

5

TEMPERATURE EFFECTS IN HOMOGENEOUS REACTORS

Nonuniform temperatures, or a temperature level different from that of the surroundings, are common in operating reactors. The temperature may be varied deliberately to achieve optimum rates of reaction, or high heats of reaction and limited heat-transfer rates may cause unintended nonisothermal conditions. Reactor design is usually sensitive to small temperature changes because of the exponential effect of temperature on the rate (the Arrhenius equation). The temperature profile, or history, in a reactor is established by an energy balance such as those presented in Chap. 3 for ideal batch and flow reactors.

In an endothermic reaction the temperature decreases as the conversion increases, unless energy is added to the system in excess of that absorbed by the reaction. Both the reduction in concentration of reactants, due to increasing conversion, and the reduction in temperature cause the rate to fall (Fig. 5-1a). Hence the conversion in a nonisothermal reactor will normally be less than that for an isothermal one. Adding energy to reduce the temperature drop will limit the reduction in conversion. If the

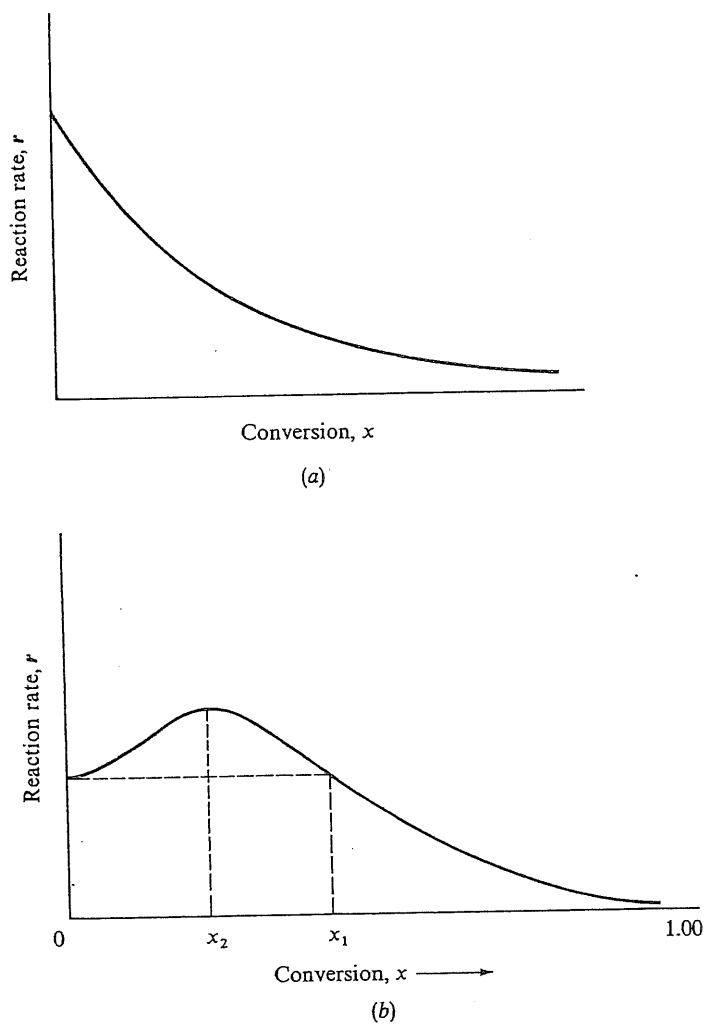


Fig. 5-1 Rate vs conversion in an adiabatic reactor: (a) endothermic reaction (b) exothermic reaction

reaction is reversible, adding energy provides the further advantage of increasing the maximum (equilibrium) conversion. A practical example is the dehydrogenation of butenes to butadiene. Only at an elevated temperature is the equilibrium conversion high enough for the process to be profitable. Also, only at high temperatures will the reaction rate be high enough to assure a close approach to the equilibrium conversion.

Successful designs for such processes must provide for the addition

of energy to counteract the heat of reaction. Energy can be added in many ways: by passing a hot fluid through a jacket around the reactor; by adding a large amount of diluent to the feed, which will absorb the heat of reaction and so prevent a large temperature drop; by a simultaneous exothermic reaction involving part of the reactants or other components added to the feed; or by inserting heaters in the reactor.

In an exothermic reaction the temperature increases as the conversion increases. At low conversions the rising temperature increases the rate more than it is reduced by the fall in reactants concentration. Normally the conversion will be greater than for isothermal operation. However, undesirable side reactions and other factors may limit the permissible temperatures. In these cases successful design depends on effective removal of the heat of reaction to prevent excessive temperatures (hot spots). In general, the same methods are employed as for adding energy in endothermic reactions.

The increase in rate as an exothermic reaction progresses is hindered by the limit on the conversion: The limit for an irreversible reaction is 100%. As the limit is approached, the concentration of reactants and the rate both approach zero, regardless of the temperature level. Hence the curve of reaction rate vs conversion for an exothermic reaction in an adiabatic reactor has a maximum, as shown in Fig. 5-1*b*. At low conversions the relative change in reactants concentration with conversion is small, and the rate increases exponentially because of the dominant temperature effect. At high conversions the reactants concentration approaches zero, and so does the rate.

In Examples 5-2 and 5-3 we shall see a quantitative comparison of the efficiency of tubular-flow and stirred-tank reactors for converting reactant into product. Some conclusions can be given here on the basis of the curves in Fig. 5-1*a* and *b*. In a tubular-flow reactor the conversion in the product stream will be the sum of the conversions in each volume element. The total conversion thus depends on the whole curve of rate vs conversion, as shown in Fig. 5-1*a* and *b*. In fact, the *average* rate over the conversion range will be a measure of the total conversion in the product stream. In a stirred-tank reactor, however, the conversion is determined solely by the rate in the *exit* stream, that is, by the *point* at the exit conversion in Fig. 5-1*a* and *b*. If the rate-vs-conversion curve is a falling one, as in Fig. 5-1*a*, the average rate will be higher than the rate at the end point. Hence a tubular-flow reactor is better for this case, which is descriptive of an endothermic reaction system. For an exothermic reaction the answer is not as clear cut because of the maximum in the curve in Fig. 5-1*b*. At low conversions a stirred-tank unit is most efficient, while at high conversions a tubular-flow unit is preferable. At intermediate conversion levels the choice

depends on whether the average rate is greater or less than the rate at the exit conversion. At any conversion greater than x_1 (the conversion where the rate is the same as that at zero conversion) the average rate will be greater than that at the end point, so that a tubular-flow reactor is best. At some exit conversion less than x_1 , but greater than x_2 , the stirred tank will become more efficient and will remain so down to zero conversion.

We have been discussing adiabatic reactors in Fig. 5-1a and b, but heat-transfer rates are usually insufficient to change the form of the curves. Hence the same conclusions apply to almost all nonisothermal conditions.

The shape of the curve in Fig. 5-1b introduces the possibility of multiple, stable operating conditions for exothermic reactions in stirred-tank reactors. This is discussed in Sec. 5-4.

5-1 Ideal Batch Reactors

The energy balance developed in Chap. 3 for batch reactors, Eq. (3-11), expressed the time rate of change of temperature in terms of the rate of reaction and the energy exchange with the surroundings. This equation may be used with the mass balance, Eq. (3-9) [or Eq. (4-2) if the density is constant], to calculate the temperature and composition of the reaction mixture at any time. Also required is a rate equation giving r as a function of temperature and composition. Normally a stepwise numerical solution is necessary. This is accomplished by writing the balances in difference form and solving them for successive time increments.

The energy balance can be expressed in terms of the conversion rather than the rate by combining Eqs. (3-11) and (3-9) to eliminate r . Thus

$$m_t c_v \frac{dT}{dt} = \frac{-\Delta H}{M} m \frac{dx}{dt} + UA_h(T_s - T) \quad (5-1)$$

where m = mass of limiting reactant (corresponding to zero conversion)

M = molecular weight of reactant

A_h = heat-transfer area

T_s = temperature of surroundings

This form is advantageous for adiabatic operation, for then time is not involved; that is, the equation reduces to

$$m_t c_v dT = \frac{-\Delta H}{M} m dx \quad (5-2)$$

All the coefficients except c_v and ΔH are constant during the course of the reaction, and the variation in these is usually small. If they are taken as

constants, Eq. (5-2) can be immediately integrated to give the following relationship between temperature and conversion:

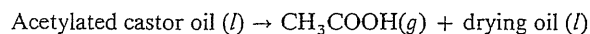
$$T_f - T_0 = \frac{-\Delta H}{Mc_p} \frac{m}{m_t} (x - x_0)$$

or

$$T - T_0 = \frac{-\Delta H}{Mc_p} w(x - x_0) \quad (5-3)$$

where w is the weight fraction of limiting reactant, corresponding to zero conversion. If the conversion initially is zero ($x_0 = 0$), w is the weight fraction of reactant at initial conditions. For adiabatic operation Eq. (5-3) eliminates the need for simultaneous stepwise solution of the mass and energy balances. Both adiabatic and nonadiabatic design calculations are illustrated in the following example.

Example 5-1 In a study of the production of drying oils by the decomposition of acetylated castor oil, Grummitt and Fleming¹ were able to correlate decomposition data on the basis of a first-order reaction written as



$$r = kC$$

where r is rate of decomposition, in grams of acetic acid produced per minute per milliliter, and C is concentration of acetic acid, in grams per milliliter, equivalent to acetylated castor oil. Data obtained over the temperature range 295 to 340°C indicated an activation energy of 44,500 cal/g mole in accordance with the following expression for the specific-reaction-rate constant k :

$$\ln k = \frac{-44,500}{R_g T} + 35.2$$

where T is in degrees Kelvin.

If a batch reactor initially contains 500 lb of acetylated castor oil at 340°C (density 0.90) and the operation is adiabatic, plot curves of conversion (fraction of the acetylated oil that is decomposed) and temperature vs time. It is estimated that the endothermic heat effect for this reaction is 15,000 cal/g mole of acetic acid vapor. The acetylated oil charged to the reactor contains 0.156 g of equivalent acetic acid per gram of oil; i.e., complete decomposition of 1 g of the oil would yield 0.156 g of acetic acid. Assume that the specific heat of the liquid reaction mixture is constant and equal to 0.6 Btu/(lb)(°F). Also assume that the acetic acid vapor produced leaves the reactor at the temperature of the reaction mixture.

¹*Ind. Eng. Chem.*, 37, 485 (1945).

