let us carry out the solution first with this assumption.

SIMPLIFIED SOLUTION (REACTION 2 ASSUMED UNIMPORTANT)   Since $x_2 = 0$, Eq. (E) simplifies to

$$r = 6.23[(1 - x_1)^2 - 0.801(x_1)^2] \tag{G}$$

This may be substituted in design Eq. (C) and integrated directly:

$$\frac{V}{F} = \frac{1}{6.23} \int_0^{x_1} \frac{dx_1}{(1 - x_1)^2 - 0.801(x_1)^2} = \frac{1}{6.23} \int_0^{x_1} \frac{dx_1}{(1 - 0.105x_1)(1 - 1.895x_1)}$$

$$= \frac{0.559}{6.23} \ln \frac{1 - 0.105x_1}{1 - 1.895x_1} \tag{H}$$

Table 4-8

| x_1, lb moles C_6H_6 decomposed/ lb mole feed	V/F, ft^3 (hr)/ (lb mole feed)	Space velocity, hr^{-1}
0.0	0	∞
0.1	0.0179	21,200
0.2	0.0409	9,280
0.3	0.0725	5,230
0.4	0.123	3,080
0.5	0.260	1,460
0.52	0.382	990
0.528*	∞	0

*Equilibrium conditions.

Table 4-8 gives the values of V/F corresponding to successive values of x_1 obtained by substituting in Eq. (H). A particular V/F value represents the ratio of volume of reactor to feed rate necessary to give the corresponding conversion. Figure 4-9 is a plot of the data given in the table.

The equilibrium conversion is 52.8%, as that is the value corresponding to infinite time. The same result could have been obtained by using the equilibrium constant $K_1 = 0.312$ to compute the equilibrium yield by the method described in Chap. 1.

Fig. 4-9   Dehydrogenation of benzene (simplified solution)
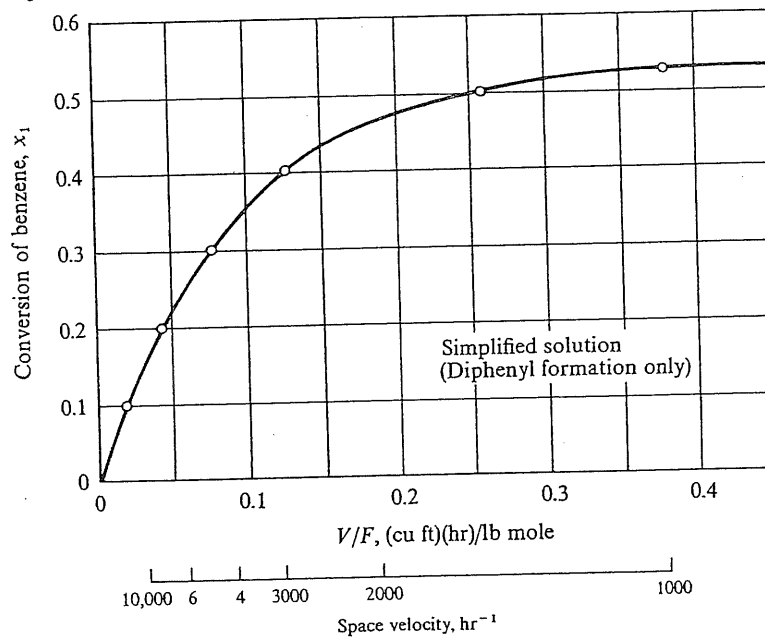
GENERAL SOLUTION (BOTH REACTIONS 1 AND 2 CONSIDERED) The rate equations (E) and (F) and the design equations (C) and (D) provide the means for determining x_1 and x_2 as a function of V/F. If (C) and (D) are written in difference form, the integration can be accomplished by a stepwise numerical approach. In a small element of volume ΔV the conversions Δx_1 and Δx_2 are

$$\Delta x_1 = \frac{\Delta V}{F}\bar{r}_1 = \Delta\left(\frac{V}{F}\right)\bar{r}_1 \qquad\qquad (C')$$

$$\Delta x_2 = \frac{\Delta V}{F}\bar{r}_2 = \Delta\left(\frac{V}{F}\right)\bar{r}_2 \qquad\qquad (D')$$

where $\bar{r}_1$ and $\bar{r}_2$ are average values of the rate for the conversion range x_1 to $x_1 + \Delta x_1$ and $x_2 + \Delta x_2$.

