

With this value of  $[B]_0 + [A]_0$  we can express Eq. (2-72) in terms of  $[A] - [A]_{\text{eq}}$ ,

$$-\frac{d[A]}{dt} = \frac{k_1(K+1)}{K}([A] - [A]_{\text{eq}})$$

or

$$-\frac{d[A]}{dt} = k_R([A] - [A]_{\text{eq}}) \quad (2-74)$$

where

$$k_R = \frac{k_1(K+1)}{K} \quad (2-75)$$

Written in this form, the rate expression is similar to that for an irreversible first-order reaction. Thus if  $[A'] = [A] - [A]_{\text{eq}}$ , Eq. (2-74) becomes

$$-\frac{d[A']}{dt} = k_R[A'] \quad (2-76)$$

Then, according to Eq. (2-54), the integrated result is

$$\ln \frac{[A] - [A]_{\text{eq}}}{[A]_0 - [A]_{\text{eq}}} = -k_R t \quad (2-77)$$

If experimental concentration-time data are plotted as  $\ln ([A] - [A]_{\text{eq}})/([A]_0 - [A]_{\text{eq}})$  vs  $t$ , the result is a straight line with a slope of  $-k_R$ . If the equilibrium constant is known,  $k_1$  can be evaluated from Eq. (2-75). Note that  $[A]_{\text{eq}}$  is determined solely by  $K$  and the initial concentrations by means of Eq. (2-73).

Illustrations of first-order reversible reactions are gas-phase cis-trans isomerizations, isomerizations in various types of hydrocarbon systems, and the racemization of  $\alpha$  and  $\beta$  glucoses. An example of a catalytic reaction is the ortho-para hydrogen conversion on a nickel catalyst. This reaction is used to illustrate other forms of Eq. (2-74) in the following example.

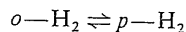
**Example 2-4** The ortho-para hydrogen reaction has been studied at  $-196^\circ\text{C}$  and constant pressure in a flow reactor, with a nickel-on- $\text{Al}_2\text{O}_3$  catalyst.<sup>1</sup> The rate data can be explained with an expression of the form

$$r = k(y_{\text{eq}} - y)_p \quad (\text{A})$$

where  $y_p$  is the mole fraction of para hydrogen. Show that this expression follows from the first-order reversible rate equation (2-74).

<sup>1</sup>N. Wakao, P. W. Selwood, and J. M. Smith, *AIChE J.*, **8**, 478 (1962).

*Solution* The reaction is



so that  $[A]$  in Eq. (2-74) refers to the concentration of ortho hydrogen. Assuming hydrogen is an ideal gas at reaction conditions and that  $P$  is the total pressure, we have

$$[A] = \frac{P}{R_g T} y_o \quad (\text{B})$$

Since the system is a binary one,  $y_p = 1 - y_o$ , and Eq. (B) becomes

$$[A] = \frac{P}{R_g T} (1 - y)_p$$

and

$$[A]_{\text{eq}} = \frac{P}{R_g T} (1 - y_{\text{eq}})_p$$

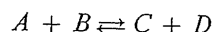
Substituting these results in Eq. (2-74) yields

$$-\frac{d[A]}{dt} = r = k_R \frac{P}{R_g T} (y_{\text{eq}} - y)_p = \frac{k_1(K+1)}{K} \frac{P}{R_g T} (y_{\text{eq}} - y)_p \quad (\text{C})$$

Equation (C) is equivalent to Eq. (A), with

$$k = \frac{k_1(K+1)}{K} \frac{P}{R_g T} \quad (\text{D})$$

**Second Order** For a second-order reversible reaction, where the stoichiometry is



the rate equation will be

$$-\frac{d[A]}{dt} = k_2[A][B] - k'_2[C][D] \quad (2-78)$$

If  $[X]$  is the amount of  $A$  which has reacted, expressed as a concentration, the concentration of  $A$  at any time will be

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

Rewriting Eq. (2-78) in terms of  $[X]$  and replacing  $k'_2$  with  $k_2/K$  gives

$$\begin{aligned} \frac{d[X]}{dt} &= k_2 \left\{ ([A]_0 - [X])([B]_0 - [X]) - \frac{1}{K} ([C]_0 \right. \\ &\quad \left. + [X])([D]_0 + [X]) \right\} \\ &= \alpha + \beta[X] + \gamma[X]^2 \end{aligned} \quad (2-79)$$

where

$$\alpha = k_2 \left\{ [A]_0 [B]_0 - \frac{1}{K} [C]_0 [D]_0 \right\} \quad (2-80)$$

$$-\beta = k_2 \left\{ ([A]_0 + [B]_0) + \frac{1}{K} ([C]_0 + [D]_0) \right\} \quad (2-81)$$

$$\gamma = k_2 \left( 1 - \frac{1}{K} \right) \quad (2-82)$$

Integration of Eq. (2-79) with the initial condition

$$[A] = [A]_0 \quad [B] = [B]_0 \quad [C] = [C]_0 \quad [D] = [D]_0$$

at  $t = 0$

gives

$$\ln \left| \frac{\{2\gamma[X]/(\beta - q^{1/2})\} + 1}{\{2\gamma[X]/(\beta + q^{1/2})\} + 1} \right| = q^{1/2}t \quad (2-83)$$

where

$$q = \beta^2 - 4\alpha\gamma \quad (2-84)$$

In practice it is difficult to use this result with concentration-time data to determine  $k_2$ . The solution is a trial-and-error one, requiring successive choices of  $k_2$  and comparison of the data with Eq. (2-83) for each choice to establish the best value. For special initial conditions the equations are simplified so that direct evaluation of  $k_2$  is possible. This case is illustrated in Example 2-5.

Rate and integrated equations for the various forms of irreversible and reversible reactions are summarized in Table 2-5. The complex analysis for reversible reactions, indicated by the complicated equations, can be avoided if measurements are made before much reaction has occurred. Under these conditions the concentrations of the products will be small, making the reverse rate negligible. Then the data can be analyzed as though the system were irreversible to determine the forward-rate constant. With this result and the equilibrium constant, the rate constant for the reverse reaction can be obtained. This *initial-rate* approach is frequently used to simplify kinetic studies. Besides the fact that the reverse reaction is eliminated, the composition of the reaction system is usually known more precisely at the initial state than at subsequent times. This is because compositions at later times are generally evaluated from a limited experimental analysis plus assumptions that certain reactions have occurred. Particularly in complex systems, knowledge of the reactions taking place may not be exact. When the rate equation determined from the concentration depen-

INTEGRATION METHOD The solution of Eq. (B) is given by Eqs. (2-83) and (2-84), where  $[X] = [I]$  and

$$\alpha = k_2[M]_0^2$$

$$\beta = -2k_2[M]_0$$

$$\gamma = k_2 \frac{K-1}{K}$$

$$q = 4k_2^2[M]_0^2 - 4k_2^2[M]_0^2 \frac{K-1}{K} = \frac{4k_2^2[M]_0^2}{K}$$

Substituting these values in Eq. (2-83) and simplifying gives

$$\frac{2k_2[M]_0}{K^{1/2}} t = \ln \frac{[M]_0 + [I](K^{-1/2} - 1)}{[M]_0 - [I](K^{-1/2} + 1)} \quad (C)$$

The data are given as the fraction  $x$  of the toluidine (or, in this example, methyl-iodide) reacted. Hence  $[I] = x[M]_0$ . Then Eq. (C) becomes

$$k_2 = \frac{K^{1/2}}{2[M]_0 t} \ln \frac{1 + x(K^{-1/2} - 1)}{1 - x(K^{-1/2} + 1)} \quad (D)$$

Substituting numerical values for  $K$  and  $[M]_0$  gives the following expression relating  $x$  and  $t$ :

$$k_2 = \frac{1.43^{1/2}}{2(0.05)t} \ln \frac{1 - 0.165x}{1 - 1.835x}$$

This expression and the data in Table 2-6 can be used to calculate a value of  $k_2$  for each run. The results are shown in Table 2-7.

As a matter of interest, the values of  $k_2$  evaluated with the assumption that the reaction is irreversible are shown in the last column of the table. They were computed from Eq. (2-59); for example,

$$k_2 t = \frac{[I]}{[M]_0([M]_0 - [I])}$$

The steady trend in the values of  $k_2$  indicates that the irreversible assumption is a poor one.

Table 2-7

Run	$\theta$ , sec	$k_2$ , liters/(g mole)(sec)	$k_2$ (neglecting reverse reaction)
1	612	$7.05 \times 10^{-3}$	$6.93 \times 10^{-3}$
2	1,590	$7.06 \times 10^{-3}$	$6.57 \times 10^{-3}$
3	2,160	$7.06 \times 10^{-3}$	$6.23 \times 10^{-3}$
4	4,680	$7.97 \times 10^{-3}$	$4.68 \times 10^{-3}$

In studies of rate data trends in  $k$  are of more significance than random variations. The former suggest that the assumed order is open to question, while the latter suggest errors in the experimental data. Of course, if the precision of the data is poor, random variations can mask trends in computed  $k$  values.