Solution: The mass balance, assuming no change in volume during the course of the reaction, is Eq. (4-2),

$$t_1 = C_0 \int_0^{x_1} \frac{dx}{r}$$

where C_0 and r are measured in terms of equivalent acetic acid. If we replace r with the rate equation, this expression becomes

$$t_1 = \int_0^{x_1} \frac{C_0 dx}{C e^{35.2 - 44,500/R_g T}} \quad (\text{A})$$

The relationship between the concentration and the conversion is

$$C = C_0(1 - x)$$

In terms of x , Eq. (A) may be written

$$t_1 = \int_0^{x_1} \frac{dx}{(1-x)e^{35.2 - 44,500/R_g T}} \quad (\text{B})$$

Since the reactor operates adiabatically, Eq. (5-3) is applicable. In this example $w = 0.156$ g of equivalent acetic acid per gram of oil. Hence

$$T - T_0 = -\frac{15,000(0.156)}{60(0.6)}(x - 0) \quad (\text{C})$$

$$T - (340 + 273) = -65x$$

or

$$T = 613 - 65x \quad (\text{D})$$

There are two methods of obtaining a curve of t vs x from Eqs. (B) and (D). The first approach is to write Eq. (B) in difference form for a small change in conversion, Δx , and solve by stepwise numerical integration. As an illustration let us follow through three incremental calculations using the modified Euler method. We write Eq. (B) as

$$\Delta t = \left[\frac{1}{(1-x)e^{35.2 - 44,500/R_g T}} \right]_{\text{av}} \Delta x = \left(\frac{1}{R} \right)_{\text{av}} \Delta x \quad (\text{B}')$$

Note that it is the multiplier of Δx that must be averaged. This means that the reciprocal of the rate, not the rate itself, is averaged over the increment. Entering the reactor,

$$T_0 = 613^\circ\text{K}$$

$$x_0 = 0$$

$$\frac{1}{R_0} = \frac{1}{(1-0)e^{35.2 - 44,500/1.98(613)}} = 4.15$$

For the first increment choose $\Delta x = 0.1$. Then at $x = 0.1$, from Eq. (D) we have

$$T_1 = 613 - 65(0.10) = 606.5^\circ\text{K}$$

$$\frac{1}{R_1} = \frac{1}{(1 - 0.1)e^{35.2 - 44,500/1.98(606.5)}} = 6.15$$

For the first increment of Δx the average value of $1/R$ will be

$$\left(\frac{1}{R}\right)_{\text{av}} = \frac{4.15 + 6.15}{2} = 5.15$$

Substituting this result in Eq. (B') gives the time at the end of the first increment,

$$\Delta t = t_1 - 0 = 5.2(0.1) = 0.52 \text{ min}$$

The procedure for the second increment would be similar. A value of $1/R_2$ is calculated at $x_2 = 0.2$ and $T_2 = 606.5 - 6.5 = 600^\circ\text{K}$. This is averaged with $1/R_1$, and Eq. (B') is used to compute Δt_2 and t_2 . The results for three increments are shown in Table 5-1. The smaller the size of the increment of conversion, the more appropriate the use of an arithmetic average value of $1/R$, and the more accurate the final results.

Table 5-1

Conversion	T , °K	t , min
0	613	0
0.10	606.5	0.52
0.20	600.0	1.40
0.30	593.6	3.00

An alternate approach, instead of stepwise numerical integration, is to plot temperature vs conversion from Eq. (D), and then from this information plot $1/r$ vs conversion. Graphical integration under this second curve up to any conversion x corresponds to the value of the integral of dx/r , which, multiplied by C_0 , equals the time required for that conversion. Figure 5-2 represents the temperature-conversion relationship corresponding to Eq. (D). At any conversion the temperature and $1/r$ can be evaluated. For example, at $x = 0.2$, $T = 600^\circ\text{K}$ from Fig. 5-2, and

$$r = C_0(1 - x)e^{35.2 - 44,500/R_g T} = 0.8e^{-2.2}C_0 = 0.0886C_0$$

$$\frac{1}{r} = \frac{11.3}{C_0}$$

Also shown in Fig. 5-2 is a plot of the $1/r$ values obtained in this manner. Graphical integration under this curve yields the time t for any x , as shown by Eq. (4-2). The results are summarized in Table 5-2. The conversion-vs-residence-time values obtained by the numerical-integration process are approximately equivalent to those listed in Table 5-1.

The final curves of temperature and conversion vs time (Fig. 5-3) show the necessity of supplying energy (as heat) to a highly endothermic reaction if large conversions are desired. In the present case, where no energy was supplied, the temperature decreased

Table 5-2

Conversion	0	0.10	0.20	0.30	0.40
θ , min	0	0.54	1.43	2.93	5.53

so rapidly that the reaction essentially stopped after a conversion of 50% was reached. If, instead of operating adiabatically, a constant rate of energy Q_s , Btu/min had been added to the reactor, the energy balance, according to Eq. (5-1), would have been

$$500(0.6)(1.8) \frac{dT}{dt} = \frac{-15,000}{60} 0.156(500)(1.8) \frac{dT}{dt} + Q_s$$

Integration gives the desired relation between T and x_1 , but in this case the time is also involved:

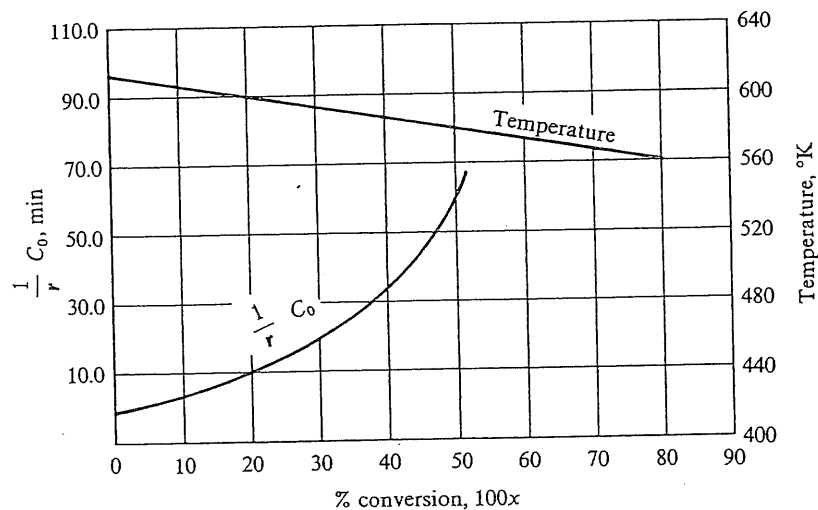
$$\Delta T = 0.00185Q_s \Delta t - 65 \Delta x \quad (D')$$

Equation (D') is analogous to Eq. (D) for the adiabatic case. The graphical solution cannot be employed in this case because curves of T and $1/r$ vs conversion cannot be easily determined independently of the time. However, the numerical-solution approach is satisfactory. The equations involved would be (D') and

$$\Delta t = \left[\frac{1}{(1-x)e^{35.2-44,500/R_g T}} \right]_{av} \Delta x \quad (B'')$$

These twin expressions can be solved by choosing an increment of conversion, assuming a corresponding time interval Δt , and evaluating T_1 at $x_1 = 0 + \Delta x$ from Eq. (D'); the assumed values of Δt may then be checked from Eq. (B''). For example, let $Q_s =$

Fig. 5-2 Temperature vs conversion for decomposition of acetylated castor oil



3,000 Btu/min and choose Δx equal to 0.10. As a first trial, assume $\Delta t = 0.50$ min, which is somewhat less than the adiabatic case. Then from Eq. (D')

$$T_1 = 613 + \Delta T_1 = 613 - 65(0.1) + 0.00185(3,000)0.50$$

$$T_1 = 613 - 6.5 + 2.8 = 609.3^\circ\text{K}$$

Now Δt can be obtained from Eq. (B''). First the average value of $1/R$ over the increment must be determined. At $x = 0.0$

$$R_0 = (1 - 0)e^{35.2 - 44,500/R_0(613)} = e^{-1.4}$$

$$\frac{1}{R_0} = 4.15$$

At $x_1 = 0.1$

$$R_1 = (1 - 0.1)e^{35.2 - 44,500/R_1(609.3)} = 0.9e^{-1.6}$$

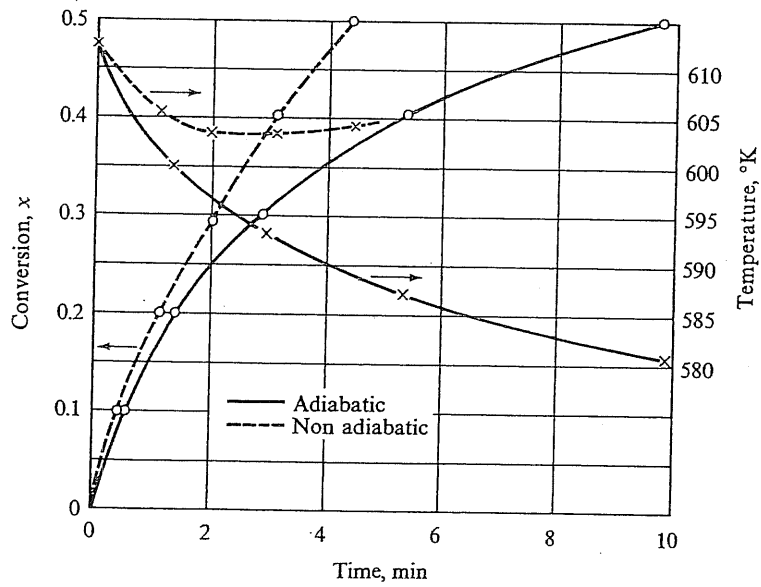
$$\frac{1}{R_1} = 5.50$$

$$\left(\frac{1}{R}\right)_{\text{av}} = \frac{4.15 + 5.50}{2} = 4.83$$

From Eq. (B'')

$$\Delta t = 4.83(0.10) = 0.48 \text{ min}$$

Fig. 5-3 Temperature and conversion vs time



This is close enough to the assumed value of $\Delta t = 0.50$ to be satisfactory. Values of Δt for successive increments can be obtained by repeating the previous calculations. The results are summarized in Table 5-3. For comparison, the adiabatic operating conditions are also shown.

Table 5-3

Conversion	Nonadiabatic		Adiabatic	
	$T, ^\circ K$	t, min	$T, ^\circ K$	t, min
0	613	0	613	0
0.10	608.7	0.48	606.5	0.54
0.20	605.5	1.08	600.0	1.43
0.30	604.0	1.97	593.5	2.93
0.40	603.9	3.10	587.0	5.53
0.50	604.3	4.39	580.5	9.85

These results show that 30% conversion is obtained in 30% less time when 3000 Btu/min, or $3,000/500 = 6$ Btu/lb of charge, is added to the reactor. Temperature and conversion curves for this nonadiabatic case are also indicated in Fig. 5-3.

5-2 Ideal Tubular-flow Reactors

The energy balance for tubular-flow reactors, Eq. (3-18), is valid for steady-state conditions and when there are no radial temperature gradients and no axial dispersion of energy. The last two requirements are satisfied by the limitation to ideal reactors. As mentioned earlier, deviations from ideal conditions are most likely to be significant for heterogeneous reactions. Therefore more general equations for tubular reactors are presented in Chap. 13, although some consideration is given to isothermal cases in Chap. 6.

Simultaneous application of Eq. (3-18), the mass balance, Eq. (3-12), and the rate equation establishes the temperature and composition as a function of reactor volume. The calculations are the same as those for batch reactors (illustrated in Example 5-1), except that the reactor volume replaces time as the independent variable. The procedure is not repeated here for single reactions; instead the treatment for multiple-reaction systems is illustrated. The most significant point is the effect of temperature on the product distribution (selectivity) in the effluent stream from the reactor. Example 5-2 concerns a nonisothermal reactor in which two parallel reactions occur, and the desired product is produced by the reaction with the higher activation energy. A case of consecutive reactions is then discussed

in which the desirable product is produced by the reaction with the lower activation energy. Some conclusions about favorable operating temperatures for systems of reactions are immediately apparent. For example, a high temperature is indicated for parallel (simultaneous) reactions when the desirable product is formed by the reaction with the highest activation energy. If the desirable reaction has the lowest activation energy, a low temperature is favored. The same conclusions are true, in general, for consecutive reactions of the form

1. $A + B \xrightarrow{k_1} R$
2. $R + B \xrightarrow{k_2} S$

where R is the desirable product. That is, high selectivity of R with respect to S is favored by high temperature if $E_1 > E_2$ and low temperature if $E_1 < E_2$. Numerical substantiation of some of these conclusions is shown in Example 5-2 and the subsequent discussion. The literature may be consulted for more thorough treatment of optimum temperatures in reactors.¹

For multiple-reaction systems the maximum selectivity for a given product will require operation at a different temperature for each location in the reactor. However, it is rarely of value to find this optimum temperature-vs-position relationship because of the practical difficulty in achieving a specified temperature profile. It is important to be able to predict the general type of profile that will give the optimum yield, for it may be possible to design the reactor to conform to this general trend. These comments apply equally to batch reactors, where the temperature-time relationship rather than the temperature-position profile is pertinent.

