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KINETICS OF
HOMOGENEOUS REACTIONS

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Kinetics is concerned with the rates of chemical reactions and the factors which influence these rates. The first kinetic measurements were made before 1820, but interpretation in terms of quantitative laws began with the studies on the inversion of sucrose by Wilhelmy,[1] the esterification of ethanol with acetic acid by Bethelot and St. Gilles,[2] and the reaction between oxalic acid and potassium permanganate by Harcourt and Esson.[3] These investigations established the relations between rate and concentration of reactants. The important contribution of Arrhenius[4] for the effect of temperature was also made in the nineteenth century.

In this chapter the definitions and concepts used in kinetics are presented, followed by a brief description of theories for reaction velocity.

[1] L. Wilhelmy, *Pogg. Ann.*, **81**, 413, 499 (1850).

[2] M. Berthelot and L. P. St. Gilles, *Ann. Phys.*, **63**, 385 (1862).

[3] A. V. Harcourt and W. Esson, *Proc. Roy. Soc. (London)*, **14**, 470 (1865); *Phil. Trans.*, **156**, 193 (1866); *Phil. Trans.*, **157**, 117 (1867).

[4] S. Arrhenius, *Z. Physik Chem.*, **4**, 226 (1889).

Then the use of rate equations for studying the kinetics of reactions is illustrated for simple systems and some complex ones. Only homogeneous reactions, devoid of any physical resistances, are considered here. The kinetics of heterogeneous reactions is taken up in Chaps. 8 and 9.

2-1 Rate of Reaction

The *rate of reaction* is formally defined as the change in moles of a component with respect to time, per unit volume of reaction mixture. This quantity is negative if the component is a reactant and positive if the component is a product. It is important that there be but one definition of rate, regardless of the type of reactor—flow or batch, tank or tube. Thus the rate must be a local, or point, value; that is, it must refer to a differential volume of reaction mixture. With this restriction the rate becomes a unique property for a given system. If the rate is to be the same throughout the volume of a tank reactor, the concentrations and temperature must be uniform. Otherwise the rate will vary from point to point in the reaction volume. In heterogeneous reactions, particularly those with solid phases, it may be convenient to base the rate on a unit mass or surface rather than volume, but it will always refer to a point in the reaction region.

For the *batch tank* reactor, with uniform concentrations and temperature, the independent variable is time, and the mathematical expression for the rate r is

$$r = \frac{1}{V} \frac{dN}{dt} = \frac{\text{moles}}{\text{volume} \times \text{time}} \qquad (2\text{-}1)$$

where V is the volume of the reaction mixture and N is the number of moles of a product species. If N refers to moles of reactant, so that dN/dt is negative, a minus sign is commonly used in front of the derivative so that the rate is always positive. For a *tubular* reactor with a steady flow of material in and out, the independent variable is position in the tube, or reactor volume, and the composition and rate change with this variable instead of time. To formulate the *point rate* a differential element of reactor volume, dV, must be chosen. If N' is the molal rate of flow of a component into the volume element, the rate will be

$$r = \frac{dN'}{dV} \qquad (2\text{-}2)$$

These two equations will be used throughout the book to describe the rate of reaction quantitatively.

The course of a reaction is normally measured by the change in *concentration* of a reactant or product. Particularly in gaseous reactions,

volume changes may also occur (for example, because of a change in total moles). Then concentration changes arise from a change in volume as well as from reaction. The influence of volume change can be examined by writing $N = CV$. Thus Eq. (2-1) becomes

$$r = \frac{1}{V} \frac{d(CV)}{dt}$$ (2-3)

If the volume, or density, of the reaction mixture is constant, Eq. (2-3) reduces to the common form

$$r = \frac{dC}{dt}$$ (2-4)

Care must be exercised in deciding when Eq. (2-4) is applicable. In a flow reactor, used for a gaseous reaction with a change in moles, it is not correct (see Examples 4-3 and 4-4). However, it is correct for all gas-phase reactions in a tank-type reactor, since the gaseous reaction mixture fills the entire vessel, so that the volume is constant. For many liquid-phase systems density changes during the reaction are small, and Eq. (2-4) is valid for all types of reactors. The use of Eqs. (2-1) to (2-4) will become clear as we consider various kinds of reactions and reactors.
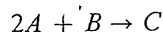
If the stoichiometric coefficients for two reactants are different, the rate expressed in terms of one reactant will not be the same as the rate expressed in terms of the other. Suppose the reaction

$$aA + bB \rightarrow cC + dD$$
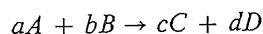
occurs at constant volume, so that Eq. (2-4) is applicable. The concentration changes for the four reactants and products are related as follows:

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$ (2-4′)

where $[A]$ is the concentration of reactant A, etc. For example, if the reaction is

$$2A + B \rightarrow C$$

$$-\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

or

$$-\frac{d[A]}{dt} = -2 \frac{d[B]}{dt} = 2 \frac{d[C]}{dt}$$

For reactions with nonequal stoichiometric coefficients, Eq. (2-4′) shows that a rate which is the same for all components can be defined as[1]

$$r = \frac{1}{a_i} \frac{dC_i}{dt}$$ (2-4″)

where the stoichiometric coefficient a_i is negative for reactant i and positive for product i, and C_i is the concentration.