**DIFFERENTIAL METHOD** Replacing  $1/K$  and  $[M]_0$  with their numerical values and taking logarithms of the rate equation (B) yields

$$\log r = \log \frac{d[I]}{dt} = \log k_2 + \log \left\{ (0.05 - [I])^2 - 0.70[I]^2 \right\} \quad (\text{E})$$

According to Eq. (E), a plot on logarithmic coordinates of the rate vs  $(0.05 - [I])^2 - 0.70[I]^2$  should yield a straight line of slope equal to unity.

Figure 2-5 shows a plot of  $[I]$  vs  $t$ . Slopes of this curve give the rate values shown in Table 2-8. Also shown is a plot of Eq. (E). Observe that the first four points establish a line with a slope close to unity, as required by the second-order mechanism. The last point deviates from the line, just as the  $k$  value for this point obtained by the integration method was not in agreement with the other values.

**Example 2-6** The interpretation of kinetic data for gaseous reactions is similar to that for liquid systems. The analysis for a reversible case is well illustrated by the vapor-phase decomposition of hydrogen iodide,

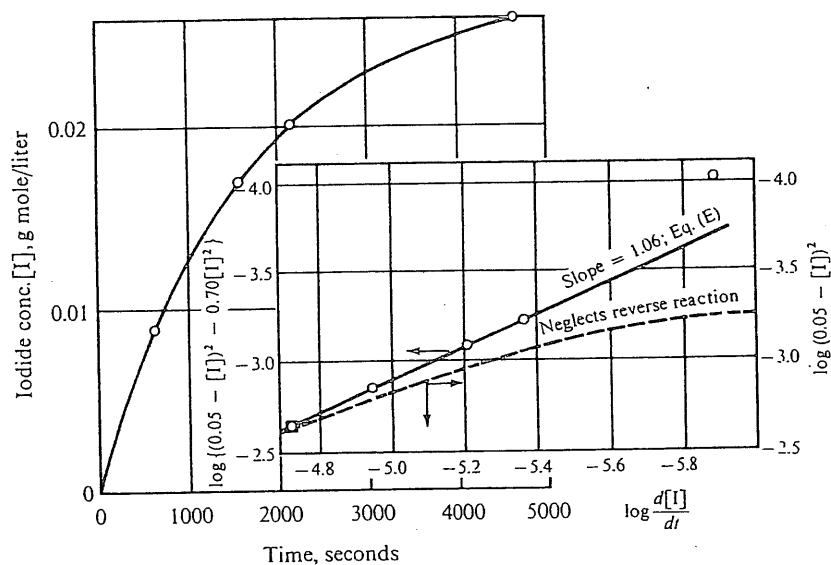
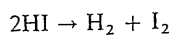


Fig. 2-5

Table 2-8

$t$ , sec	$[I]$ g mole/liter	$\frac{d[I]}{dt}$	$\log \frac{d[I]}{dt}$	$(0.05 - [I])^2 - 0.70[I]^2$	$\log \{(0.05 - [I])^2 - 0.70[I]^2\}$
0	0	$1.93 \times 10^{-5}$	-4.71	$25.0 \times 10^{-4}$	-2.60
612	0.00875	$1.12 \times 10^{-5}$	-4.95	$16.5 \times 10^{-4}$	-2.78
1,590	0.0171	$0.62 \times 10^{-5}$	-5.20	$8.75 \times 10^{-4}$	-3.05
2,160	0.0201	$0.42 \times 10^{-5}$	-5.37	$6.13 \times 10^{-4}$	-3.21
4,680	0.0261	$0.13 \times 10^{-5}$	-5.89	$0.96 \times 10^{-4}$	-4.01

This reaction has been carefully studied by a number of investigators,<sup>1</sup> and it is generally considered one of the most certain examples of a second-order reaction, at least at low pressures. The equilibrium values of the fraction  $x$  of HI decomposed can be accurately represented by Bodenstein's equation,

$$x_{\text{eq}} = 0.1376 + 7.22 \times 10^{-5}t + 2.576 \times 10^{-7}t^2 \quad t = ^\circ\text{C}$$

Kistiakowsky used a static experimental method to study the reaction. Pure hydrogen iodide was sealed in glass bulbs, immersed in a constant-temperature bath for various time intervals, and then removed and cooled, and the contents were analyzed for all three chemical species. The initial pressure (and hence the initial concentration) of HI and the size of the reaction bulb were varied over a wide range. The data obtained at an average temperature of 321.4°C are given in Table 2-9.

(a) From this information estimate the specific-reaction-rate constants [liters/(g mole)(sec)] for the forward and reverse reactions, both of which may be taken as second order. (b) What would be the values of the specific-reaction-rate constants in units of g moles/(liter)(sec)(atm)<sup>2</sup>? (c) Could the course of this reaction be followed by measuring the total pressure in the reaction vessel at various times?

*Solution* This reaction system is somewhat simpler than the second-order reversible system whose solution is given by Eq. (2-83), since the concentrations of products are very low and there is only one reactant. The extent of reaction, noted by the percentage of HI decomposed, is always low. The series of runs constitute *initial rate* data, with each run corresponding to a different concentration of HI.

If the rate is followed by the concentration of iodine, Eq. (2-79) becomes

$$\frac{d[I_2]}{dt} = k_2([HI]_0 - 2[I_2])^2 - k'_2[I]^2 = k_2 \left\{ ([HI]_0 - 2[I_2])^2 - \frac{1}{K} [I_2]^2 \right\}$$

where  $[HI]_0$  is the initial concentration of HI and the second equality indicates the assumption that the reaction is an elementary one.

<sup>1</sup>M. Bodenstein, *Z. Physik Chem.*, **13**, 56 (1894); *Z. Physik Chem.*, **22**, 1 (1897); *Z. Physik Chem.*, **29**, 295 (1898); H. A. Taylor, *J. Phys. Chem.*, **28**, 984 (1924); G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **50**, 2315 (1928).

Table 2-9

Run	$t$ , sec	% of HI decomposed	Volume of reaction bulb, cm <sup>3</sup>	$[\text{HI}]_0$ , g moles/liter
1	82,800	0.826	51.38	0.02339
2	172,800	2.567	59.80	0.03838
3	180,000	3.286	51.38	0.04333
4	173,100	3.208	51.38	0.04474
5	81,000	2.942	7.899	0.1027
6	57,560	2.670	7.899	0.1126
7	61,320	4.499	7.899	0.1912
8	19,200	2.308	7.899	0.3115
9	18,000	2.202	7.899	0.3199
10	16,800	2.071	7.899	0.3279
11	17,400	2.342	7.899	0.3464
12	17,700	2.636	7.899	0.4075
13	18,000	2.587	7.899	0.4228
14	23,400	4.343	7.899	0.4736
15	6,000	2.224	3.28	0.9344
16	5,400	1.903	0.778	0.9381
17	8,160	3.326	0.781	1.138
19	5,400	2.741	0.713	1.231

(a) If the rate equation is integrated, with the initial condition  $[\text{I}_2] = 0$  at  $t = 0$ , the result is very similar to Eq. (C) of the previous example:

$$\frac{2k_2[\text{HI}]_0}{K^{1/2}} t = \ln \frac{[\text{HI}]_0 + [\text{I}_2](K^{-1/2} - 2)}{[\text{HI}]_0 - [\text{I}_2](K^{-1/2} + 2)} \quad (\text{A})$$

The equilibrium constant is related to the concentrations at equilibrium by

$$K = \left( \frac{[\text{I}_2][\text{H}_2]}{[\text{HI}]^2} \right)_{\text{eq}}$$

If the fraction of HI decomposed is  $x$ , then

$$[\text{I}_2] = [\text{H}_2] = \frac{1}{2}[\text{HI}]_0 x$$

$$[\text{HI}] = [\text{HI}]_0(1 - x)$$

Hence

$$K = \frac{1}{4} \frac{x_{\text{eq}}^2}{(1 - x_{\text{eq}})^2}$$

From the expression given for  $x_{\text{eq}}$  at 321.4°C,

$$x_{\text{eq}} = 0.1376 + 7.221 \times 10^{-5} (321.4) + 2.576 \times 10^{-7} (321.4)^2 = 0.1873$$

Hence

$$K = \frac{1}{4} \frac{(0.1873)^2}{(1 - 0.1873)^2} = 0.0133$$

Substituting this value of  $K$  in Eq. (A) and introducing the fraction decomposed, we have

$$k_2 = \frac{1}{2(8.67)[\text{HI}]_0 t} \ln \frac{[\text{HI}]_0 + \frac{1}{2}[\text{HI}]_0(8.67 - 2)x}{[\text{HI}]_0 - \frac{1}{2}[\text{HI}]_0(8.67 + 2)x}$$

or

$$k_2 = \frac{1}{2(8.67)[\text{HI}]_0 t} \ln \frac{1 + 3.335x}{1 - 5.335x} \quad (\text{B})$$

The experimental data for  $x$  can be used directly in Eq. (B) to compute values of the specific reaction rate  $k_2$ . However, another form of the expression is more useful when the  $x$  values are very low, as in this case (the maximum value of  $x$  is 0.04499 for run 7). Equation (B) may be written in the form

$$k_2 = \frac{1}{2(8.67)[\text{HI}]_0 t} \ln \left( 1 + \frac{8.67x}{1 - 5.335x} \right)$$