For adiabatic operation Eq. (3-18) reduces to an integrable form,

$$F_t c_p dT = F \frac{-\Delta H}{M} dx \quad (5-4)$$

If c_p and ΔH are constant, this may be integrated to give an expression analogous to Eq. (5-3) for batch reactors,

$$T - T_0 = \frac{-\Delta H}{M c_p} w(x - x_0) \quad (5-5)$$

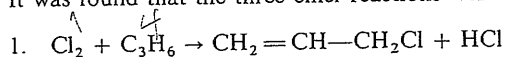
where $w = F/F_t$ is the weight fraction of reactant in the feed and the subscript zero denotes feed conditions.

¹Octave Levenspiel, "Chemical Reaction Engineering," chap. 8, John Wiley & Sons, Inc., New York, 1962; K. G. Denbigh, "Chemical Reactor Theory," chaps. 5 and 6, Cambridge University Press, New York, 1965; K. G. Denbigh, *Chem. Eng. Sci.*, **8**, 125 (1958); O. Bilous and N. R. Amundson, *Chem. Eng. Sci.*, **5**, 81 (1956).

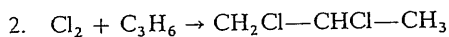
Example 5-2 It is proposed to design a pilot plant for the production of allyl chloride. The reactants consist of 4 moles propylene/mole chlorine and enter the reactor at 200°C. The reactor will be a vertical tube of 2 in. ID. If the combined feed rate is 0.85 lb mole/hr, determine the conversion to allyl chloride as a function of tube length. The pressure may be assumed constant and equal to 29.4 psia.

The reactants will be preheated separately to 200°C and mixed at the entrance to the reactor. At this low temperature explosion difficulties on mixing are not serious. The reactor will be jacketed with boiling ethylene glycol, so that the inside-wall temperature will be constant and equal to 200°C. The inside-heat-transfer coefficient may be taken as 5.0 Btu/(hr)(ft²)(°F).

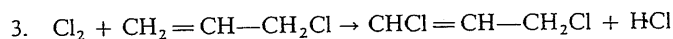
ADDITIONAL DATA AND NOTES The basic development of the allyl chloride process has been reported by Groll and Hearne¹ and Fairbairn, Cheney, and Cherniavsky.² It was found that the three chief reactions were allyl chloride formation,



the parallel addition reaction giving 1,2-dichloropropane,



and consecutive chlorination of allyl chloride to give 1;3-dichloro-1-propene



To simplify the kinetic treatment of the problem we shall consider only the first two reactions. The heats of reaction, in calories per gram mole, are shown in Table 5-4. The molal heat capacities C_p will be assumed constant and equal to the values given in Table 5-5.

No information is published for the rate-of-reaction equations, although it is known that reaction 2 takes place at temperatures as low as 100°C, while reaction 1 has an insignificant rate below 200°C. As the temperature increases above 200°C, the rate of reaction 1 increases rapidly, until at 500°C it is several times as fast as that of reaction 2. From this general information and some published data on the effect of residence time and temperature on the conversion, the proposed rate equations are

$$r_1 = 206,000e^{-27,200/R_s T} p_{\text{C}_3\text{H}_6} p_{\text{Cl}_2}$$

$$r_2 = 11.7e^{6,860/R_s T} p_{\text{C}_3\text{H}_6} p_{\text{Cl}_2}$$

Table 5-4

ΔH	273°K	355°K
Reaction 1	-26,800	-26,700
Reaction 2	-44,100	-44,000

¹H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, 31, 1530 (1939).

²A. W. Fairbairn, H. A. Cheney, and A. J. Cherniavsky, *Chem. Eng. Progr.*, 43, 280 (1947).

Table 5-5

Component	C_p , Btu/(lb mole)(°R)
Propylene (g)	25.3
Chlorine (g)	8.6
Hydrogen chloride (g)	7.2
Allyl chloride (g)	28.0
1,2-Dichloropropane (g)	30.7

where r_1 and r_2 are in lb moles of Cl_2 converted per hour per cubic foot, T is in degrees Rankine, and the partial pressure p is in atmospheres.

Solution Since there will be heat transfer from the reaction gases to the glycol jacket, the temperature in the reactor will depend on the length z , and the design calculations have to be carried out by the stepwise integration of the rate and energy equations. The conversion resulting from each of the simultaneous reactions must be obtained separately. It is convenient in this problem to define the conversion as moles of chlorine reacted per mole of *total* feed rather than per mole of chlorine in the feed. If this conversion is $(x_i)_1$ for reaction 1 and $(x_i)_2$ for 2, the mass-balance equation, Eq. (3-12), are

$$r_1 dV = F_i d(x_i)_1$$

$$r_2 dV = F_i d(x_i)_2$$

or, in difference form,

$$\Delta(x_i)_1 = \bar{r}_1 \Delta\left(\frac{V}{F_i}\right)$$

$$\Delta(x_i)_2 = \bar{r}_2 \Delta\left(\frac{V}{F_i}\right)$$

where the overbar indicates average value and F_i is the total *molar* feed rate.

The energy balance defining the temperature is given by Eq. (3-18). It is convenient for numerical solution to write this in terms of the rates of reaction instead of the conversion. This can be done by substituting for dx/dV the quantities in Eqs. (A) and (B). If we take both reactions into account and note that $F_i dx_i = F dx$, Eq. (3-18) becomes¹

$$F_i C_p \frac{dT}{dV} = U(T_s - T) \frac{dA_h}{dV} - (r_1 \Delta H_1 + r_2 \Delta H_2)$$

If z is the reactor length and d is its diameter,

$$dV = \frac{\pi d^2}{4} dz$$

$$dA_h = \pi d dz$$

¹The molecular weight M is not necessary as it is in Eq. (3-18), because the rates are expressed in moles.

Using these relations and writing the result in difference form gives

$$F_t C_p \Delta T = \pi d \Delta z U (T_s - T)_{av} - (\bar{r}_1 \Delta H_1 + \bar{r}_2 \Delta H_2) \frac{\pi d^2}{4} \Delta z \quad (C)$$

Equations (A) to (C) and the rate expressions can be solved for $(x_t)_1$, $(x_t)_2$, and T as a function of reactor length. Equations (A) and (B) may be expressed in terms of Δz by noting

$$\Delta \left(\frac{V}{F_t} \right) = \frac{\pi d^2}{4 F_t} \Delta z \quad (D)$$

Then they may be written

$$\Delta(x_t)_1 = \bar{r}_1 \frac{\pi d^2}{4 F_t} \Delta z \quad (A')$$

$$\Delta(x_t)_2 = \bar{r}_2 \frac{\pi d^2}{4 F_t} \Delta z \quad (B')$$

The solution procedure is as follows:

1. From the known initial conversion $[(x_t)_1 = 0 \text{ and } (x_t)_2 = 0]$ and temperature (200°C), r_1 and r_2 entering the reactor are computed.
2. An arbitrary increment of reactor length Δz is chosen. The smaller this increment, the more accurate the solution (and the more time consuming the calculations).
3. For the chosen Δz , first estimates of the conversion occurring within the increment are obtained from Eqs. (A') and (B'). It is convenient to assume that the average values of r_1 and r_2 are equal to the initial values evaluated in step 1.
4. The change in temperature within the increment ΔT is determined from Eq. (C). An estimate of the mean temperature difference $(T_s - T)_{av}$ in the increment is required in order to evaluate the heat-loss term. Once ΔT has been computed, the estimate of $(T_s - T)_{av}$ can be checked. Hence a trial-and-error calculation is necessary to evaluate ΔT .
5. From the conversion and temperature at the end of the first increment, as determined in steps 3 and 4, the rate of reaction is computed at this position in the reactor. Then steps 3 and 4 are repeated, using for \bar{r}_1 and \bar{r}_2 the arithmetic average of the values at the beginning and end of the increment. This, in turn, will give more precise values of the conversion and temperature at the end of the first increment and permit a third estimate of the average values of the rates. If this third estimate agrees with the second, the next increment of reactor length is chosen and the procedure is repeated.

The steps will be illustrated by carrying out the numerical calculations for the first two increments. Note that these kinds of calculations are well suited for digital-machine computation.

The rate equations should be converted to a form involving the conversions rather than partial pressures. If 4 moles propylene/mole chlorine enter the reactor, then at a point where the conversions are $(x_t)_1$ and $(x_t)_2$, the moles of each component will be as follows:

$$\text{Chlorine}^1 = 1 - 5(x_{i1}) - 5(x_{i2})$$

$$\text{Propylene} = 4 - 5(x_{i1}) - 5(x_{i2})$$

$$\text{Allyl chloride} = 5(x_{i1})$$

$$\text{Dichloropropane} = 5(x_{i2})$$

$$\text{Hydrogen chloride} = 5(x_{i1})$$

$$\text{Total moles} = 5[1 - (x_{i2})]$$

If we assume that all the components behave as ideal gases at $p_t = 29.4$ psia, the partial pressures of chlorine and propylene, in atmospheres, are given by

$$p_{\text{C}_2\text{H}_6} = \frac{29.4}{14.7} \left[\frac{4 - 5(x_{i1}) - 5(x_{i2})}{5[1 - (x_{i2})]} \right] = 2 \frac{0.8 - (x_{i1}) - (x_{i2})}{1 - (x_{i2})}$$

$$p_{\text{Cl}} = \frac{29.4}{14.7} \left[\frac{1 - 5(x_{i1}) - 5(x_{i2})}{5[1 - (x_{i2})]} \right] = 2 \frac{0.2 - (x_{i1}) - (x_{i2})}{1 - (x_{i2})}$$

These expressions can be substituted in the original proposed rate equations to relate the rates to the conversions and the temperature. The results are

$$r_1 = 824,000 e^{-13,700/T} \frac{[0.8 - (x_{i1}) - (x_{i2})][0.2 - (x_{i1}) - (x_{i2})]}{[1 - (x_{i2})]^2} \quad (\text{E})$$

$$r_2 = 46.8 e^{-3,460/T} \frac{[0.8 - (x_{i1}) - (x_{i2})][0.2 - (x_{i1}) - (x_{i2})]}{[1 - (x_{i2})]^2} \quad (\text{F})$$

Equations (A) to (F) can now be employed to carry out the steps in the solution.

STEP 1 The rates of reaction at the reactor entrance are given by Eqs. (E) and (F), with $T = (200 + 273)(1.8) = 852^\circ\text{R}$ and $(x_{i1}) = (x_{i2}) = 0$:

$$r_1 = 824,000 e^{-16.1}(0.16) = 0.0135 \text{ lb mole}/(\text{hr})(\text{ft}^3)$$

$$r_2 = 46.8 e^{-4.06}(0.16) = 0.129 \text{ lb mole}/(\text{hr})(\text{ft}^3)$$

STEP 2 An increment of reactor length is chosen as $\Delta z = 4.0$ ft.