2-2 Concepts of Kinetics

The early workers in kinetics found that simple relations existed between rates of reaction and concentrations of reactants. Thus Berthelot and St. Gilles[2] discovered that the rate of esterification was proportional to the first power of the concentration of ethanol and to the first power of the concentration of acetic acid. The rate is said to be *first order* with respect to each reactant. In general terms, suppose that the rate of the reaction

$$aA + bB \rightarrow cC + dD$$
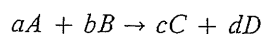
may be written

$$r = k[A]^\alpha[B]^\beta$$ (2-5)

Then α is the *order* of the reaction with respect to A, and β is the *order* with respect to B. In subsequent sections kinetics will be discussed with respect to a batch tank reactor, usually at constant density, so that Eq. (2-4) is applicable. Measured in terms of reactant A, this limitation means that Eq. (2-5) may be written

$$r = -\frac{d[A]}{dt} = k[A]^\alpha[B]^\beta$$ (2-6)

The order of the reaction is determined by comparison of experimental data with Eq. (2-6) or integrated forms of it, as described in Secs. 2-7 to 2-10. As such, order is an empirical quantity, and α and β do not always have integer values.

There is no necessary connection between order and the stoichiometric coefficients in the reaction equation; that is, it is not required that $\alpha = a$ and $\beta = b$ in reaction (2-5). For example, the stoichiometry of the ammonia-synthesis reaction is

$$2N_2 + 3H_2 \rightarrow 2NH_3$$
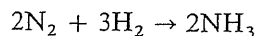
[1]This concept of a unique rate has been used to develop a measure of the amount of reaction which is the same regardless of the component used to follow the course of the reaction. This so-called *extent* of reaction is described in Michel Boudart, "Kinetics of Chemical Processes," p. 10, Prentice-Hall, Inc., Englewood Cliffs, N.J., 1968.

[2]M. Berthelot and L. P. St. Gilles, *Ann. Phys.*, 63, 385 (1862).

but for many catalysts the rate equation that best fits experimental data is
first order in N_2 and zero order in hydrogen.

As kinetic studies of many kinds of reactions have accumulated, it
has become increasingly clear that formation of the final products from the
original reactants usually occurs in a series of relatively simple steps. The
number of overall reactions that take place in a single step is small. Herein
lies the explanation for the difference between order and stoichiometric
coefficients. The rates of the individual steps will normally be different,
and the rate of the overall reaction will be determined primarily by the
slowest of these steps. The *mechanism* of a reaction is the sequence of steps
that describe how the final products are formed from the original reactants.
If the mechanism is known, it is usually possible to evaluate a rate equation
such as (2-6) and, hence, the order of the reaction. In contrast, it is generally
not possible to infer a mechanism from the rate equation alone.

These points are well illustrated by the gaseous photochlorination
of propane,

$$C_3H_8 + Cl_2 \rightarrow C_3H_7Cl + HCl$$
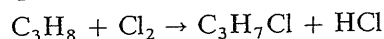
At certain concentrations stoichiometry and order do not agree, for the
rate is found[1] to be second-order in chlorine and independent of propane
concentration (zero order) according to the rate equation

$$-\frac{d[Cl_2]}{dt} = k[Cl_2]^2 \qquad (2\text{-}7)$$

However, the actual mechanism of the reaction probably entails many
steps comprising an initiation reaction in which light is absorbed, propaga-
tion steps involving the free radicals C_3H_7 and Cl, and termination steps
in which the radicals are eliminated.