Expanding the logarithmic term in a power series and retaining the first two terms gives

$$k_2 = \frac{1}{2(8.67)[\text{HI}]_0 t} \left[ \frac{8.67x}{1 - 5.335x} - \frac{1}{2} \left( \frac{8.67x}{1 - 5.335x} \right)^2 \right] \quad (\text{C})$$

The use of Eq. (C) may be illustrated with run 1:

$$\begin{aligned} k_2 &= \frac{1}{2(8.67)(0.02339)(82,800)} \\ &\quad \times \left\{ \frac{8.67(0.00826)}{1 - 5.335(0.00826)} - \frac{1}{2} \frac{[(8.67)(0.00826)]^2}{[(1 - 5.335)(0.00826)]^2} \right\} \\ &= 2.97 \times 10^{-5} (0.0749 - 0.0028) \\ &= 2.14 \times 10^{-6} \text{ liter/(g mole)(sec)} \end{aligned}$$

The results for the other runs are summarized in Table 2-10. The average value of  $k_2$  is  $1.99 \times 10^{-6}$ . For the reverse reaction.

$$k'_2 = \frac{k_2}{K_1} = \frac{1.99 \times 10^{-6}}{0.0133} = 1.50 \times 10^{-4} \text{ liter/(g mole)(sec)}$$

(b) The rate equations could also have been written in terms of partial pressures. These are proportional to the concentrations in a gas-phase reaction, provided the gas mixture follows perfect-gas behavior. In terms of pressures the net rate may be written

$$\frac{d[\text{I}]}{dt} = k_p p_{\text{HI}}^2 - k'_p p_{\text{I}_2} p_{\text{H}_2}$$



Table 2-10

Run	Conversion	$k_2 \times 10^6$ , liters/(sec)(g mole)
1	0.00826	2.14
2	0.02567	2.01
3	0.03286	2.20
4	0.03208	2.17
5	0.02942	1.92
6	0.02670	2.08
7	0.04499	2.04
8	0.02308	1.99
9	0.0202	1.80
10	0.02071	1.77
11	0.02342	2.00
12	0.02636	1.90
13	0.02587	1.75
14	0.04343	2.08
15	0.02224	2.05
16	0.01903	1.93
17	0.03326	1.87
19	0.02741	2.15

According to the perfect-gas law, the partial pressure of  $I_2$ , for example, is given by the expression

$$p_{I_2} = \frac{N_i R_g T}{V} = [I_2] R_g T$$

Substituting partial-pressure relationships in the rate equation, we have

$$\frac{d[I]}{dt} = k_p (R_g T)^2 [HI]^2 - k'_p (R_g T)^2 [I_2] [H_2]$$

Comparison with the original rate equation shows that  $k_p$  is related to  $k_2$  as follows:

$$\begin{aligned} k_p &= \frac{k_2}{(R_g T)^2} = \frac{1.99 \times 10^{-6}}{0.082^2 (273.1 + 321.4)^2} \\ &= 0.84 \times 10^{-9} \text{ g mole/(liter)(atm)}^2 \text{(sec)} \end{aligned}$$

and

$$k'_p = \frac{k'_2}{(R_g T)^2} = 6.40 \times 10^{-8} \text{ g mole/(liter)(atm)}^2 \text{(sec)}$$

Although no pressures are given in the tabulated data, approximate values can be computed from the perfect-gas law. Thus the total pressure will be given by

$$p_t = \frac{N_t R_g T}{V}$$

Initially the only substance present is HI, so that  $N_i/V$  represents the initial concentration of HI. For run 1

$$p_t = [\text{HI}]_0 R_g T = 0.02339(0.082)(594.5) = 1.14 \text{ atm}$$

The highest pressure will be for run 19, where the initial concentration is the greatest. In this case

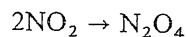
$$p_t = 1.2310(0.082)(594.5) = 60 \text{ atm}$$

(c) In this reaction the number of moles does not change with reaction. Hence the total pressure does not change with the extent of the reaction.

### 2-9 The Total-pressure Method of Studying Kinetics

The treatment in this chapter has been limited to nonflow systems at constant temperature and constant volume so that the rate can be represented by the rate of change of concentration of a reactant or product. With these restrictions there will be little change in the total pressure for a gaseous reaction unless the total number of moles changes.<sup>1</sup> However, if there is an increase in number of moles as the reaction proceeds, there will be an increase in pressure. This increase is uniquely related to the extent of reaction. Hence measuring the total pressure as a function of time is a suitable method for studying the kinetics of such a system and has been widely used.

As an illustration of the method, consider the reaction



In this instance the pressure decreases, and this change will depend on the extent of the reaction. If the initial number of moles of  $\text{NO}_2$  is  $N_0$  (initial concentration  $[\text{NO}_2]_0$ ) and no  $\text{N}_2\text{O}_4$  is present, the total moles at any time is

$$N_t = N_{\text{N}_2\text{O}_4} + N_{\text{NO}_2} = N_{\text{N}_2\text{O}_4} + N_0 - 2N_{\text{N}_2\text{O}_4} = N_0 - N_{\text{N}_2\text{O}_4}$$

Then the total pressure will be

$$p_t = \frac{N_t R_g T}{V} = \frac{N_0 - N_{\text{N}_2\text{O}_4}}{V} R_g T \quad (2-85)$$

If the initial total pressure is  $p_0$ ,

$$p_0 = \frac{N_0 R_g T}{V}$$

<sup>1</sup>Any change in pressure for a reaction with no change in number of moles would be due to deviations from ideal-gas behavior. If the deviation of the reaction mixture changes with composition, a change in total pressure with extent of reaction would occur, but it would be relatively small.

Hence the expression for  $p_t$  may be written in terms of  $p_0$  and the concentration of  $\text{N}_2\text{O}_4$  as

$$p_t = p_0 - \frac{N_{\text{N}_2\text{O}_4}}{V} R_g T = p_0 - [\text{N}_2\text{O}_4] R_g T \quad (2-86)$$

To compute the rate constant from total-pressure measurements we first write the rate equation in the usual way,

$$\frac{d[\text{N}_2\text{O}_4]}{dt} = k_2[\text{NO}_2]^2 = k_2([\text{NO}_2]_0 - 2[\text{N}_2\text{O}_4])^2 \quad (2-87)$$

Then Eq. (2-86) is used to replace the concentration of  $\text{N}_2\text{O}_4$  with the total pressure. For example, differentiation of Eq. (2-86) yields

$$\frac{d[\text{N}_2\text{O}_4]}{dt} = -\frac{1}{R_g T} \frac{dp_t}{dt}$$

Also,

$$[\text{NO}_2]_0 = \frac{p_0}{R_g T}$$

$$[\text{N}_2\text{O}_4] = \frac{p_0 - p_t}{R_g T}$$

Substituting these equalities in Eq. (2-87), we have

$$r = \frac{d[\text{N}_2\text{O}_4]}{dt} = -\frac{1}{R_g T} \frac{dp_t}{dt} = k_2 \left( \frac{p_0}{RT} - 2 \frac{p_0 - p_t}{RT} \right)^2$$

or

$$-\frac{dp_t}{dt} = \frac{k_2}{R_g T} (2p_t - p_0)^2$$

This differential equation can be integrated, using the initial condition  $p_t = p_0$  at  $t = 0$ , to give

$$\frac{1}{2} \left( \frac{1}{2p_t - p_0} - \frac{1}{p_0} \right) = \frac{k_2}{R_g T} (t - 0)$$

or

$$k_2 = \frac{R_g T}{2t} \left( \frac{1}{2p_t - p_0} - \frac{1}{p_0} \right) \quad (2-88)$$

The total pressure-vs-time data can be used directly in Eq. (2-88) to evaluate  $k_2$ .

## ANALYSIS OF COMPLEX RATE EQUATIONS

A *complex* system is one in which more than one reaction occurs. This can lead to multiple products, some of which are more desirable than others from a practical standpoint. For example, in the air oxidation of ethylene the desired product is ethylene oxide, but complete oxidation to carbon dioxide and water also occurs. The important performance factor is the production rate of ethylene oxide and its purity in the reaction products, rather than the total amount of ethylene reacted. To characterize this performance two parameters are used: yield and selectivity. The *yield* of a specific product is defined as the fraction of reactant converted to that product. The *point selectivity* is the ratio of the rate of production of one product to the rate for another product. With multiple products there is a separate selectivity based on each pair of products. The *overall*, or integrated, *selectivity* is the ratio of the amount of one product produced to the amount of another. Selectivity and yield are related to each other through the total conversion, i.e., the total fraction of reactant converted to all products.