STEP 3 Assuming that the rates computed in step 1 are average values for the increment, the first estimates of the conversion in the increment are given by Eqs. (A) and (B):

$$\frac{\pi d^2}{4} = \frac{\pi}{4} \left(\frac{2}{12} \right)^2 = 0.0218 \text{ ft}^2$$

$$\frac{\pi d^2}{4F_t} = \frac{0.0218}{0.85} = 0.0257$$

¹The coefficient 5 appears in this equation because x_i is the conversion based on 1 mole of total feed. Note that the maximum value for the sum of (x_{i1}) and (x_{i2}) is 0.2, which corresponds to complete conversion of the chlorine to either allyl chloride or dichloropropane.

hence

$$\Delta(x_i)_1 = 0.0135(0.0257)(4.0) = 0.0014$$

$$(x_i)_1 = 0 + 0.0014 = 0.0014$$

Similarly, for the second reaction we obtain

$$\Delta(x_i)_2 = 0.129(0.0257)(4.0) = 0.0133$$

$$(x_i)_2 = 0 + 0.0133 = 0.0133$$

STEP 4 To use Eq. (C) for estimating ΔT for the increment we must know ΔH_1 , ΔH_2 , T_s , U , F_i , C_p , and $(T_s - T)_{av}$: The heat-of-reaction data in Table 5-4 are at low temperatures, but they show little change with temperature; hence ΔH_1 and ΔH_2 will be assumed constant:

$$\Delta H_1 = -26,700(1.8) = -48,000 \text{ Btu/lb mole}$$

$$\Delta H_2 = -44,000(1.8) = -79,200 \text{ Btu/lb mole}$$

$$T_s = (200 + 273)(1.8) = 852^\circ\text{R}$$

$$h = 5 \text{ Btu/(hr)(ft}^2\text{)(}^\circ\text{F)}^1$$

Since the conversion is small during the first increment, the heat capacity per unit time of the total reaction mixture is essentially that of the chlorine and propylene in the feed to the reactor,

$$\begin{aligned} F_i C_p &= \frac{0.85}{5} (8.6) + \frac{4}{5} (0.85)(25.3) \\ &= 0.85(21.8) = 18.5 \text{ Btu/(hr)(}^\circ\text{F)} \end{aligned}$$

If the mean temperature difference $(T_s - T)_{av}$ for the first increment is *estimated* to be -20°F , substitution in Eq. (C) gives

$$18.5 \Delta T = \pi \frac{2}{12}(5)(-20)(4) - [0.0135(-48,000) + 0.129(-79,200)](0.0218)(4)$$

$$\Delta T = \frac{946 - 210}{18.5} = 40^\circ\text{F}$$

$$T_1 = 852 + 40 = 892^\circ\text{R} \quad \text{temperature at end of first increment}$$

$$T_s - T \text{ at entrance} = 0$$

$$T_s - T \text{ at end of increment} = 852 - 892 = -40^\circ\text{F}$$

$$(T_s - T)_{av} = \frac{0 + (-40)}{2} = -20^\circ \quad \text{vs } -20^\circ \text{ assumed}$$

¹In the expression for h , since the inside-wall temperature is known, the heat transfer with the surroundings can be evaluated from $h(T_s - T)_{av}\pi d \Delta z$, where h is the inside-film coefficient and T_s is the inside-wall-surface temperature. The overall coefficient U is not necessary in this case.

STEP 5 At the end of the first increment the first estimate of the conversions and temperature is

$$(x_i)_1 = 0.0014$$

$$(x_i)_2 = 0.0133$$

$$T_1 = 852 + 40 = 892^\circ\text{R}$$

Substitution of these conditions in rate equations (E) and (F) yields

$$r_1 = 0.0256 \quad r_2 = 0.143$$

A second, and more accurate, estimate of the average values of the rates for the first increment can now be made:

$$\bar{r}_1 = \frac{0.0135 + 0.0256}{2} = 0.0195$$

$$\bar{r}_2 = \frac{0.129 + 0.143}{2} = 0.136$$

The second estimate of the conversion in the increment, obtained from these rates and Eqs. (A') and (B'), is

$$\Delta(x_i)_1 = 0.0195(0.0257)(4.0) = 0.0020$$

$$(x_i)_1 = 0 + 0.0020 = 0.0020$$

$$\Delta(x_i)_2 = 0.136(0.0257)(4.0) = 0.0140$$

$$(x_i)_2 = 0 + 0.0140 = 0.0140$$

The second estimate of ΔT , determined from Eq. (C), is

$$\Delta T = 41^\circ\text{F}$$

$$T_1 = 852 + 41 = 893^\circ\text{R}$$

At the revised values of $(x_i)_1$, $(x_i)_2$, and T (at the end of the first increment) the rates are

$$r_1 = 0.0258$$

$$r_2 = 0.144$$

Since these values are essentially unchanged from the previous estimate, the average rates will also be the same, and no further calculations for this increment are necessary.

For the second increment Δz is again chosen as 4 ft, and the average rates are estimated to be

$$\bar{r}_1 = 0.032$$

$$\bar{r}_2 = 0.15$$

Then from Eqs. (A') and (B'),

$$\Delta(x_i)_1 = 0.032(0.0257)(4) = 0.0033$$

$$(x_i)_1 = 0.0020 + 0.0033 = 0.0053$$

$$\Delta(x_i)_2 = 0.15(0.0257)(4.0) = 0.0154$$

$$(x_i)_2 = 0.0140 + 0.0154 = 0.0294$$

From Eq. (C), estimating $(T_s - T)_{av} = -55^\circ\text{F}$, we have

$$18.5 \Delta T = \pi \frac{2}{12} (5)(-20)(4) - [0.032(-48,000) + 0.15(-79,200)](0.0218)(4)$$

$$\Delta T = 32^\circ\text{F}$$

$$T_2 = 893 + 32 = 925^\circ\text{R}$$

The estimated $(T_s - T)_{av}$ for the second increment can be checked by evaluating the temperature differences at the beginning and end of the increment:

$$T_s - T = 852 - 893 = -41^\circ\text{F} \quad \text{beginning of increment}$$

$$T_s - T = 852 - 925 = -73^\circ\text{F} \quad \text{end of increment}$$

$$(T_s - T)_{av} = -57^\circ\text{F} \quad \text{vs } -55^\circ\text{F assumed}$$

According to the first estimate, the conversions and temperature at the end of the second increment are

$$(x_i)_1 = 0.0053$$

$$(x_i)_2 = 0.0294$$

$$T_2 = 925^\circ\text{R}$$

Using these quantities in the rate equations, we obtain

$$r_1 = 0.0400$$

$$r_2 = 0.145$$

A second estimate of the average rates during the increment is given by the expressions

$$\bar{r}_1 = \frac{0.0258 + 0.0400}{2} = 0.0329$$

$$\bar{r}_2 = \frac{0.144 + 0.145}{2} = 0.144$$

Since these values are close to the first estimates, additional rate calculations for the increment are unnecessary. The revised values for conversion at the end of the increment are

$$(x_i)_1 = 0.0020 + 0.0329(0.0257)(4.0) = 0.0054$$

$$(x_i)_2 = 0.0140 + 0.144(0.0257)(4.0) = 0.0288$$

The revised temperature is given by

$$F_t C_p \Delta T = -[0.0329(-48,000) + 0.144(-79,200)](0.0218)(4) \\ + 5(-57)(0.524)(4) = 536$$

Since the total conversion is becoming significant at the end of the second increment, it may be necessary to evaluate $F_t C_p$ in terms of the actual mixture in the reactor instead of assuming that it equals that for the feed. This may be approximated by noting that $F_t C_p = \sum_i F_i(C_p)_i$. To evaluate this summation molal units will be used. The rate of flow of each component at the end of the second increment will be

$$\text{Allyl chloride} = F_t(x_t)_1 = 0.85(0.0054) = 0.0046 \text{ mole/hr}$$

$$\text{Dichloropropane} = F_t(x_t)_2 = 0.85(0.0288) = 0.0245$$

$$\text{Chlorine} = F_t[0.2 - (x_t)_1 - (x_t)_2] = 0.85(0.1658) = 0.1410$$

$$\text{Propylene} = F_t[0.8 - (x_t)_1 - (x_t)_2] = 0.85(0.7658) = 0.6510$$

$$\text{Hydrogen chloride} = F_t(x_t)_1 = 0.85(0.0054) = 0.0046$$

Thus

$$\begin{aligned} \sum F_i(C_p)_i &= 0.0046(28) + 0.0245(30.7) + 0.1410(8.6) \\ &\quad + 0.6510(25.3) + 0.0046(7.2) \\ &= 18.6 \text{ Btu/(hr)(}^\circ\text{R)} \end{aligned}$$

This result turns out not to be appreciably different from that based on the feed, but it will become so when the conversion reaches larger values. Hence, from the energy balance

$$\Delta T = \frac{536}{18.6} = 29^\circ\text{F}$$

and the revised temperature at the end of the increment is

$$T_2 = 893 + 29 = 922^\circ\text{R}$$

The results of these calculations indicate two trends. First, the rate of reaction 1 is relatively low with respect to reaction 2 at low temperatures but increases rapidly with temperature, while the rate of reaction 2 is not very sensitive to temperature changes. This is because the activation energy for reaction 1 is greater than that for reaction 2. The second trend is the increase in rate of heat transfer to the surroundings with an increase in reactor length. This effect, which is a consequence of the increase in $(T - T_s)_{\text{av}}$, offsets the rise in temperature due to the exothermic nature of the reactions, and results ultimately in a decrease in temperature with reactor length. This point is reached when the heat transferred from the reactor tube to the surroundings is greater than the heat evolved from the reactions. Additional incremental calculations (Figs. 5-4, 5-5, and Table 5-6) indicate that the point at which the temperature starts to decrease is about 18 ft from the entrance to the reactor. This point of maximum temperature occurs at too low a level for the rate of reaction 1 to become large with respect to that of reaction 2. Therefore the conversion to allyl chloride never reaches a high

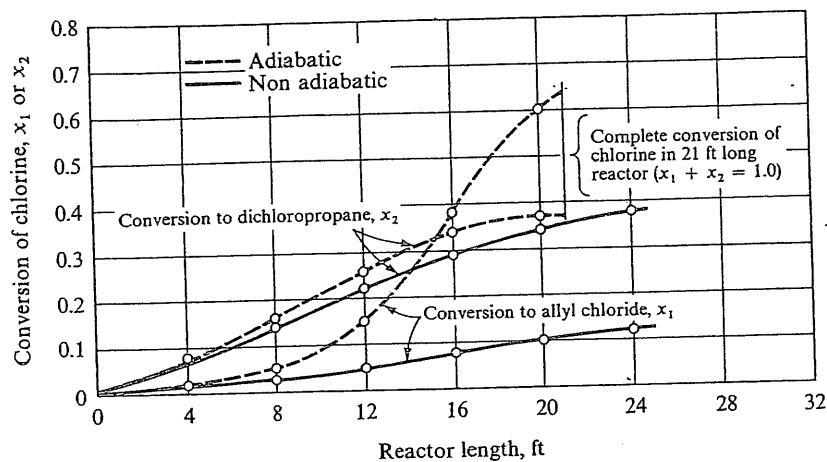


Fig. 5-4 Conversion curves for allyl chloride production in a tubular reactor

Fig. 5-5 Temperature profiles for allyl chloride production in a tubular reactor

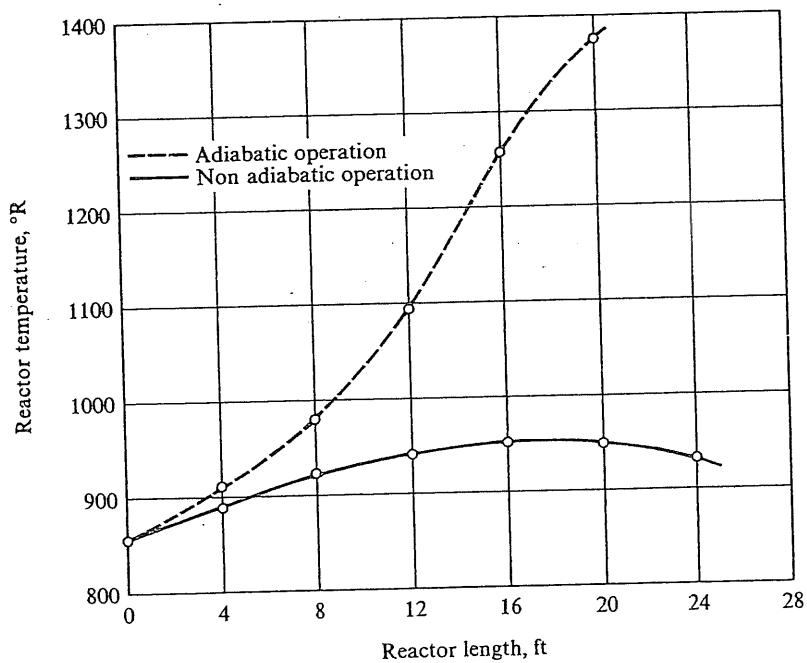


Table 5-6 Conversion vs reactor length for chlorination of propylene

NON ADIABATIC OPERATION

Reactor volume, ft ³	Reactor length, ft ³	Conversion per mole feed			T, °R	Conversion of chlorine in feed			Selectivity $S_o = x_1/x_2$
		(x_i) ₁	(x_i) ₂	Total		x_1	x_2	Total	
0	0	0.0	0.0	0.0	852	0.0	0.0	0.0	...
0.087	4	0.0020	0.0140	0.0160	893	0.0100	0.070	0.080	0.14
0.174	8	0.0054	0.0288	0.0342	922	0.0270	0.145	0.172	0.19
0.261	12	0.0098	0.0435	0.0533	940	0.0490	0.217	0.266	0.23
0.349	16	0.0147	0.0575	0.0723	949	0.0735	0.287	0.361	0.36
0.436	20	0.0193	0.0698	0.0891	949	0.0964	0.349	0.445	0.28