To illustrate the method of solving Eqs. (C') and (D') let us start at the entrance to the reactor and carry out several stepwise calculations. The rates at the entrance are given by Eqs. (E) and (F) with $x_1 = x_2 = 0$,

$$(r_1)_0 = 6.23(1 - 0) = 6.23 \text{ lb moles } C_6H_6 \text{ converted/(hr)(ft}^3)$$

$$(r_2)_0 = 3.61(0) = 0$$

Choose an interval of $\Delta(V/F) = 0.005 \text{ ft}^3/(\text{lb mole feed})(\text{hr})$. If the initial rates are constant over this interval, the conversions at the end of the interval are, according to Eqs. (C') and (D'),

$$x_1 = 0 + 0.005(6.23) = 0.03115$$

$$x_2 = 0 + 0.005(0) = 0$$

The rates at the end of the interval are

$$(r_1)_1 = 6.23\left[(1 - 0.03115)^2 - \frac{1}{4}\,\frac{0.03115^2}{0.312}\right] = 6.23(0.938) = 5.84$$

$$(r_2)_1 = 3.61\left[(1 - 0.03115)\frac{0.03115}{2} - 0\right] = 0.0544$$

The average values of the rates in the first increment of $\Delta(V/F)$ may be taken as the arithmetic average of the rates entering and leaving the increment; for example,

$$\bar{r}_1 = \frac{(r_1)_0 + (r_1)_1}{2} = \frac{6.23 + 5.84}{2} = 6.04$$

$$\bar{r}_2 = \frac{(r_2)_0 + (r_2)_1}{2} = \frac{0 + 0.0544}{2} = 0.0272$$

With these revised values the conversions at the end of the first increment are, again according to Eqs. (C') and (D'),

$$(x_1)_1 = 0 + 0.005(6.04) = 0.0302$$

$$(x_2)_1 = 0 + 0.005(0.0272) = 0.000136$$

Proceeding to the second increment of $\Delta(V/F)$, we can speed up the computations

by anticipating the average rates in the increment instead of using the values at the beginning of the increment. Estimate that the average rates will be

$$\bar{r}_1 = 6.04 - (6.23 - 5.84) = 5.65$$

$$\bar{r}_2 = 0.0272 + (0.0544 - 0) = 0.0816$$

With these values the conversion occurring within the second increment is given by Eqs. (C′) and (D′). Thus

$$\Delta x_1 = 0.005(5.65) = 0.0282$$

$$(x_1)_2 = x_{1_1} + \Delta x_1 = 0.0302 + 0.0282 = 0.0584$$

and

$$\Delta x_2 = 0.005(0.0816) = 0.000408$$

$$(x_2)_2 = 0.000136 + 0.000408 = 0.000544$$

The estimated values of the average rates can be checked by evaluating rates at the beginning and end of the increment. At the end of the increment

$$(r_1)_2 = 6.23 \left[(1 - 0.0584 - 0.0005)^2 - \left(\frac{0.0584}{2} - 0.0005 \right) \right.$$
$$\left. \left(\frac{0.0584}{2} + 0.0005 \right) \frac{1}{0.312} \right]$$

$$= 6.23(0.883) = 5.50$$

$$(r_2)_2 = 3.61 \left[(1 - 0.0584 - 0.0005) \left(\frac{0.0584}{2} - 0.0005 \right) - 0.000544 \right.$$
$$\left. \left(\frac{0.0584}{2} + 0.0005 \right) \frac{1}{0.480} \right]$$

$$= 3.61(0.0270) = 0.0975$$

At the beginning of the increment

$$(r_1)_1 = 6.23 \left[(1 - 0.0302 - 0.0001)^2 - \left(\frac{0.0302}{2} - 0.0001 \right) \right.$$
$$\left. \left(\frac{0.0302}{2} + 0.001 \right) \left(\frac{1}{0.312} \right) \right]$$

$$= 5.86$$

$$(r_2)_1 = 3.61 \left[(1 - 0.0302 - 0.0001) \left(\frac{0.0302}{2} - 0.0001 \right) - 0.000136 \right.$$
$$\left. \left(\frac{0.0302}{2} + 0.0001 \right) \left(\frac{1}{0.480} \right) \right]$$

$$= 0.0529$$

Thus the average values are

$$\bar{r}_1 = \frac{r_{1_1} + r_{1_2}}{2} = \frac{5.86 + 5.50}{2} = 5.68 \qquad \text{vs 5.65 estimated}$$

$$\bar{r}_2 = \frac{r_{2_1} + r_{2_2}}{2} = \frac{0.0529 + 0.0975}{2} = 0.0752 \qquad \text{vs 0.0816 estimated}$$