As an illustration of these terms consider the simultaneous reaction system



Suppose the total conversion of  $A$  is  $x_t$ , consisting of the fraction  $x_B$  of reactant  $A$  converted to  $B$  and the fraction  $x_C$  converted to  $C$ . The *yield* of  $B$  is simply  $x_B$  and that of  $C$  is  $x_C$ . The amount of a product produced is proportional to the yield. Hence the *overall selectivity* of  $B$  is the ratio of the yields of  $B$  and  $C$ ,

$$S_o = \frac{x_B}{x_C} \quad (2-90)$$

If both reactions are first order and irreversible, the *point selectivity* is

$$S_p = \frac{d[B]/dt}{d[C]/dt} = \frac{k_1[A]}{k_2[A]} = \frac{k_1}{k_2} \quad (2-91)$$

Under the restriction of constant density, the amount of a product produced is proportional to its concentration. Thus the overall selectivity can also be written as

$$S_o = \frac{[B]}{[C]} \quad (2-92)$$

The simple form of Eq. (2-91) shows that selectivity and yield calculations can advantageously be carried out by dividing the rate for one reaction by that for another, eliminating time in the process. Since yield and selectivity are usually more important than total conversion for complex-reaction systems, this procedure will be emphasized in the following section. The possible combinations of simultaneous, parallel, and consecutive reactions are very large. A few irreversible first-order cases will be analyzed in Sec. 2-10 to illustrate the method of approach. Then in Sec. 2-11 a different type of complex system, chain reactions, will be discussed.

### 2-10 First-order Complex Reactions

Consider first the *simultaneous* reactions described by Eq. (2-89). The rates of formation of the components are given by the following three equations

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] \quad (2-93)$$

$$\frac{d[B]}{dt} = k_1[A] \quad (2-94)$$

$$\frac{d[C]}{dt} = k_2[A] \quad (2-95)$$

Our goal is to integrate these equations to establish  $[B]$  and  $[C]$  for an  $[A]$ . Then all yields and selectivities can be obtained from equations like (2-90). In this simple example Eq. (2-93) can be immediately integrated to give  $[A] = f(t)$ . This result, used in Eqs. (2-94) and (2-95), allows these two equations to be integrated, so that  $[B]$  and  $[C]$  are also known as a function of time. However, in more complicated cases (see Example 2-8) integration with respect to time is not as easy. Therefore the solution will be obtained by dividing Eqs. (2-94) and (2-95) by Eq. (2-93), to eliminate time:

$$\frac{d[B]}{d[A]} = -\frac{k_1}{k_1 + k_2} \quad (2-96)$$

$$\frac{d[C]}{d[A]} = -\frac{k_2}{k_1 + k_2} \quad (2-97)$$

If Eqs. (2-96) and (2-97) are integrated with the conditions that at  $t = 0$ ,  $[A] = [A]_0$ , and  $[B] = [C] = 0$ , then the yields of  $B$  and  $C$  are

$$x_B = \frac{[B]}{[A]_0} = \frac{k_1}{k_1 + k_2} \left( 1 - \frac{[A]}{[A]_0} \right) = \frac{k_1}{k_1 + k_2} x_t \quad (2-98)$$

$$x_C = \frac{[C]}{[A]_0} = \frac{k_2}{k_1 + k_2} \left( 1 - \frac{[A]}{[A]_0} \right) = \frac{k_2}{k_1 + k_2} x_t \quad (2-99)$$

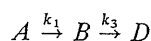
where  $x_t$  is the total conversion of  $A$  to  $B$  plus  $C$ .

From Eqs. (2-98) and (2-99), the overall selectivity is

$$S_o = \frac{x_B}{x_C} = \frac{k_1}{k_2} \quad (2-100)$$

The point selectivity, given by Eq. (2-91) for first-order simultaneous reactions, is also equal to  $k_1/k_2$ . Although point and overall selectivities are identical for this type of first-order system, the two selectivities differ for most complex reactions.

Next let us consider a *consecutive* set of reactions,



and take  $[B] = [D] = 0$  and  $[A] = [A]_0$  at  $t = 0$ . The rates are

$$\frac{d[A]}{dt} = -k_1[A] \quad (2-101)$$

$$\frac{d[B]}{dt} = k_1[A] - k_3[B] \quad (2-102)$$

$$\frac{d[D]}{dt} = k_3[B] \quad (2-103)$$

Dividing Eqs. (2-102) and (2-103) by Eq. (2-101) yields

$$\frac{d[B]}{d[A]} = -1 + \frac{k_3[B]}{k_1[A]} \quad (2-104)$$

$$\frac{d[D]}{d[A]} = -\frac{k_3[B]}{k_1[A]} \quad (2-105)$$

Since Eq. (2-104) is a linear first-order differential equation, it has an analytic solution. With the stated initial condition the result can be expressed in terms of the yield of  $B$ ,

$$x_B = \frac{[B]}{[A]_0} = \frac{k_1}{k_1 - k_3} \left\{ \left( \frac{[A]}{[A]_0} \right)^{k_3/k_1} - \frac{[A]}{[A]_0} \right\} \quad (2-106)$$

This expression for  $[B]$  can be substituted in Eq. (2-105). Then integration of Eq. (2-105) gives

$$x_D = \frac{[D]}{[A]_0} = \frac{k_1}{k_1 - k_3} \left\{ 1 - \left( \frac{[A]}{[A]_0} \right)^{k_3/k_1} \right\} - \frac{k_3}{k_1 - k_3} \left( 1 - \frac{[A]}{[A]_0} \right) \quad (2-107)$$

From these two expressions the overall selectivity  $x_B/x_D$  is seen to depend on the fraction unconverted,  $[A]/[A]_0$ , as well as on the rate constants. This means that the yield of  $B$  and the overall selectivity will vary with time. This is in contrast to the result for simultaneous reactions, Eq. (2-100).

**Example 2-7** If  $[B] = [D] = 0$  initially for the consecutive reaction system described by Eqs. (2-101) to (2-103), what is the time at which the yield of  $B$  is a maximum? What is the maximum yield?

**Solution** Equation (2-106) gives the yield of  $B$  in terms of  $[A]/[A]_0$ . This ratio can be expressed as a function of time by integrating Eq. (2-101). The result is

$$\frac{[A]}{[A]_0} = e^{-k_1 t} \quad (A)$$

Then Eq. (2-106) becomes

$$x_B = \frac{k_1}{k_1 - k_3} (e^{-k_3 t} - e^{-k_1 t}) \quad (B)$$

To obtain the maximum value of  $x_B$  we differentiate Eq. (B) with respect to time and set the derivative equal to zero:

$$\frac{dx_B}{dt} = 0 = \frac{k_1}{k_1 - k_3} (-k_3 e^{-k_3 t} + k_1 e^{-k_1 t})$$

$$t_{\max B} = \frac{\ln(k_1/k_3)}{k_1 - k_3} \quad (C)$$

Substituting this value for the time in Eq. (B) gives the maximum yield,

$$(x_B)_{\max} = \left( \frac{k_1}{k_3} \right)^{k_3/(k_3 - k_1)} \quad (D)$$

The form of the concentration-vs-time curves are shown in Fig. 2-6.

Solutions of assemblies of ordinary differential equations with time as the independent variable are ideally suited for solution by analog computation. Hence complex kinetics equations of the type considered in this section may conveniently be solved with an analog computer. This is illustrated in the problems at the end of this chapter.

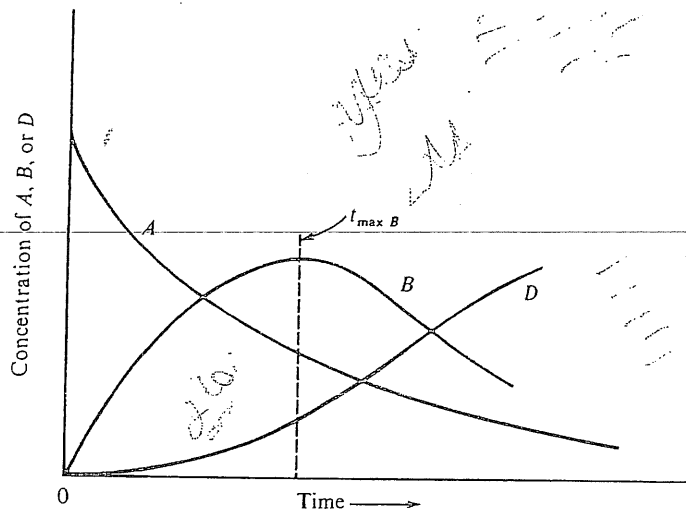


Fig. 2-6 Concentration vs time for consecutive-reaction system  $A \rightarrow B \rightarrow D$  for  $B = \dot{B} = 0$  at  $t = 0$

Example 2-8 Benzene is chlorinated in the liquid phase in a kettle-type reactor operated on a semibatch basis; i.e., the reactor is initially charged with liquid benzene, and then chlorine gas is bubbled into the well-agitated solution. The reactor is equipped with a reflux condenser which will condense the benzene and chlorinated products but will not interfere with the removal of hydrogen chloride. Assume that the chlorine is added sufficiently slowly that (1) the chlorine and hydrogen chloride concentrations in the liquid phase are small and (2) all the chlorine reacts.

At the constant operating temperature of 55°C the significant reactions are the three substitution ones leading to mono-, di-, and trichlorobenzene.

1.  $C_6H_6 + Cl_2 \xrightarrow{k_1} C_6H_5Cl + HCl$
2.  $C_6H_5Cl + Cl_2 \xrightarrow{k_2} C_6H_4Cl_2 + HCl$
3.  $C_6H_4Cl_2 + Cl_2 \xrightarrow{k_3} C_6H_3Cl_3 + HCl$

MacMullin<sup>1</sup> found the ratios of the rate constants to have the following values at 55°C:

$$\frac{k_1}{k_2} = 8.0 \quad \frac{k_2}{k_3} = 30$$

<sup>1</sup>R. B. MacMullin, *Chem. Eng. Progr.*, 44, 183 (1948).