ADIABATIC OPERATION

0	0	0.0	0.0	0.0	852	0.0	0.0	0.0	...
0.087	4	0.0023	0.0144	0.0167	905	0.0115	0.0720	0.0835	0.16
0.174	8	0.0088	0.0315	0.0403	981	0.0440	0.157	0.201	0.28
0.261	12	0.0283	0.0505	0.0788	1,093	0.142	0.252	0.394	0.56
0.349	16	0.0779	0.0667	0.1446	1,261	0.389	0.334	0.723	1.16
0.436	20	0.1204	0.0739	0.1943	1,380	0.602	0.369	0.971	1.63

value (most of the reaction is to the dichloropropane), and the selectivity for allyl chloride is always less than unity, as noted in the last column of Table 5-6. A reactor of this type is not well suited for the production of allyl chloride. An adiabatic reactor would eliminate the maximum in the temperature and result in higher temperatures, which in turn would favor the production of allyl chloride. The only change in the calculations for such an adiabatic case is that the term $U(T_s - T)_{av} \pi d \Delta z$ would be zero. For comparison purposes the temperature and conversion results for such an adiabatic reactor are also shown in Figs. 5-4 and 5-5 and Table 5-6. The selectivity now is greater than unity at high conversions.

Even adiabatic operation results in the formation of considerable amounts of the undesirable dichloropropane. This occurs in the first part of the reactor, where the temperature of the flowing mixture is low. This is an illustration of the discussion at the beginning of the chapter with respect to Fig. 5-1a and b. The conditions correspond to the low-conversion range of Fig. 5-1b before the maximum rate is reached. A tubular-flow reactor is less desirable for these conditions than a stirred-tank unit. The same reaction system is illustrated in Example 5-3 for a stirred-tank unit.

Consider next an illustration of consecutive reactions where the intermediate component is the desired product. Suppose *A* and *B* produce products *X*, *Y*, and *Z* according to the following homogeneous reactions, which follow second-order kinetics:

1. $A + B \rightarrow X + Z$
2. $X + B \rightarrow Y + Z$

The system has a constant density and the reactions are irreversible. The specific reaction rates for each reaction are

$$k_1 = A_1 e^{-E_1/R_g T} \quad (5-6)$$

$$k_2 = A_2 e^{-E_2/R_g T} \quad (5-7)$$

The problem is to find the constant operating temperature in a tubular-flow reactor for which the yield of X will be a maximum. We would also like to know the value of the yield and the overall selectivity of X with respect to Y at this condition. For these objectives it is not necessary to know the individual values of A_1 , A_2 , E_1 , and E_2 in Eqs. (5-6) and (5-7), but only the ratio k_2/k_1 . Suppose this is defined by

$$\frac{A_2}{A_1} = 7.95 \times 10^{11} \quad (5-8)$$

$$E_2 - E_1 = 16,700 \text{ cal/g mole} \quad (5-9)$$

and that we take the permissible range of operating temperatures as 5 to 45°C. This problem involves consecutive reactions for which the activation energy of the reaction producing the desired product is less than that of the other reaction; that is, $E_1 < E_2$. According to the discussion at the beginning of the section, the lowest temperature, 5°C, would give the best yield of X . We wish to verify this and calculate the maximum yield and the selectivity.

The reactions represent a common type of substitution reaction; for example, the successive chlorination of benzene considered in Example 2-8 is of this form. In that example yields of primary and secondary products were obtained for an isothermal batch reactor. As pointed out in Sec. 4-4, the results for batch reactors may be used for tubular-flow reactors if the time is replaced by the residence time. Actually, in Example 2-8 the yield equations were expressed in terms of fraction of benzene unreacted rather than time. Therefore identical results apply for the tubular-flow reactor. Hence the yield of X is given by Eq. (F) of Example 2-8,¹ with $[A]/[A]_0$ replacing $[B]/[B]_0$; that is,

$$x_x = \frac{[X]}{[A]_0} = \frac{1}{1 - \alpha} \left[\left(\frac{[A]}{[A]_0} \right)^\alpha - \frac{[A]}{[A]_0} \right] \quad (5-10)$$

¹ Actually, by the equation immediately preceding Eq. (F). The same result is also given by Eq. (2-106), which was developed for consecutive first-order reactions. As shown in Example 2-8, in this case the results are the same for first- or second-order kinetics.

where

$$\alpha = \frac{k_2}{k_1} = \frac{A_2 e^{-E_2/R_g T}}{A_1 e^{-E_1/R_g T}} = 7.95 \times 10^{11} e^{-16,700/R_g T} \quad (5-11)$$

The yield of X , described by Eq. (5-10), has a maximum value at an intermediate value of $[A]/[A]_0$, that is, at an intermediate value of the conversion $(1 - [A]/[A]_0)$. We first find this local maximum, and then express it as a function of α . Once this is done, we can find the value of α , and hence the temperature, that gives the overall maximum within the allowable temperature range.

To determine the local maximum let us set the derivative of x_X with respect to $[A]/[A]_0$ (call this z) equal to zero; that is,

$$\frac{dx_X}{dz} = 0 = \frac{1}{1 - \alpha} \left[\alpha(z)^{\alpha-1} - 1 \right]$$

or

$$z = \frac{[A]}{[A]_0} = \left(\frac{1}{\alpha} \right)^{1/(\alpha-1)} \quad (5-12)$$

This is the value of $[A]/[A]_0$ for the local maximum of x_X . Substituting this value in Eq. (5-10) gives the local maximum in terms of α ,¹

$$(x_X)_{\max} = \frac{1}{1 - \alpha} \left(\frac{1}{\alpha} \right)^{1/(\alpha-1)} \left(\frac{1}{\alpha} - 1 \right) = \left(\frac{1}{\alpha} \right)^{\alpha/(\alpha-1)} \quad (5-13)$$

From Eq. (5-11) we can find the value of α for any temperature over the range 5 to 45°C. Substituting these results for α in Eq. (5-13) gives the corresponding local-maximum yields of X . The results are shown in Fig. 5-6, plotted as $(x_X)_{\max}$ vs temperature. As expected, the overall maximum occurs at 5°C and is about 0.84. The corresponding value of α is 0.06.

The total conversion at maximum yield conditions is, from Eq. (5-12),

$$\begin{aligned} x_t &= 1 - \frac{[A]}{[A]_0} = 1 - \left(\frac{1}{\alpha} \right)^{1/(\alpha-1)} \\ &= 1 - \left(\frac{1}{0.06} \right)^{1/(0.06-1)} = 1 - 0.05 = 0.95 \quad \text{or } 95\% \end{aligned}$$

From the stoichiometry of the reactions, the mass balance of A is

$$[A] = [A]_0 - [X] - [Y]$$

¹This same result was obtained in Example 2-7 for a batch reactor.

or

$$\frac{[A]}{[A]_0} = 1 - \frac{[X]}{[A]_0} - \frac{[Y]}{[A]_0}$$

$$x_Y = \frac{[Y]}{[A]_0} = 1 - \frac{[A]}{[A]_0} - \frac{[X]}{[A]_0} = x_t - x_X \quad (5-14)$$

Hence

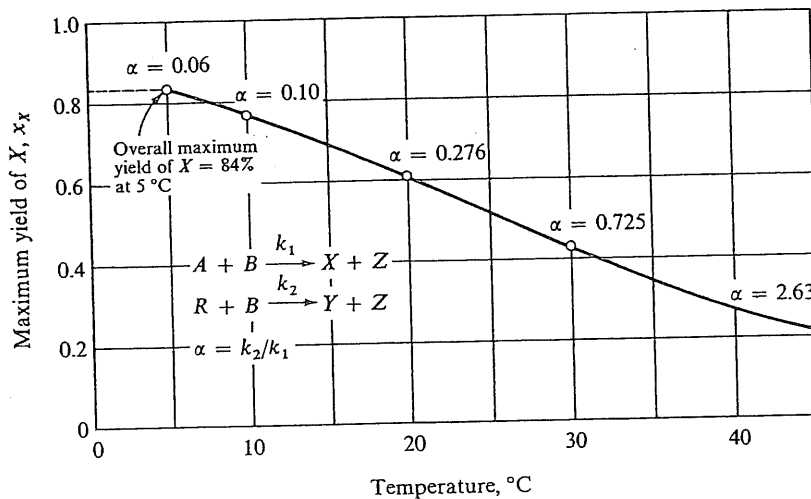
$$x_Y = 0.95 - 0.84 = 0.11$$

Of the total conversion of 95%, 84% is to X and 11% is to Y . The overall selectivity of X to Y is $0.84/0.11 = 7.6$ at the maximum yield of X . The selectivity is not necessarily a maximum at the conditions of maximum yield. If the separation of X from Y in the product stream requires an expensive process, it might be more profitable to operate the reactor at a conversion level at which x_X is less than 84% but the selectivity is higher than 7.6. The selectivity may be evaluated for any total conversion and α from Eqs. (5-10) and (5-14); thus the selectivity is

$$S_o = \frac{x_X}{x_Y} = \frac{1/(1-\alpha)[(1-x_t)^\alpha - (1-x_t)]}{x_t - 1/(1-\alpha)[(1-x_t)^\alpha - (1-x_t)]} \quad (5-15)$$

Equation (5-15) indicates that S_o decreases sharply with x_t . The relationship is shown for 5°C by the dotted curve in Fig. 5-7. This curve suggests that

Fig. 5-6 Maximum yield of intermediate product (X) for consecutive reactions



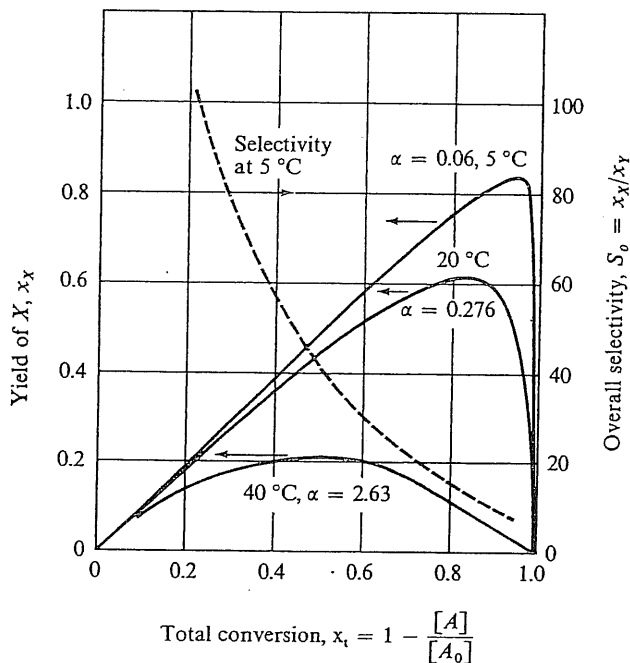
if a selectivity of 20 is required to reduce separation costs, the reactor should be designed to give a conversion of about 73%, at which the yield of X is only 70%. In this case the maximum yield occurs at a conversion of 95%, while the maximum selectivity is at a conversion approaching zero. Figure 5-7 also includes the curves for yield vs total conversion for several temperatures.