The agreement with the estimated average rates is sufficiently close that a second calculation is unnecessary. The final values for the conversion leaving the second increment ($V/F = 0.005 + 0.005 = 0.01$) will be

$$(x_1)_2 = 0.0302 + 0.005(5.68) = 0.0586$$

$$(x_2)_2 = 0.000136 + 0.005(0.0752) = 0.000512$$

This stepwise procedure may be repeated until any desired value of $x_1 + x_2$ is reached. Such iterative calculations are most easily carried out by machine computation. The results from zero to equilibrium are shown in Table 4-9 and Fig. 4-10. Space velocities $v_F F/V$, based on $v_F = 379$ ft^3/mole (60°F, 1 atm), are also shown.

(b) The reactor volume required to process 10,000 lb/hr of benzene may be computed from the V/F data in Table 4-9. For a total conversion of 41.7%, for example, $V/F = 0.12$ and the reactor volume is

$$V = 0.12F = 0.12\frac{10,000}{78} = 15.4 \text{ ft}^3$$

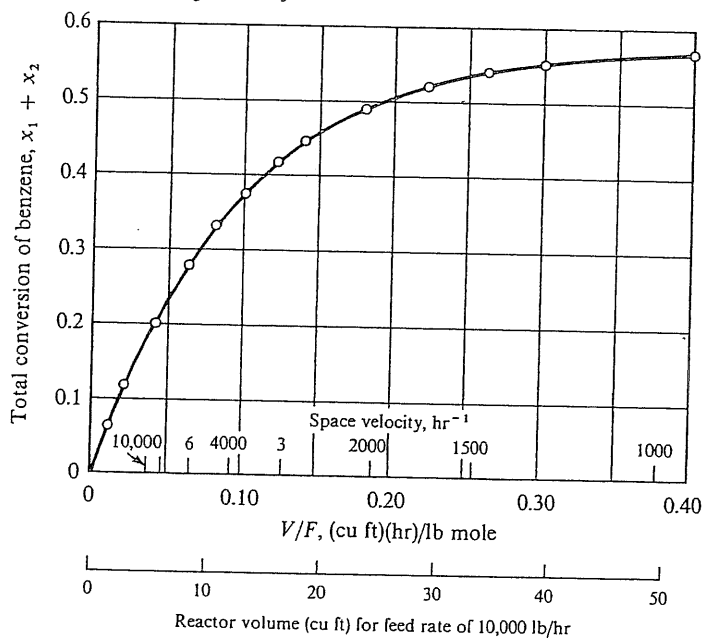*Fig. 4-10 Dehydrogenation of benzene*

Table 4-9   Conversion vs V/F for the dehydrogenation of benzene

V/F	Space velocity, hr^{-1}	Conversion			Composition of mixture (molal)			
		x_1	x_2	x_t	C_6H_6	$C_{12}H_{10}$	$C_{18}H_{14}$	H_2
0	∞	0	0	0	1.000	0	0	0
0.005	75,800	0.0302	0.00014	0.0303	0.970	0.0150	0.00014	0.0152
0.010	37,900	0.0586	0.00051	0.0591	0.941	0.0288	0.00051	0.0298
0.020	18,950	0.1105	0.00184	0.112	0.888	0.0534	0.00184	0.0571
0.040	9,500	0.197	0.0062	0.203	0.797	0.0923	0.0062	0.1047
0.060	6,320	0.264	0.0119	0.276	0.724	0.1201	0.0119	0.1439
0.080	4,740	0.316	0.0180	0.334	0.666	0.140	0.0180	0.176
0.100	3,790	0.356	0.0242	0.380	0.620	0.154	0.0242	0.202
0.120	3,160	0.387	0.0302	0.417	0.583	0.163	0.0302	0.224
0.140	2,710	0.411	0.0359	0.447	0.533	0.170	0.0359	0.241
0.180	2,110	0.445	0.0459	0.491	0.509	0.177	0.0459	0.268
0.220	1,720	0.468	0.0549	0.523	0.477	0.179	0.0549	0.289
0.260	1,460	0.478	0.0617	0.540	0.460	0.177	0.0617	0.301
0.300	1,260	0.485	0.0673	0.552	0.448	0.175	0.0673	0.310
0.400	950	0.494	0.0773	0.571	0.429	0.170	0.0773	0.324
∞*	0	0.496	0.091	0.587	0.413	0.157	0.091	0.339

*Equilibrium conditions.