Find the yields of each product as a function of the moles of chlorine added per mole of benzene charged to the reactor.<sup>1</sup> The holdup in the reflux condenser is negligible.

*Solution*<sup>2</sup> The process described is neither flow nor batch, but semibatch in nature. However, with assumptions which are reasonably valid, the problem can be reduced to that for a constant-density batch reactor. If the density of the solution remains constant and the hydrogen chloride vaporizes and leaves the solution, the volume of the liquid-phase reaction will be constant. Then the relationship between the composition of the substances in the liquid phase is governed by rate expressions of the type used in this chapter. Assume that the reactions are second order. Then the rate of disappearance of benzene, determined entirely by the first reaction, is

$$-\frac{d[B]}{dt} = k_1[B][Cl_2] \quad (A)$$

Similarly the net rates of formation of the mono-, di-, and trichlorobenzenes are

$$\frac{d[M]}{dt} = k_1[B][Cl_2] - k_2[M][Cl_2] \quad (B)$$

$$\frac{d[D]}{dt} = k_2[M][Cl_2] - k_3[D][Cl_2] \quad (C)$$

$$\frac{d[T]}{dt} = k_3[D][Cl_2] \quad (D)$$

These four rate equations, along with the mass balance, can be solved for the desired yields of the products (in terms of the amount of benzene reacted) by eliminating time as a variable. The expressions cannot be solved directly to give compositions as a function of time because the magnitudes of the individual rate constants are not known (only their ratios are known). Although the rate equations are second order, the chlorine concentration appears in all the expressions and cancels out. Hence the reaction system is equivalent to the consecutive first-order system already considered, except that three reactions are involved.

If Eq. (B) is divided by Eq. (A), we obtain

$$\frac{d[M]}{d[B]} = -1 + \frac{k_2}{k_1} \frac{[M]}{[B]} \quad (E)$$

This is similar to Eq. (2-104), and so its solution can be written immediately by reference to Eq. (2-106). Thus the yield of monochlorobenzene is

$$x_M = \frac{[M]}{[B]_0} = \frac{k_1}{k_1 - k_2} \left\{ \left( \frac{[B]}{[B]_0} \right)^{k_2/k_1} - \frac{[B]}{[B]_0} \right\}$$

<sup>1</sup>From the standpoint of determining rate equations from experimental data it would be more appropriate to reverse this example, i.e., to require the evaluation of the ratios of the rate constants from given composition curves. Actually, the calculations are essentially the same in both cases.

<sup>2</sup>This problem was originally solved by MacMullin in a somewhat different manner.

or

$$x_M = [M] = \frac{[B]}{1 - \alpha} ([B]^{\alpha-1} - 1) \quad (F)$$

where  $\alpha \doteq k_2/k_1$ .

Similarly, Eq. (C) can be divided by Eq. (A) to give

$$\frac{d[D]}{d[B]} = -\alpha \frac{[M]}{[B]} + \beta \frac{[D]}{[B]} \quad (G)$$

where  $\beta = k_3/k_1$ . Equation (F) can be used in Eq. (G) to replace  $[M]$  with a function of  $[B]$ . Then another linear first-order differential equation in  $[D]$  results. Integrating this, and noting that  $[D]_0 = 0$  when  $[B]_0 = 1$ , gives the yield of  $D$ ,

$$x_D = \frac{[D]}{[B]_0} = [D] = \frac{\alpha}{1 - \alpha} \left( \frac{[B]}{1 - \beta} - \frac{[B]^\alpha}{\alpha - \beta} \right) + \frac{\alpha[B]^\beta}{(\alpha - \beta)(1 - \beta)} \quad (H)$$

The concentration of trichlorobenzene can be determined by difference, with a mass balance of aromatic components. Since the initial concentration of benzene is 1.0, and 1 mole of each chlorobenzene is produced per mole of benzene, the total molal concentration is constant and equal to unity. Hence

$$1.0 = [B] + [M] + [D] + [T] \quad (I)$$

Equations (F), (H), and (I) give the concentrations of  $[M]$ ,  $[D]$ , and  $[T]$  in terms of  $[B]$ . The corresponding amount of chlorine added can be determined from a mass balance on chlorine. If  $[Cl_2]$  represents the total moles of chlorine added (or reacted) per mole of benzene, then

$$[Cl_2] = [M] + 2[D] + 3[T] \quad (J)$$

As an illustration of the numerical calculations choose the point at which one-half the benzene has reacted. Then  $[B] = 0.5$ . It is given that

$$\alpha = \frac{1}{8} = 0.125$$

$$\beta = \frac{k_3}{k_1} = \frac{k_3}{k_2} \frac{k_2}{k_1} = \frac{1}{30} \left( \frac{1}{8} \right) = 0.00417$$

Then in Eq. (F)

$$x_M = [M] = \frac{1}{1 - 0.125} (0.5^{0.125} - 0.5) = 0.477$$

Equations (H) and (I) give

$$x_D = [D] = \frac{0.125}{1 - 0.125} \left( \frac{0.5}{1 - 0.00417} - \frac{0.50^{0.125}}{0.125 - 0.00417} \right) + \frac{0.125(0.50)^{0.00417}}{(0.125 - 0.00417)(1 - 0.00417)} = 0.022$$

$$[T] = 1 - [B] - [M] - [D] = 1 - 0.50 - 0.477 - 0.022 = 0.001$$

Finally, from Eq. (J),

$$[\text{Cl}_2] = 0.477 + 2(0.022) + 3(0.001) = 0.524$$

Hence, with 0.524 mole of chlorine reacted per mole of benzene, most of the product is monochlorobenzene, with a little dichlorobenzene, and a negligible quantity of trichlorobenzene.

To obtain the composition at a much later time we choose  $[B] = 0.001$ . Then, proceeding in the same manner, we find most of the product to be mono- and dichlorobenzene, with a little trichlorobenzene substituted product. The results for a range of  $[\text{Cl}_2]$  up to 2.14 are summarized in Table 2-11. Note that the maximum yield of monochlorinated product is obtained when approximately 1 mole of  $\text{Cl}_2$  has been reacted, and the maximum yield of dichlorinated product results when about 2 moles of  $\text{Cl}_2$  have been reacted. Selectivities for any two products can easily be found by taking ratios of the yields, Eq. (2-90). Since the problem has been solved on a basis of 1 mole of initial benzene,  $[M]$ ,  $[D]$ ,  $[T]$  also are equivalent to mole fractions.

Table 2-11 Composition of chlorinated benzenes

Compound	Mole fractions, or yields per mole of benzene							
	1.0	0.50	0.10	0.01	0.001	$10^{-4}$	$10^{-10}$	$10^{-20}$
Monochlorobenzene	0	0.477	0.745	0.632	0.482	0.362	0.064	0.004
Dichlorobenzene	0	0.022	0.152	0.353	0.509	0.625	0.877	0.852
Trichlorobenzene	0	0.001	0.003	0.005	0.008	0.013	0.059	0.144
Total	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Moles of chlorine used per mole of original benzene	0	0.524	1.06	1.35	1.52	1.65	1.99	2.14

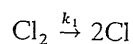
### 2-11 Chain Reactions

Chain mechanisms are a significant class of complex reactions since they explain many photochemical, combustion, and polymerization processes.<sup>1</sup>

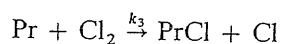
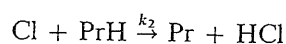
<sup>1</sup>For more complete discussions of chain reactions see A. A. Frost and R. G. Pearson "Kinetics and Mechanisms," John Wiley & Sons, Inc., New York, 1961; S. A. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Company, New York, 1960; S. W. Benson, *Ind. Eng. Chem.*, 56, 18 (1964).

Chain reactions consist of three kinds of elementary steps: initiation (or activation), propagation, and termination. As an illustration, consider the chlorination of propane (PrH). The experimental evidence suggests the following sequence:

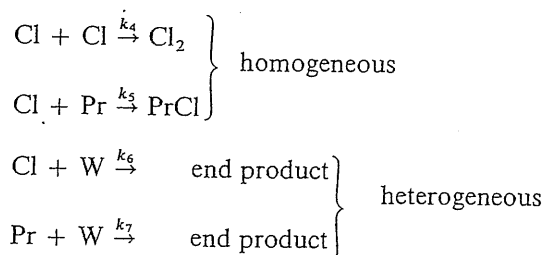
INITIATION



PROPAGATION



TERMINATION



In the initiation step the activated chlorine atoms can be obtained from intermolecular collisions of molecules heated to a high temperature (thermal activation). Alternately, the chlorine molecule can absorb radiant energy of the proper wavelength and dissociate (photochemical activation). The propagation steps are generally reactions which produce unstable intermediates (the Pr radical in our illustration) and also regenerate the activated reactant (Cl). These two reactions produce stable products (PrCl, HCl) and continuously regenerate activated reactant. Pr and Cl are *chain carriers*. Only a small amount of initiation is required to start the chain and lead to large rates of product formation. Hence chain reactions may be very fast. The overall rate is reduced by the termination processes, which convert the unstable intermediate and activated reactant into stable, end products. Termination may be homogeneous (occurring by intermolecular collisions) or heterogeneous (occurring by collision with the wall *W*, of the reactor).