One final point is of significance. As conditions have been attained for the maximum yield of X , the reactor has become relatively large. At 5°C the reaction rate will be low and the total conversion is approaching 100%. Whether it is advisable to operate at these conditions for maximum conversion of X depends on the economics of reactor costs, separation costs, and price of product X .

5-3 Ideal Stirred-tank Reactors (Flow)

The ideal stirred-tank reactor operates isothermally and hence at a constant rate. However, an energy balance is needed to predict the constant temperature when the heat of reaction is sufficient (or the heat exchange between the surroundings and reactor is insufficient) to cause a difference between

Fig. 5-7 Yield of intermediate product (X) vs total conversion for consecutive reactions



feed and reactor temperatures. The proper energy balance is the algebraic relation presented as Eq. (3-6). This expression, the mass balance [Eq. (3-3)], and the rate equation are sufficient to fix the temperature and composition of the reaction mixture leaving the reactor. Sometimes simultaneous solution of the equations is required. For example, if a reactor of known volume is to be used, the calculation of the conversion and the temperature requires a simultaneous trial-and-error solution of Eqs. (3-3), (3-6), and the rate equation expressing the temperature dependency of r . In contrast, if the objective is the reactor volume needed to obtain a specified conversion, Eq. (3-6) can be solved independently for the reactor exit temperature T_e . The rate at T_e can be found from the rate equation and used in Eq. (3-3) to obtain the reactor volume. When more than one reaction occurs, a separate mass balance is necessary for each reaction.

A stirred tank may give better or worse selectivities than a tubular-flow unit in multiple-reaction systems. As usual, the key point is the relative values of the activation energies for the reactions. In particular, for a set of parallel reactions, where the desired product is formed by the reaction with the higher activation energy, the stirred tank is advantageous. The production of allyl chloride considered in Example 5-2 is a case in point. The performance of a stirred-tank reactor for this system is discussed next, and the results are compared with the performance of the tubular-flow reactor.

Example 5-3 Consider the design of a continuous stirred-tank reactor for the production of allyl chloride from propylene, using the reaction-rate data given in Example 5-2. So that we may compare the two types of reactors, the same feed condition will be employed:

$$\begin{aligned} F_i &= 0.85 \text{ mole/hr} \\ T &= 200^\circ\text{C} \\ P &= 29.4 \text{ psia} \\ \text{Molal ratio of propylene to chlorine} &= 4.0 \end{aligned}$$

The operation is adiabatic. Also, suitable baffles and entrance nozzles will be used so that, although the contents of the reactor are gaseous, they will be of uniform temperature, pressure, and composition.

Using the heats of reaction and heat capacities given in Example 5-2, determine the conversion of chlorine to allyl chloride expected for a range of sizes of reactors (i.e., reactor volumes).

Solution The rate of each reaction (allyl chloride and dichloropropane formation) will be a constant and should be evaluated at the temperature and composition of the stream leaving the reactor. The temperature is determined by Eq. (3-6). For adiabatic operation and zero conversion in the feed this becomes, using molal units for F ,

$$F_i C_p (T_f - T_e) - F[(x_i)_1 \Delta H_1 + (x_i)_2 \Delta H_2] = 0 \quad (\text{A})$$

where the subscript e is omitted from the conversion for convenience. Thus $(x_t)_1$ and $(x_t)_2$ refer to conversion in the product, based on total feed (as in Example 5-2).

If only one reaction were involved, this energy balance could be used to calculate T_e for a series of arbitrarily chosen conversions $(x_t)_1$. Then each value of $(x_t)_1$ would fix a rate r_1 . Substitution of these rates in the mass balance, Eq. (3-3), would give the reactor volumes corresponding to the conversions. However, in this case two equations of the form of (3-3) must be satisfied,

$$(x_t)_1 - 0 = r_1 \frac{V}{F_t} \quad (\text{B})$$

$$(x_t)_2 - 0 = r_2 \frac{V}{F_t} \quad (\text{C})$$

The rate expressions are obtained by substituting T_e for the temperature in Eqs. (E) and (F) of Example 5-2. Thus

$$r_1 = 824,000 e^{-13,700/T_e} \frac{[0.8 - (x_t)_1 - (x_t)_2][0.2 - (x_t)_1 - (x_t)_2]}{[1 - (x_t)_2]^2} \quad (\text{D})$$

$$r_2 = 46.8 e^{-3,460/T_e} \frac{[0.8 - (x_t)_1 - (x_t)_2][0.2 - (x_t)_1 - (x_t)_2]}{[1 - (x_t)_2]^2} \quad (\text{E})$$

The problem is solution of Eqs. (A) to (E) for the five unknowns $(x_t)_1$, $(x_t)_2$, T_e , r_1 , and r_2 at different values of the reactor volume V . One procedure which is not tedious is first to choose a value of T_e . Then, from the ratio of Eqs. (B) and (C), using (D) and (E) for r_1 and r_2 , we obtain the ratio $(x_t)_1/(x_t)_2$. Employing this ratio in Eq. (A) will give separate values for each conversion. Finally, the corresponding reactor volume can be obtained from either Eq. (B) or Eq. (C). This approach will be illustrated by including the numerical calculations for an exit temperature of 1302°R (450°C),

$$\frac{(x_t)_1}{(x_t)_2} = \frac{r_1}{r_2} = \frac{824,000 e^{-13,700/1,302}}{46.8 e^{-3,460/1,302}} = 6.77$$

Using this ratio in Eq. (A) and noting that the heat capacity of the feed $F_t C_p$ was determined in Example 5-2 as 18.5 Btu/(hr)(°F), we have

$$\begin{aligned} 18.5(T_F - T_e) + 0.85[6.77(x_t)_2 (48,000) + (x_t)_2(79,200)] \\ = 18.5(852 - 1,302) + 343,000(x_t)_2 = 0 \end{aligned}$$

$$(x_t)_2 = 0.0243$$

$$(x_t)_1 = 6.77(0.0243) = 0.164$$

The reactor volume required for these conversions is, from Eq. (B),

$$0.164 = \frac{V}{0.85} (824,000 e^{-13,700/1,302}) \frac{(0.8 - 0.164 - 0.024)(0.2 - 0.164 - 0.024)}{(1 - 0.0243)^2}$$

$$V = \frac{0.164(0.85)}{0.167} = 0.83 \text{ ft}^3$$

Table 5-7 Conversion vs reactor volume for adiabatic tank reactor: allyl chloride production

Reactor (or exit) temperature		Conversion per mole feed		Conversion of chlorine in feed		Reactor volume, ft ³	Selectivity $S_o = x_1/x_2$
°R	°C	$(x_1)_1$	$(x_1)_2$	x_1	x_2		
960	260	0.0098	0.0237	0.049	0.119	0.12	0.41
1032	300	0.0282	0.0324	0.14	0.162	0.15	0.86
1122	350	0.0660	0.0341	0.33	0.171	0.18	1.93
1212	400	0.114	0.0298	0.57	0.149	0.24	3.82
1257	425	0.138	0.0273	0.69	0.136	0.34	5.07
1302	450	0.164	0.0243	0.82	0.121	0.83	6.78

The corresponding values of the conversions and volume for other temperatures are summarized in Table 5-7. Comparing the results with those of Example 5-2, we see that the adiabatic stirred-tank reactor gives much higher yields and selectivities for allyl chloride than the tubular-flow type for the same reactor volume. In the tubular-flow equipment considerable dichloropropane is formed in the initial sections of the reactor, where the temperature is relatively low. This is avoided in the adiabatic tank reactor by operation at a constant temperature high enough to favor allyl chloride formation. For example, if the adiabatic tank reactor is operated at 450°C, 82% of the chlorine is converted to allyl chloride and 12% is converted to dichloropropane; the total conversion is 94%. In the adiabatic tubular reactor of Example 5-2 the products contained much greater amounts of dichloropropane for all reactor volumes. These conclusions are summarized in Fig. 5-8, where the fraction of chlorine converted to each product is shown plotted against reactor volume for the tubular and the tank reactors.

5-4 Stable Operating Conditions in Stirred-tank Reactors¹

In Example 5-3 the temperature and conversion leaving the reactor were obtained by simultaneous solution of the mass and energy balances. The results for each temperature in Table 5-7 represented such a solution and corresponded to a different reactor, i.e., a different reactor volume. However, the numerical trial-and-error solution required for this multiple-reaction system hid important features of reactor behavior. Let us therefore reconsider the performance of a stirred-tank reactor for a simple single-reaction system.

Suppose an exothermic irreversible reaction with first-order kinetics is carried out in an adiabatic stirred-tank reactor, as shown in Fig. 5-9. The

¹For more complete discussions of this subject see C. van Heerden, *Ind. Eng. Chem.*, 45, 1242 (1953); K. G. Denbigh, *Chem. Eng. Sci.*, 8, 125 (1958).

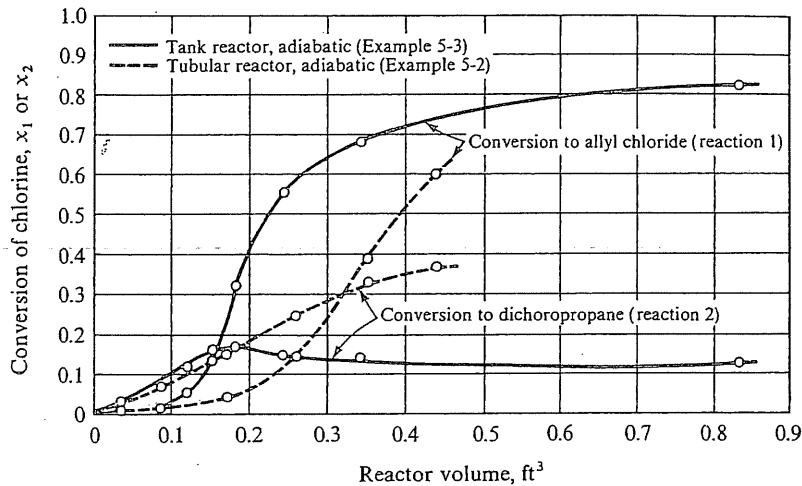


Fig. 5-8 Comparison of tubular and tank reactors for allyl chloride production

permissible, or stable, operating temperatures and conversions can be shown analytically and graphically for this system by combining the mass and energy balances. If the density is constant, Eq. (4-7) represents the mass balance for this case. Since V/Q is the average residence time, Eq. (4-7) may be written

$$x = \frac{k\bar{\theta}}{1 + k\bar{\theta}} \quad (5-16)$$

In terms of temperature, Eq. (5-16) takes the form

$$x = \frac{\bar{\theta}Ae^{-E/R_gT}}{1 + \bar{\theta}Ae^{-E/R_gT}} \quad (5-17)$$

where E is the activation energy and A is the frequency factor. At a fixed $\bar{\theta}$ (that is, for a given reactor), Eq. (5-17) expresses the result of the combined effects of temperature and reactant concentration on the rate as referred to in Fig. 5-1b. At low conversion levels the conversion increases approximately exponentially with temperature, since the exponential term in the denominator is small with respect to unity. At high temperatures the reactant composition, and hence the rate, approaches zero; then the exponential term dominates the denominator and the conversion approaches a constant value. For an irreversible reaction Eq. (5-17) shows that this value is unity (100% conversion). The S-shaped curve representing this T -vs- x relationship is sketched in Fig. 5-9.