If a 4-in.-ID tubular reactor were used, a length of about 175 ft would be required. The complete curve of volume vs total conversion is also shown in Fig. 4-10.

The equilibrium total conversion of 49.6 + 9.1 = 58.7% and the equilibrium composition are shown as the values for V/F at infinity in Table 4-9. These results could also have been obtained from Eqs. (E) and (F). Thus at equilibrium, $r_1 = r_2 = 0$, and

$$(1 - x_1 - x_2)^2 = \frac{(\frac{1}{2}x_1 - x_2)(\frac{1}{2}x_1 + x_2)}{0.312}$$

$$(1 - x_1 - x_2)(\frac{1}{2}x_1 - x_2) = \frac{x_2(\frac{1}{2}x_1 + x_2)}{0.480}$$

Simultaneous solution of these two equations leads to values of $x_1 = 0.496$ and $x_2 = 0.091$, as shown.

The rates of each reaction as a function of V/F are shown in Fig. 4-11. In both cases the rates fall off toward zero as V/F approaches high values. The rate of reaction 2 also approaches zero at very low values of V/F because diphenyl is not present in the benzene entering the reactor.

The last four columns in Table 4-9 give the composition of the reaction mixture. With a fixed feed rate the increasing V/F values correspond to moving through the reactor, i.e., increasing reactor volume. Hence these columns show how the composition varies with position in the reactor. Note that the mole fraction of benzene decreases
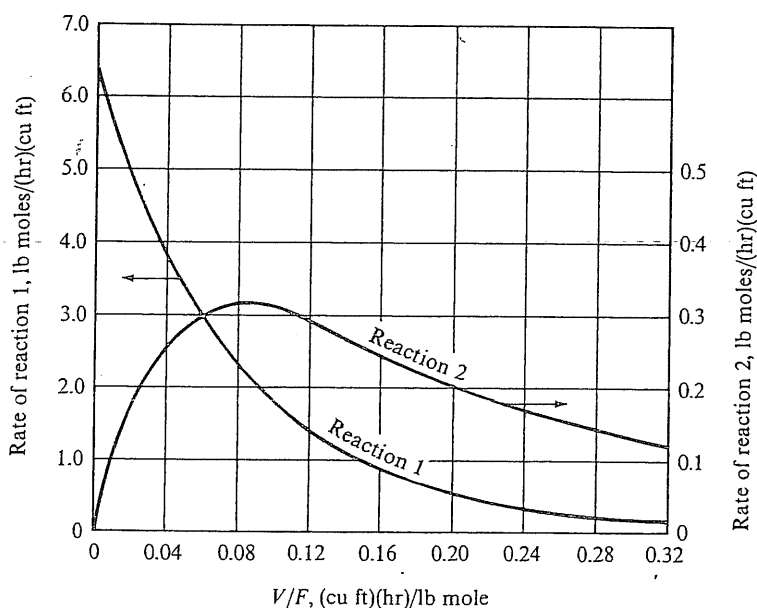
Fig. 4-11 Rates of reaction for dehydrogenation of benzene

continuously as the reaction mixture proceeds through the reactor, while the diphenyl content reaches a maximum at a V/F value of about 0.22, typical of the intermediate product in consecutive reactions.

Example 4-6 illustrates the design procedure for a homogeneous flow reactor operating at constant temperature and pressure. When the pressure is not constant and the rate of reaction varies significantly with the pressure (gaseous components), the pressure drop in the reactor must be taken into account. The method of accomplishing this involves no new principles. In comparison with the case in Example 4-6, the differences are as follows:

1. The effect of pressure on the rate of reaction must be accounted for; i.e., rate equations (A) and (B) would be used instead of (E) and (F), which are based upon 1 atm pressure.
2. The same stepwise numerical procedure is applicable, except that the pressure at any point in the reactor must be computed and the appropriate value used in Eqs. (A) and (B).

The changes in pressure are due to friction, potential-energy changes, and kinetic-energy changes in the flow process in the reactor. Hence the pressure drop may be computed from the Bernoulli equation, with suitable