If the propagation steps are rapid with respect to the termination process, the overall rate of product formation can be very large. When the propagation steps produces *two* chain carriers for every one consumed, the extra radical may cause further propagation or it may be destroyed by termination processes. If it is not destroyed, the growth in propagation

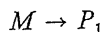
(and product formation) approaches infinity, resulting in an explosion. The oxidation of hydrogen is an example. After initiation produces H, this may react with O<sub>2</sub> producing *two* chain carriers, OH and O. Both chain carriers then propagate further to form product and regenerate themselves. Thus the sequence of reactions is

1.  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$
2.  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$
3.  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$

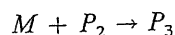
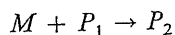
Reactions such as reaction 1 are called *chain-branching steps*.

Polymerization does not occur by a normal chain-reaction sequence, since the activated reactant is not regenerated. There is no chain carrier. Nevertheless, the overall process can be effectively analyzed in many instances as a combination of initiation, propagation, and termination steps. For example, suppose  $P_r$  represents a reactive polymer containing  $r$  molecules of monomer and  $M_{r+n}$  represents an inactive polymer of  $r+n$  molecules of monomer. The polymerization process might then be described by the following reactions, in which  $M$  is the monomer feed and  $P_1$  an activated form of the monomer:

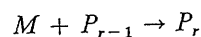
INITIATION



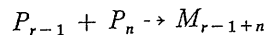
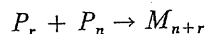
PROPAGATION



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TERMINATION



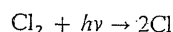
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The kinetics problems of interest in chain reactions, as in all complex systems, are to predict the conversion and product distribution as a function of time from the rate equations for the individual reactions, or to decide on the reactions involved and evaluate their rate constants from experimental data on the conversion and product distribution. The methods are illustrated

with a photochemical reaction in Example (2-9). Polymerization will be discussed in more detail in Chap. 4, after we have considered the nature of reactor performance.

**Example 2-9** Experimental measurements for the photochlorination of propane at 25°C and 1 atm pressure showed that the rate of consumption of  $\text{Cl}_2$  was independent of propane, second order in chlorine, and first order in light intensity.<sup>1</sup> If the controlling termination step is the heterogeneous termination of propyl radicals, show that the description of elementary steps given earlier for the chlorination of propane satisfactorily explains the experimental data.

**Solution** If  $h$  is Planck's constant and  $\nu$  is the frequency of radiation, the initiation reaction for a photochemical activation may be written as



The rate of production of Cl atoms depends on the volumetric rate of adsorption of radiant energy,  $Ia$ , according to the expression

$$r_i = 2\phi_i Ia \quad (\text{A})$$

where  $\phi_i$  is the quantum yield of the initiation step.<sup>2</sup> The rate of energy absorption is equal to the intensity of radiation,  $I$ , multiplied by the absorptivity  $\alpha$  and the chlorine concentration, so that Eq. (A) becomes

$$r_i = 2\phi_i \alpha [\text{Cl}_2] I$$

Suppose that the concentrations of intermediates rapidly attain constant low values; that is, the stationary-state hypothesis is valid.<sup>3</sup> Then a steady state will quickly be reached, after which the production and destruction rates of Pr and Cl will balance each other, or

$$\frac{d[\text{Pr}]}{dt} = \frac{d[\text{Cl}]}{dt} = 0 \quad (\text{B})$$

We can write two independent equations from Eq. (B), one for Pr and the other for Cl, using the elementary steps described in the text.<sup>4</sup>

$$\frac{d[\text{Pr}]}{dt} = 0 = k_2[\text{Cl}][\text{PrH}] - k_3[\text{Pr}][\text{Cl}_2] - k_7[\text{Pr}]$$

$$\frac{d[\text{Cl}]}{dt} = 0 = 2\phi_i \alpha [\text{Cl}_2] I - k_2[\text{Cl}][\text{PrH}] + k_3[\text{Pr}][\text{Cl}_2]$$

<sup>1</sup>A. E. Cassano and J. M. Smith, *AIChE J.*, **12**, 1124 (1966).

<sup>2</sup>The quantum yield is the molecules of product produced per quantum of energy absorbed. For a primary step  $\phi_i$  approaches unity. Note that the coefficient 2 in Eq. (A) takes account of the production of two atoms of chlorine for each molecule of  $\text{Cl}_2$ .

<sup>3</sup>Note that the requirement for the stationary-state hypothesis to be valid is that the concentrations of intermediates be small with respect to those of the reactants and products.

<sup>4</sup>In writing these expressions only the one termination step involving  $k_7$  is needed, since it is assumed to control the termination process.

Adding these two expressions gives  $[\text{Pr}]$  in terms of the concentration of stable species and the rate constants,

$$[\text{Pr}] = \frac{2\phi_i \alpha [\text{Cl}_2] I}{k_7} \quad (\text{C})$$

The rate of consumption of  $\text{Cl}_2$  or production of propyl chloride is obtained from the second of the propagation reactions. Thus

$$-\frac{d[\text{Cl}_2]}{dt} = k_3 [\text{Pr}] [\text{Cl}_2] \quad (\text{D})$$

The concentration of  $[\text{Pr}]$  is small but unknown. However, the stationary-state hypothesis has allowed us to develop Eq. (C) for  $[\text{Pr}]$  in terms of known quantities. Using Eq. (C) in Eq. (D) gives

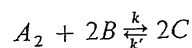
$$-\frac{d[\text{Cl}_2]}{dt} = \frac{2k_3 \phi_i}{k_7} \alpha [\text{Cl}_2]^2 I \quad (\text{E})$$

This is the desired result, giving the rate as second order in chlorine and first order in light intensity. By choosing different termination steps to be controlling, we can obtain different expressions for  $-d[\text{Cl}_2]/dt$ , some involving  $[\text{Pr}]$ ,  $[\text{Cl}_2]$ , and  $[I]$  to other powers. Comparison of the various results with experimentally determined rates allows us to choose the best form of the rate equation and to evaluate the ratio of rate constants; for example,  $k_3 \phi_i / k_7$  in Eq. (E). From measurements only on stable species, individual values of  $k$  cannot, in general, be established.

No mention has been made of the effects of wavelength, measurement of light intensity, and other complications in photochemical studies. These questions and others are discussed in the literature.<sup>1</sup>

### 2-12 Rate Constants and Equilibrium

In Sec. 2-8 it was shown that for an elementary process the ratio of rate constants in the forward and reverse directions is equal to the equilibrium constant. When order and stoichiometry do not agree this is not necessarily true. To explain with a simple example, suppose the reversible, overall reaction



is found to be first order in  $A_2$  and  $B$  in the forward direction, and first order in  $C$  in the reverse direction. The net rate of consumption of  $A_2$  is

$$r_{A_2} = k[A_2][B] - k'[C] \quad (2-108)$$

<sup>1</sup>J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, 1966; W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corporation, New York, 1941.

At equilibrium the net rate will be zero, so that

$$\frac{k}{k'} = \frac{[C]}{[A_2][B]} \quad (2-109)$$

The stoichiometry of the reaction requires that the equilibrium constant be defined as

$$K = \frac{[C]^2}{[A_2][B]^2} \quad (2-110)$$

Comparison of Eqs. (2-109) and (2-110) shows that  $k/k'$  is not equal to  $K$  for this case.

It has been suggested<sup>1</sup> that if the mechanism of the overall reaction is known, and if one of the elementary steps controls the rate, the relationship between rate constants and the overall equilibrium constant is

$$\frac{k}{k'} = K^{1/n} \quad (2-111)$$

The coefficient  $n$  is defined by Horiuti as the stoichiometric number of the particular elementary process which controls the rate. This is the number of times this step must occur to accomplish the overall reaction. Suppose that the mechanism of the reaction we have chosen consists of the elementary steps

1.  $A_2 \rightleftharpoons 2A$
2.  $A + B \rightleftharpoons C$

For the overall reaction  $A_2 + 2B \rightleftharpoons 2C$  to result, the first step must occur once and the second step twice. Accordingly, the stoichiometric numbers are 1 and 2 for these steps.

### 2-13 Precision of Kinetic Measurements

Errors in experimental data may arise from random causes or inherent difficulties in the system. The latter type can be corrected once the performance of the system is fully understood. For example, in kinetics studies erroneous rates may be caused by some appreciable unknown reaction not accounted for in the treatment of the data. Random errors, such as temperature fluctuations in a thermostat, can be reduced by improvements in apparatus and technique but usually cannot be eliminated. These residual random errors may be evaluated from the known precision of the experi-

<sup>1</sup>M. Manes, L. Hofer, and S. Weller, *J. Chem. Phys.*, **18**, 1355 (1950); J. Horiuti, in *Advan. Catalysis*, **9**, 339 (1957).



mental observations. It is important in kinetics to be able to calculate the precision of rates of reaction, rate constants, and activation energies from the errors in the measurements.