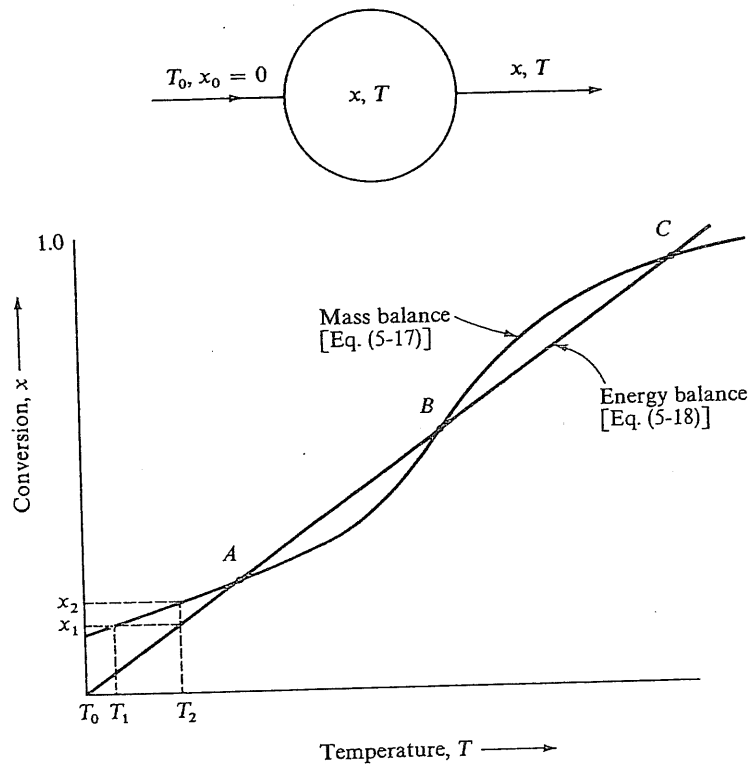


Fig. 5-9 Temperature vs conversion for a first-order irreversible reaction in an adiabatic stirred-tank reactor

The energy balance [Eq. (3-6)] for adiabatic operation and zero conversion in the feed is

$$x - 0 = \frac{MF_i c_p (T - T_0)}{F(-\Delta H)} = \frac{M c_p (T - T_0)}{w_0 (-\Delta H)}$$

where w_0 is the weight fraction of reactant in the feed. For constant-density systems it is convenient to express M/w_0 as ρ/C_0 , so that

$$x = \frac{\rho c_p}{C_0 (-\Delta H)} (T - T_0) \quad (5-18)$$

Since the heat of reaction usually varies little with temperature, Eq. (5-18) shows a linear relationship between $T - T_0$ and conversion and is represented by the straight line in Fig. 5-9.

For a given reactor and kinetics the operating temperature and con-

version in the effluent stream are established by the simultaneous solution of Eqs. (5-17) and (5-18). The intersections shown in Fig. 5-9 indicate that such solutions are possible at three points, A , B , and C . Stable steady-state operation cannot exist at other temperatures. For example, suppose that the initial temperature is below the temperature at point A , say, at T_1 . Figure 5-9 shows that the conversion required by the mass balance is greater than that corresponding to the energy balance. Thus the energy evolved at the conversion x_1 , corresponding to T_1 from Eq. (5-17), will raise the temperature to T_2 . This is the temperature corresponding to x_1 in Eq. (5-18). The conversion at T_2 is x_2 , from Eq. (5-17). Hence a further heating of the reaction mixture occurs. This transient heating will continue until point A is reached. At initial temperatures between points A and B the reaction rate is too small to justify steady-state operation, and the reaction mixture cools to the point A . Initial temperatures between B and C would be similar to temperatures below point A , so that transient heating will occur until point C is reached. At initial temperatures above C transient cooling will take place until the temperature drops to C . The temperature-vs-time relationship may be evaluated by writing and solving the *transient* energy balance.

Point B is different from A and C . After small initial displacements from B the system does not return to B , whereas disturbances from points A and C are followed by a return to these stable points.

The relative position of the mass-balance curve and the energy-balance line in Fig. 5-9 depends on the chemical properties (A , E , and ΔH) and physical properties (ρ and c_p) of the system and the operating conditions ($\bar{\theta}$ and C_0), according to Eqs. (5-17) and (5-18). These properties and conditions determine whether or not stable operating conditions are possible and how many stable operating points exist. For example, consider a series of reactions with the same A and E at constant $\bar{\theta}$. Then the relation between x and T determined by Eq. (5-17) is fixed, as shown by the S-shaped curve in Fig. 5-10. Suppose also that ρ , c_p , and C_0 are constant, and that the reactions are distinguished by different heats of reaction. For reaction 1, which has the lowest $-\Delta H$, the energy-balance line will be steep and will intersect the mass-balance curve at a small value of $T - T_0$. This point is the only stable operating condition. The reactor will operate at a low conversion and at a temperature only slightly above the feed temperature T_0 . For reaction 2, with an intermediate value of $-\Delta H$, there will be two stable operating conditions, points A and C in Fig. 5-10, and a metastable point, B . This is the situation described in Fig. 5-9. Reaction 3 has a high $-\Delta H$; there is just one intersection, and this occurs at nearly complete conversion. As shown in Fig. 5-10, point D , the reactor temperature is far above T_0 .

Stability behavior in heterogeneous reactions is similar. For example, the interaction of chemical and physical processes (rates of chemical reaction

and mass and heat transfer) in reactions between gases and solid particles causes results analogous to those discussed here. We shall return to this subject in Chap. 10.

Calculations of stable operating conditions are illustrated in the following example.

Example 5-4 A first-order homogeneous (liquid-phase) reaction is carried out in an ideal stirred-tank reactor. The concentration of reactant in the feed is 3.0 g moles/liter and the volumetric flow rate is 60 cm³/sec. The density and specific heat of the reaction mixture are constant at 1.0 g/cm³ and 1.0 cal/(g)(°C), respectively. The reactor volume is 18 liters. There is no product in the feed stream and the reactor operates adiabatically. The heat and rate of the irreversible reaction are

$$\Delta H = -50,000 \text{ cal/g mole}$$

$$r = 4.48 \times 10^6 e^{-15,000/R_g T} C \quad \text{g moles/(sec)(cm}^3\text{)}$$

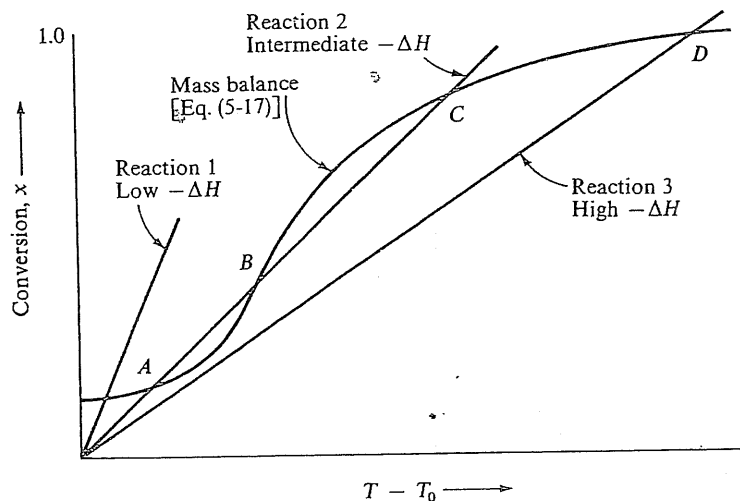
where C is the reactant concentration, in gram moles per cubic centimeter, and T is in degrees Kelvin. If the feed stream is at 25°C, what are the steady-state conversions and temperatures in the product stream?

Solution Stable operating conditions correspond to the solutions of Eqs. (5-17) and (5-18). Starting with Eq. (5-17),

$$\bar{\theta}A = \frac{V}{Q}A = \frac{18,000}{60} (4.48 \times 10^6) = 1.34 \times 10^9$$

so that Eq. (5-17) becomes

Fig. 5-10 Temperature rise vs conversion as a function of heat of reaction in an adiabatic stirred-tank reactor



$$x = \frac{1.34 \times 10^9 e^{-15,000/R_p T}}{1 + 1.34 \times 10^9 e^{-15,000/R_p T}} \quad (\text{A})$$

This relation between x and T is shown as the S-shaped curve in Fig. 5-11. With the given numerical values, Eq. (5-18) takes the form

$$x = \frac{1.0(1.0)}{3.0 \times 10^{-3} (50,000)} (T - T_0) = \frac{1}{150} (T - 298) \quad (\text{B})$$

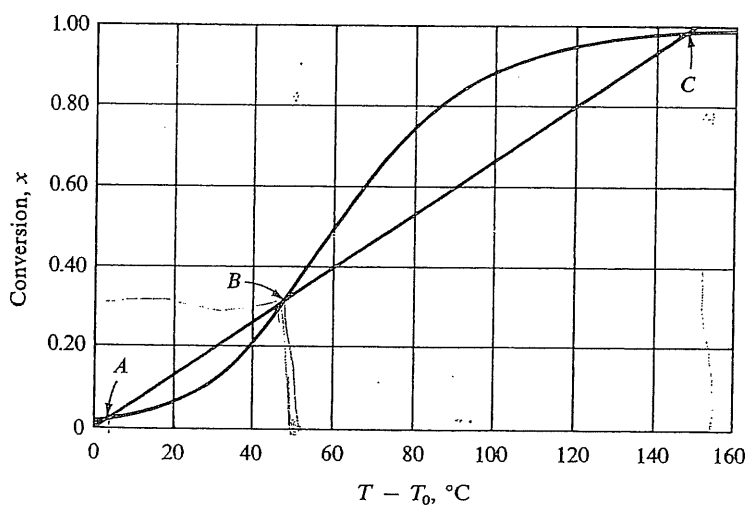
This energy balance is the straight line shown in Fig. 5-11.

Table 5-8

Intersection	$T - T_0, ^\circ\text{C}$	$T, ^\circ\text{K}$	Conversion, %
A	3	301	1.5
C	146	444	98.0

The intersections of the two curves in Fig. 5-11 give the possible operating temperatures and conversions. The intersections at both ends of the curves are stable operating points and give the results shown in Table 5-8. Point B at $T = 298 + 48 = 346^\circ\text{K}$ (73°C) represents a metastable point, as described in connection with Fig. 5-9. If the reaction had been started in the usual way by adding feed at 25°C , point A would be the steady-state operating condition at $25 + 3 = 28^\circ\text{C}$ and the conversion would be only 1.5%. To obtain a high conversion the initial temperature would have to be above 73°C (point B). Then the reaction temperature would increase to $25 + 146 = 171^\circ\text{C}$ and the conversion would be 98%.

Fig. 5-11 Temperature rise vs conversion



5-5 Semibatch Reactors

The performance of semibatch reactors under isothermal conditions was studied in Sec. 4-8. When the temperature is not constant, an energy balance must be solved simultaneously with the mass-balance equation. In general, the energy balance for a semibatch reactor (Fig. 3-1c) will include all four items of Eq. (3-2). Following the nomenclature of Sec. 4-8, let F_0 and F_1 be the total mass-flow rates of feed and product streams and H_0 and H_1 the corresponding enthalpies above a reference state. Then, following Eq. (3-2) term by term, the energy balance over an element of time Δt is

$$\begin{array}{l} \text{Energy in} \quad \text{energy in} \quad \text{energy from} \quad \text{energy accumulated} \\ \text{feed stream} - \text{product stream} + \text{surroundings} = \text{in reactor} \end{array} \quad (5-19)$$

$$F_0 H_0 \Delta t - F_1 H_1 \Delta t + U A_h (T_s - T_1) \Delta t = \frac{\Delta H}{M} r V \Delta t + m_t c_v \Delta T_1$$

The accumulation term represents the energy increase due to the change in composition and the change in temperature of the reactor contents. This involves the heat of reaction ΔH and the specific heat c_p , as described in the development of Eq. (3-11) for batch reactors. Similarly, the enthalpies H_0 and H_1 depend on both temperature and composition. Let us take the reference temperature as T_1 and the reference composition as that corresponding to the composition of the feed (zero conversion). Then, following the development of Eq. (3-5),

$$H_0 = c_p (T_0 - T_1) + 0 \frac{\Delta H}{M} w_0 = c_p (T_0 - T_1) \quad (5-20)$$

$$H_1 = c_p (T_1 - T_1) + x_1 \frac{\Delta H}{M} w_1 = x_1 w_1 \frac{\Delta H}{M} \quad (5-21)$$

where w = weight fraction of reactant

M = molecular weight of reactant

x_1 = conversion

Substituting Eqs. (5-20) and (5-21) in Eq. (5-19), simplifying, and taking the limit at $\Delta t \rightarrow 0$ gives

$$F_0 c_p (T_0 - T_1) + F_1 x_1 w_1 \frac{\Delta H}{M} + U A_h (T_s - T_1) = \frac{\Delta H}{M} r V + m_t c_v \frac{dT_1}{dt} \quad (5-22)$$

This expression, along with the mass balance [Eq. (4-12)] and the rate equation, can be solved for the temperature and composition in the reactor (or product stream) as a function of time.