Let us consider as an illustration the precision of rate constants. The fractional error in dependent variable  $\Omega$ , which is a function of independent variables  $\alpha_i$ , is given by

$$\left(\frac{\Delta\Omega}{\Omega}\right)^2 = \sum_{i=1}^m \left[\frac{\partial(\ln \Omega)}{\partial(\ln \alpha_i)}\right]^2 \left(\frac{\Delta\alpha_i}{\alpha_i}\right)^2 \quad (2-112)$$

The starting point in using this expression is the relation between the quantity we want to know the precision of and the experimental observations used. For our example this is the relation between the rate constant and the rate and concentrations. Suppose the reaction is second order and of the form

$$r = k_2[A][B]$$

Then the required relationship is

$$k_2 = \frac{r}{[A][B]} \quad (2-113)$$

where  $r$ ,  $[A]$ , and  $[B]$  are the three independent variables ( $\alpha_i$ ) and  $k$  is the dependent variable ( $\Omega$ ). Evaluating the partial derivatives from Eq. (2-113) and substituting them in Eq. (2-112) yields

$$\left(\frac{\Delta k}{k}\right)^2 = \left[\frac{\partial(\ln k)}{\partial(\ln r)}\right]^2 \left(\frac{\Delta r}{r}\right)^2 + \left\{\frac{\partial(\ln [k])}{\partial(\ln [A])}\right\}^2 \left(\frac{\Delta[A]}{[A]}\right)^2 + \left\{\frac{\partial(\ln k)}{\partial(\ln [B])}\right\}^2 \left(\frac{\Delta[B]}{[B]}\right)^2$$

or

$$\left(\frac{\Delta k}{k}\right)^2 = \left(\frac{\Delta r}{r}\right)^2 + \left(\frac{\Delta[A]}{[A]}\right)^2 + \left(\frac{\Delta[B]}{[B]}\right)^2 \quad (2-114)$$

This result shows that the squares of the fractional errors in the individual measurements are additive. If the precision of the rate measurements is 8% and that of each concentration is 4%, the error in  $k$  will be

$$\left(\frac{\Delta k}{k}\right)^2 = 0.08^2 + 0.04^2 + 0.04^2 = 0.0096$$

$$\frac{\Delta k}{k} = 0.098 \quad \text{or } 9.8\%$$

The rate is not a direct measurement but is itself calculated from

observations of such variables as time and concentration. Its precision, arbitrarily chosen in the example as 8%, should be based on an evaluation similar to that illustrated for obtaining the error in  $k$ .

The evaluation of  $k$  from data for rates and concentrations should be carried out by statistically sound methods, provided sufficient data points are available. For example, Eq. (2-113) shows that a linear relationship exists between the product  $[A][B]$  and  $r$ . Hence  $k_2$  should be determined from the slope of the line of  $r$  vs  $[A][B]$  determined by a least-mean-square fit of the data points. This technique was illustrated in Example 2-1, where the best fit of the Arrhenius equation to  $k$ -vs- $T$  data was used to evaluate the activation energy.

Errors in activation energy can be evaluated from the Arrhenius equation by the same procedure described for finding the errors in  $k$ . The precision of  $E$  will depend on the uncertainty in  $k$  and  $T$ . Since  $E$  is based on differences in  $k$  and  $T$  values, the same errors in  $k$  and  $T$  will result in smaller errors in  $E$  as temperature range covered by the data is increased.

### *Bibliography*

1. S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Company, New York, 1960. The stationary-state hypothesis mentioned in Secs. 2-6 and 2-11 is defined and illustrated on pp. 50-53. In chap. XII the collision theory is considered in detail, complications related to the energy distribution of molecules and the steric factor are discussed, and the results are compared in depth with those from the transition-state theory.
2. S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, 1968. Proposes means for estimating rate constants for a variety of homogeneous reactions.
3. Michel Boudart, "Kinetics of Chemical Processes," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1968. A concise presentation of the fundamental concepts of kinetics for homogeneous and heterogeneous reactions, including a chapter on the application and validity of the stationary-state hypothesis.
4. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, 1961. Provides an excellent discussion of reaction mechanisms with applications.
5. N. N. Semenov, "Problems in Chemical Kinetics and Reactivity," vols. I and II translated by M. Boudart, Princeton University Press, Princeton, N.J., 1958. Provides large reservoirs of information on theories of kinetics and experimental data.

### *Problems*

- 2-1. A common rule of thumb is that the rate of reaction doubles for each 10°C rise in temperature. What activation energy would this suggest at a temperature of 25°C?



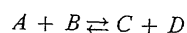
A at 600°K and compare it with the experimental result. Assume that the effective collision diameter is  $5 \times 10^{-8}$  cm.

- 2-7. From the transition-state theory and the following thermodynamic information, calculate the rate constant for the given unimolecular reactions. Assume ideal-gas behavior.

Reaction	T, °K	$\Delta H^*$ , cal/g mole	$\Delta S^*$ , cal/(g mole)(°K)
Decomposition of methyl azide, $\text{CH}_3\text{N}_3$	500	42,500	8.2
Decomposition of dimethyl ether, $\text{CH}_3\text{OCH}_3$	780	56,900	2.5

SOURCE: O. A. Hougen and K. M. Watson, "Chemical Process Principles," vol. III, "Kinetics and Catalysis," John Wiley & Sons, Inc., New York, 1947.

- 2-8. A gaseous second-order reversible reaction of the form

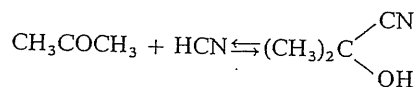


has forward-rate constants as follows:

$$k_2 = \begin{cases} 10.4 \text{ liter}/(\text{g mole})(\text{sec}) & \text{at } 230^\circ\text{C} \\ 45.4 \text{ liter}/(\text{g mole})(\text{sec}) & \text{at } 260^\circ\text{C} \end{cases}$$

The standard-state entropy and enthalpy changes for the overall reaction are approximately independent of temperature and are given by  $\Delta H^\circ = 8,400$  cal/g mole and  $\Delta S^\circ = -2.31$  cal/(g mole)(°K). Derive expressions for the forward- and reverse-rate constants as functions of temperature.

The reaction



was studied in aqueous solution by Svirbely and Roth.<sup>1</sup> In one run with initial concentrations of 0.0758 normal for HCN and 0.1164 normal for acetone, the following data were obtained:

t, min	4.37	73.2	172.5	265.4	346.7	434.4
[HCN], normal	0.0748	0.0710	0.0655	0.0610	0.0584	0.0557

Determine a reasonable rate equation from these data. ( $K_c = 13.87$  liter/mole)

- 2-10. With HCl as a homogeneous catalyst the rate of esterification of acetic acid and alcohol is increased. At 100°C the rate of the forward reaction is

$$r_2 = k_2[H][OH] \quad \text{g moles}/(\text{liter})(\text{min})$$

<sup>1</sup>J. Am. Chem. Soc., 75, 3109 (1953).

$$k_2 = 4.76 \times 10^{-4} \text{ liter}/(\text{g mole})(\text{min})$$

and the rate of the reverse reaction is

$$r'_2 = k'_2[E][W] \quad \text{g moles}/(\text{liter})(\text{min})$$

$$k'_2 = 1.63 \times 10^{-4} \text{ liter}/(\text{g mole})(\text{min})$$

where  $[H]$  = concentration of acetic acid

$[OH]$  = concentration of alcohol

$[E]$  = concentration of ester

$[W]$  = concentration of water

An initial mixture consists of equal masses of 90 wt % aqueous solution of acid and 95 wt % solution of ethanol. For constant-volume conditions calculate the conversion of acid to ester for various times of reaction. Assuming complete miscibility, estimate the equilibrium conversion.

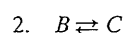
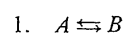
- 2-11. Smith<sup>1</sup> has studied the gas-phase dissociation of sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , into chlorine and sulfur dioxide at 279.2°C. The total-pressure method was employed to follow the course of the reaction. Under constant-volume conditions the results were as follows:

$t$ , min	3.4	15.7	28.1	41.1	54.5	68.3	82.4	96.3
$p_t$ , mm Hg	325	335	345	355	365	375	385	395

What reaction order do these data suggest? The conversion is 100% at infinite time.



For two consecutive reversible reactions (liquid-phase)



the forward-rate constants  $k$  and equilibrium constants  $K$  are

$$k_1 = 1 \times 10^{-3} \text{ min}^{-1} \quad K_1 = 0.8$$

$$k_2 = 1 \times 10^{-2} \text{ min}^{-1} \quad K_2 = 0.6$$

If the initial concentration of  $A$  is 1.0 molal, plot the concentration of  $A$  vs time from 0 to 1,000 min. Both reactions are first order.

- 2-13. The thermal decomposition of nitrous oxide ( $\text{N}_2\text{O}$ ) in the gas phase at 1030°K is studied in a constant-volume vessel at various initial pressures of  $\text{N}_2\text{O}$ . The half-life data so obtained are as follows:

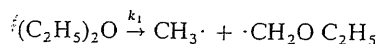
$p_0$ , mm Hg	52.5	139	290	360
$t_{1/2}$ , sec	860.0	470	255	212

Determine a rate equation that fits these data.

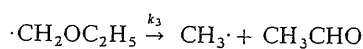
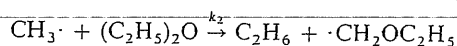
<sup>1</sup>D. F. Smith, *J. Am. Chem. Soc.*, 47, 1862 (1925).

- 2-14. It has been postulated that the thermal decomposition of diethyl ether occurs by the following chain mechanism:

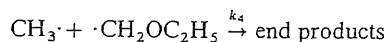
INITIATION



PROPAGATION

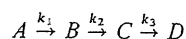


TERMINATION



Show that the stationary-state hypothesis indicates that the rate of decomposition is first order in ether concentration.

- 2-15. Consider the reaction sequence



Determine the profiles of concentration vs time for  $A$ ,  $B$ ,  $C$ , and  $D$  on an analog computer. Solve the problem in the following steps:

STEP 1 To limit the variables range from 0 to 1.0, first put the differential equations expressing the rate in dimensionless form by using the new variables

$$A^* = \frac{[A]}{[A]_0} \quad B^* = \frac{[B]}{[A]_0} \quad C^* = \frac{[C]}{[A]_0} \quad D^* = \frac{[D]}{[A]_0} \quad t^* = k_1 t$$

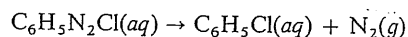
where  $[A]_0$  is the initial concentration of  $A$ . Note that the initial conditions are  $t^* = 0$ ,  $A^* = 1$ , and  $B^* = C^* = D^* = 0$ .

STEP 2 Next prepare a block diagram showing the hookup of integrators, inverters, summers, and potentiometers needed to solve the differential equations for  $A^*$ ,  $B^*$ ,  $C^*$ , and  $D^*$ . Suppose  $k_2/k_1 = k_3/k_1 = 1.0$ .

STEP 3 Hook up an analog computer according to the block diagram and display the outputs  $A^*$ ,  $B^*$ ,  $C^*$ , and  $D^*$  vs  $t^*$  on an oscilloscope or  $xy$  plotter.

- 2-16. Solve Prob. 2-15 by analytical integration of the differential equations (dimensionless form).

- 2-17. Aqueous solutions of diazobenzene decompose irreversibly according to the reaction



The kinetics are first order. In one experiment,<sup>1</sup> at 50°C the initial concentration

<sup>1</sup>O. A. Hougen and K. M. Watson, "Chemical Process Principles," vol. III, "Kinetics and Catalysis," John Wiley & Sons, Inc., New York, 1947.

of  $C_6H_5N_2Cl$  was 10 g/liter and the following amounts of  $N_2$  were liberated:

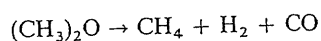
Reaction time, min	6	9	12	14	18	20	22	24	26	30
$N_2$ liberated, $cm^3$ at $50^\circ C$ , 1 atm	19.3	26.0	32.6	36.0	41.3	43.3	45.0	46.5	48.4	50.3

Complete decomposition of the diazo salt liberated  $58.3 cm^3$  of  $N_2$ . Calculate an accurate value for the rate constant.

- 2-18. The thermal decomposition of dimethyl ether in the gas phase was studied by Hinshelwood and Askey<sup>1</sup> by measuring the increase in pressure in a constant-volume reaction vessel. At  $504^\circ C$  and an initial pressure of 312 mm Hg the following data were obtained:

$t$ , sec	390	777	1,195	3,155	$\infty$
$p_t$ , mm Hg	408	488	562	779	931

Assuming that only ether was present initially and that the reaction is



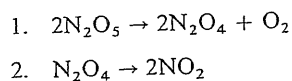
determine a rate equation for the decomposition. What is the numerical value of the specific-reaction rate at  $504^\circ C$ ?

- 2-19.<sup>2</sup> Suppose that a gaseous reaction between  $A$  and  $B$  is studied kinetically by making isothermal measurements of the half-life period for several initial compositions of reactants. The results for each of four different initial conditions are as follows:

$(p_A)_0$ , mm Hg	500	125	250	250
$(p_B)_0$ , mm Hg	10	15	10	20
$(t_{1/2})_B$ , min	80	213	160	80

If the rate is first order with respect to component  $A$  and second order with respect to  $B$ , what is the numerical value of the specific reaction rate?

- 2-20. The reaction mechanism for the decomposition of nitrogen pentoxide is complex, as described in Sec. 2-2. However, a satisfactory rate equation can be developed by considering the two reactions



Reaction 2 is rapid with respect to reaction 1, so that nitrogen dioxide and

<sup>1</sup>C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc. (London)*, **A115**, 215 (1927).

<sup>2</sup>From A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, 1953 (by permission).

nitrogen tetroxide may be assumed to be in equilibrium. Hence only reaction 1 need be considered from a kinetic standpoint. Calculate the specific reaction rate for this reaction (which is essentially irreversible) from the following total-pressure data<sup>1</sup> obtained at 25°C:

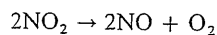
$t, \text{ min}$	0	20	40	60	80	100	120	140	160	$\infty$
$p_t, \text{ mm Hg}$	268.7	293.0	302.2	311.0	318.9	325.9	332.3	338.8	344.4	473.0

It may be assumed that only nitrogen pentoxide is present initially. The equilibrium constant  $K_p$  for the dissociation of nitrogen tetroxide into nitrogen dioxide at 25°C is 97.5 mm Hg.

2-21.<sup>2</sup> The decomposition of nitrogen dioxide follows a second-order rate equation. Data at different temperatures are as follows:

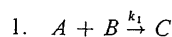
$T, \text{ }^\circ\text{K}$	592	603	627	651.5	656
$k_2, \text{ cm}^3/(\text{g mole})(\text{sec})$	522	755	1,700	4,020	5,030

Compute the energy of activation  $E_c$  from this information. If the reaction is written



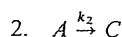
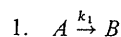
also evaluate the activation energy  $E_p$ .

2-22. Reactants  $A$  and  $B$  are placed in a reaction vessel at zero time, where  $[A]_0 = [B]_0$ . The following reactions occur at constant density:



where  $C$  is the desired product. If both reactions are second order, derive an expression for the selectivity of  $C$  with respect to  $D$  in terms of the total conversion of  $A$ . Also determine the total conversion at which the selectivity will be a maximum if  $k_2/k_1 = 1.0$ . Will the maximum conversion of  $A$  to  $C$  occur at the same total conversion as that for which the selectivity of  $C$  with respect to  $D$  is a maximum?

2-23. The parallel, first-order irreversible reaction system



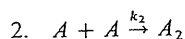
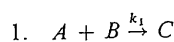
<sup>1</sup>F. Daniels and E. H. Johnston, *J. Am. Chem. Soc.*, 43, 53 (1921).

<sup>2</sup>From A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, 1953 (by permission).



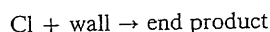
consists of three components, so that the reaction path can be conveniently represented on a triangular diagram.<sup>1</sup> Suppose that initially only  $A$  is present at a concentration  $[A]_0$ . Assume constant density, so that the sum of the concentrations of all the components will be constant and equal to  $[A]_0$ . Let one apex of the equilateral triangle represent a reaction mixture containing 100%  $A$ , the second 100%  $B$ , and the third 100%  $C$ . Use Eq. (2-100) to show how the composition of the reaction mixture can be represented on the diagram. Specifically, draw the reaction path from zero to complete conversion of  $A$  when  $k_2/k_1 = 2$ . What path would be followed if  $k_2/k_1 = 0$ ?

- 2-24. Suppose the consecutive first-order reactions described on page 77 occur at constant density in a batch reactor, with an initial mixture containing only  $A$  at a concentration  $[A]_0$ . Show on a triangular diagram the reaction paths for three cases:  $k_3/k_1 = 0.5, 1.0, \text{ and } 2.0$ .
- 2-25. The second-order reactions



occur at constant density, with an initial mixture containing only  $A$  and  $B$ , each at the same concentration. For a batch reactor, show the reaction path on a triangular diagram for  $k_2/k_1 = 1.0$ .

- 2-26. Consider that the photochlorination of propane occurs according to the reactions in Sec. 2-11. If the controlling termination step is the heterogeneous termination of chlorine radicals,



derive a rate equation for the overall reaction. What would be the form of the rate equation if the second-order homogeneous termination of  $\text{Cl}$  were controlling (i.e., according to the reaction  $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$ )?

- 2-27. The kinetics of a second-order irreversible liquid-phase reaction of the form  $A + B \rightarrow C$  are studied in a constant-volume apparatus. Starting with equal concentrations of 1.0 mole/liter for  $A$  and  $B$ , the reaction is stopped after 30 min, at which time about 20% of the reactants have disappeared. Random errors will amount to about 5 sec in the time readings and 0.002 moles/liter in the concentration measurements. Estimate the fractional error in the rate constants computed from such data.

<sup>1</sup>The representation of reaction paths on triangular diagrams is described in detail in Kramers and Westerterp, "Chemical Reactor Design and Operation," p. 47, Academic Press, Inc., New York, 1963.