There are a multitude of variations for semibatch operation. Equation (5-22) already includes restrictions that limit its application to specific operating conditions; for example, constant mass-flow rates. A frequently encountered case for nonisothermal operation is one in which there is *no product stream*, one reactant is present in the reactor, and the temperature is controlled by the flow rate of the feed stream containing the second reactant. Figure 4-17 shows this type, and Example 4-13 illustrates the design calculations for isothermal operation. The energy balance for this situation reduces to

$$F_0 c_p (T_0 - T_1) + UA_h (T_s - T_1) = \frac{\Delta H}{M} rV + m_t c_v \frac{dT_1}{dt} \quad (5-23)$$

When temperature control is critical the reaction rate is often very fast with respect to the rate of heat transfer. Then the factors that determine the design are the rate of energy exchange with the surroundings, the feed temperature, and the feed rate. Under these circumstances only the energy balance is required. The reaction may be assumed to be at thermodynamic equilibrium, so that the chemical kinetics equation (and the mass balance) is unnecessary. The rate of reaction is equal to the rate of addition of reactant in the feed stream. Hence the quantity rV is equal to $F_0 w_0$, and Eq. (5-23) becomes

$$m_t c_v \frac{dT_1}{dt} = F_0 c_p (T_0 - T_1) + UA_h (T_s - T_1) - \frac{\Delta H}{M} F_0 w_0 \quad (5-24)$$

Solution of this expression shows how the temperature varies with time for various combinations of feed rate, feed temperature, and heat-exchange rate. The conversion obtained under such conditions is always the equilibrium value corresponding to the temperature at the end of the process. Its application to a practical problem is illustrated in Example 5-5.

- **Example 5-5** Hexamethylenetetramine (HMT) is to be produced in a semibatch reactor by adding an aqueous ammonia solution (25 wt % NH_3) at the rate of 2 gpm to an initial charge of 238 gal (at 25°C) of formalin solution containing 42% by weight formaldehyde. The original temperature of the formalin solution is raised to 50°C in order to start the reaction. The temperature of the NH_4OH solution is 25°C . The heat of reaction in the liquid phase may be assumed independent of temperature and concentration and taken as -960 Btu/lb of HMT. If the reactor can be operated at a temperature of 100°C , the rate of reaction is very fast in comparison with the rate of heat transfer with the surroundings. Temperatures higher than 100°C are not desirable because of vaporization and increase in pressure.

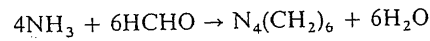
It is proposed to cool the reactor by internal coils through which water is passed. The overall heat-transfer coefficient between the stirred reaction mixture and the cooling water will be 85 Btu/(hr)(ft²)(°F). The water rate through the coils is such that

its temperature varies little, and an average value of 25°C may be used. Given the following data, calculate the length of 1-in.-OD tubing required for the cooling coils.

$$\begin{aligned} \text{Density of ammonia solution} &= 0.91 \text{ g/cm}^3 \\ \text{Density of formalin (42\%)} &= 1.10 \text{ g/cm}^3 \\ \text{Specific heat of reaction mixture (assume constant), } c_p &= 1.0 \text{ Btu/(lb)(}^\circ\text{F)} \\ \text{Specific heat of 25 wt \% NH}_3 \text{ solution, } c_p &= 1.0 \text{ Btu/(lb)(}^\circ\text{F)} \end{aligned}$$

The rate of the reverse reaction is negligible.

Solution Since the rate is very rapid and the reaction is irreversible, the ammonia in the inlet stream will be completely converted to HMT just as soon as it is added to the reactor according to the reaction



Since 4 moles of ammonia are required for 6 moles of formaldehyde, the total amount of ammonia required to react with all the charge of formalin solution will be

$$(\text{NH}_3)_t = \frac{238(8.33)(1.10)(0.42)}{30} \frac{4}{6} (17) = 346 \text{ lb}$$

From the ammonia feed rate of 2 gpm, the total time of reaction will be

$$t_t = \frac{346}{2(8.33)(0.91)(0.25)} = 91.3 \text{ min}$$

The heat-transfer surface is to be sufficient to prevent the temperature from exceeding 100°C. Hence at 100°C, dT/dt in Eq. (5-24) will be zero. At temperatures below 100°C the driving force, $T - T_s$, will be insufficient to transfer enough energy to the cooling coils to maintain a constant temperature. Thus at the start of the addition of ammonia the last term in Eq. (5-24), which is positive for an exothermic reaction, will be greater than the sum of the first and second terms, and the temperature of the reaction mixture will increase. From a practical standpoint this heating period would be reduced to a minimum by shutting off the flow of cooling water until the temperature reaches 100°C.

To determine the required heat-transfer area, Eq. (5-24) may be used when the temperature is 100°C and $dT_1/dt = 0$. Thus

$$\begin{aligned} UA_h(T_1 - T_2) &= \frac{-\Delta H}{M_{\text{NH}_3}} F_0 w_0 + F_0 c_p (T_0 - T_1) \\ 85A_h(100 - 25)(1.8) &= \frac{-\Delta H}{M_{\text{NH}_3}} F_0 w_0 + F_0(1.0)(25 - 100)(1.8) \end{aligned} \quad (\text{A})$$

The heat of reaction is -960 Btu/lb HMT. On the basis of NH_3 ,

$$\frac{\Delta H}{M_{\text{NH}_3}} = -\frac{960(140)}{4(17)} = -1,975 \text{ Btu/lb NH}_3$$

The feed rate is

$$F_0 = 2(60)(8.33)(0.91) = 910 \text{ lb/hr}$$

$$w_0 = 0.25$$

Substituting these values in Eq. (A) and solving for the heat-transfer area, we obtain

$$A_h = \frac{910(1,975)(0.25) - 1(75)(1.8)}{85(75)(1.8)} = 28.3 \text{ ft}^2$$

If the heat-transfer coefficient of 85 is based on the outside area of the tubes, the length L of 1-in.-OD coil is

$$L = \frac{28.3}{\pi D} = \frac{28.3(12)}{\pi} = 108 \text{ ft}$$

An approximate size of the reactor can be obtained by noting that the total mass of mixture at the end of the process will be

$$910 \left(\frac{91.3}{60} \right) + 238(8.33)(1.10) = 3,560 \text{ lb}$$

If we assume the density of the HMT solution to be 72 lb/ft³, the minimum reactor volume is 50 ft³. A cylindrical vessel 4 ft in diameter and 6 ft in height would provide 33% excess capacity. If the 1-in. tubing were wound into a 3-ft-diameter coil, approximately 12 loops would be needed.

The length of time necessary to raise the reaction temperature from its initial value of 50°C to 100°C can be obtained by integrating Eq. (5-24). With the water rate shut off $UA_h(T - T_1)$ is negligible, and the expression becomes

$$\int_{(T_1)_0}^{T_1} \frac{dT_1}{(-\Delta H/M_{\text{NH}_3})F_0 w_0 + F_0 c_p (T_0 - T)} = \int_0^t \frac{dt}{(m_0 + F_0 t)c_p}$$

where m_t has been replaced by $m_0 + F_0 t$. If ΔH and c_p do not vary with temperature, this equation may be integrated to yield

$$-\frac{1}{F_0 c_p} \ln \frac{(-\Delta H/M_{\text{NH}_3})F_0 w_0 + F_0 c_p (T_0 - T_1)}{(-\Delta H/M_{\text{NH}_3})F_0 w_0 + F_0 c_p [T_0 - (T_1)_0]} = \frac{1}{F_0 c_p} \ln \frac{m_0 + F_0 t}{m_0} \quad (\text{B})$$

Equation (B) expresses the temperature as a function of time during the heating period. Taking $(T_1)_0 = 50^\circ + 273^\circ$ and $T_0 = 25^\circ + 273^\circ$ and expressing t in hours, the time required for T_1 to reach 100°C is

$$-\frac{1}{(910)} \ln \frac{449,000 + (910)(1)(25 - 100)(1.8)}{449,000 + (910)(1)(25 - 50)(1.8)} = \frac{1}{910(1)} \ln \frac{2,180 + 910t}{2,180}$$

$$\ln(1 + 0.418t) = -\ln \frac{326,000}{408,000}$$

$$1 + 0.418t = 1.25$$

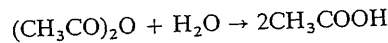
$$t = 0.60 \text{ hr} \quad \text{or } 36 \text{ min}$$

In summary, the reaction temperature would rise from 50 to 100°C in 36 min

after the ammonia feed is started, provided water is not run through the cooling coil. After 36 min the water flow would be started in order to maintain the reactor temperature at 100°C. After a total time of 93 min sufficient ammonia would have been added to convert all the formaldehyde to HMT.

Problems

- 5-1. The liquid-phase hydrolysis of dilute aqueous acetic anhydride solutions is second order and irreversible, as indicated by the reaction



A batch reactor for carrying out the hydrolysis is charged with 200 liters of anhydride solution at 15°C and a concentration of 2.16×10^{-4} g mole/cm³. The specific heat and density of the reaction mixture are essentially constant and equal to 0.9 cal/(g)(°C) and 1.05 g/cm³, respectively. The heat of reaction may be assumed constant and equal to -50,000 cal/g mole. The rate has been investigated over a range of temperatures, of which the following results are typical:

$t, ^\circ\text{C}$	10	15	25	40
$r, \text{ g mole}/(\text{cm}^3)(\text{min})$	$0.0567C$	$0.0806C$	$0.1580C$	$0.380C$

where C is acetic anhydride concentration, in gram moles per cubic centimeter.

- (a) Explain why the rate expression can be written as shown in the table even though the reaction is second-order. (b) If the reactor is cooled so that operation is isothermal at 15°C, what time would be required to obtain a conversion of 70% of the anhydride? (c) Determine an analytical expression for the rate of reaction in terms of temperature and concentration. (d) What time is required for a conversion of 70% if the reactor is operated adiabatically?
- 5-2. A reactor for the production of drying oils by the decomposition of acetylated castor oil is to be designed for a conversion of 70%. The initial charge will be 500 lb and the initial temperature 340°C, as in Example 5-1. In fact, all the conditions of Example 5-1 apply, except instead of adiabatic operation, heat will be supplied electrically with a cal-rod unit in the form of a 1-in.-OD coil immersed in the reaction mixture. The power input and the stirring in the reactor will be such that the surface temperature of the heater is maintained constant at 700°K. The heat-transfer coefficient may be taken equal to 60 Btu/(hr)(ft²)(°F). What length of heater will be required if the conversion of 70% is to be obtained in 20 min?
- 5-3. Reconsider the pilot plant discussed in Example 5-2 for the production of allyl chloride. It has been proposed to reduce the extent of the side reaction to dichloropropane by preheating the feed to 300°C. To obtain a more uniform axial temperature profile, inert nitrogen will be added to the feed to give a composition corresponding to 5 moles of N₂, 4 moles of C₃H₆, and 1 mole of Cl₂. The total feed rate will be 0.85 lb mole/hr. If all other conditions are