A fortuitous example in which order and stoichiometry are identical
is the decomposition of N_2O_5,

$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$
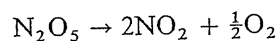
Ogg[2] has found that while the rate is first order in N_2O_5, the mechanism
probably consists of three steps:

1. $N_2O_5 \rightleftharpoons NO_2 + NO_3$

2. $NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$

3. $NO + NO_3 \rightarrow 2NO_2$

If the second step is second order and very slow with respect to the others,

[1] A. E. Cassano and J. M. Smith, *AIChE J.*, 12, 1124 (1966).
[2] R. A. Ogg, Jr., *J. Chem. Phys.*, 15, 337, 613 (1947).

the rate of the overall process will be proportional to the product of NO_2 and NO_3 concentrations. Furthermore, equilibrium will be quickly attained in the first step, so that $[NO_2][NO_3]$ will be equal to $K_1[N_2O_5]$, where K_1 is the equilibrium constant for the first step. These postulates and the three-step mechanism thus explain the first-order rate equation. Note that it would be incorrect to assume a single step for the overall reaction on a basis of the observed first-order dependency on the rate.

The individual steps, which together describe the overall reaction, are called *elementary processes*. Theories about kinetics (discussed in Secs. 2-4 to 2-6) refer to these elementary processes. Order and stoichiometric numbers are usually identical for elementary processes, but not always. The *molecularity* of an elementary step is the number of reactant molecules that take part in the reaction. This is usually equal to the total order, but exceptions exist for unimolecular reactions. For example, unimolecular reactions (molecularity = 1) are not necessarily first order; in fact, gaseous reactions which involve one molecule always become second order at low pressures (see Sec. 2-6).

Up to this point we have considered the influence only of concentration on the rate. The *specific rate constant* k in Eq. (2-6) includes the effects of all other variables. The most important of these is temperature, but others may be significant. For example, a reaction may be primarily homogeneous but have appreciable wall or other surface effects. In such cases k will vary with the nature and extent of the surface. A reaction may be homogeneous but also require a catalyst. An example is the reaction for the inversion of sugar, where the acid acts as a catalyst. In these instances k may depend on the concentration and nature of the catalytic substance. However, when the concentration effect of the catalyst is known, it is better to include the catalyst concentration in Eq. (2-5), so that k is independent of all concentrations.

The dependency of k on temperature for an elementary process follows the Arrhenius equation (see Sec. 2-3),

$$k = Ae^{-E/R_gT} \tag{2-8}$$

where A is the frequency (or preexponential) factor and E is the activation energy. Combining Eqs. (2-8) and (2-6) yields

$$-\frac{d[A]}{dt} = Ae^{-E/R_gT}[A]^\alpha[B]^\beta \tag{2-9}$$

This provides a description of the rate in terms of the measurable variables, concentration and temperature. It is rigorously limited to an elementary process because the Arrhenius equation is so restricted. However, the exponential effect of temperature often accurately represents experimental

rate-data for an overall reaction, even though the activation energy is
not clearly defined and may be a combination of E values for several of
the elementary steps.

2-3 The Arrhenius Law

Arrhenius developed his concepts about the variation of rate with tem-
perature through thermodynamic arguments.[1] For a reaction whose rates are
rapid enough to achieve a dynamic equilibrium the *van't Hoff equation*
states that

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{R_g T^2} \tag{2-10}$$

If the reaction may be written

$$A + B \rightleftharpoons C$$
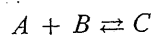
the equilibrium constant[2] is

$$K = \frac{[C]}{[B][A]} \tag{2-11}$$

Since this is an elementary process, the rates of the forward and reverse
reactions may be formulated [by Eq. (2-6)] with order and stoichiometric
numbers identical:

Forward rate $= k_2[A][B]$

Reverse rate $= k_1'[C]$

At equilibrium the two rates are equal. This fact, plus Eq. (2-11), yields

$$k_2[A][B] = k_1'[C] \tag{2-12}$$

or[3]

$$\frac{[C]}{[A][B]} = \frac{k_2}{k_1'} = K \tag{2-13}$$

Using this result in Eq. (2-10) gives

$$\frac{d(\ln k_2)}{dT} - \frac{d(\ln k_1')}{dT} = \frac{\Delta H}{R_g T^2} \tag{2-14}$$

[1]S. Arrhenius, Z. *Physik Chem.*, 4, 226 (1889).
[2]To simplify the reasoning the complexities introduced by the differences between activities,
upon which K in Eq. (2-10) is based, and concentrations, which express K in Eq. (2-11), are
ignored.
[3]The form of Eq. (2-13) for an overall reaction is considered in Sec. 2-12.

The right-hand side of Eq. (2-14) may be divided into two enthalpy changes, ΔH_1 and ΔH_2, such that

$$\Delta H = \Delta H_2 - \Delta H_1 \tag{2-15}$$

Then Eq. (2-14) may be split into two equations, one for the forward reaction and another for the reverse reaction, which will have a difference in agreement with (2-15):

$$\frac{d(\ln k_2)}{dT} = \frac{\Delta H_2}{R_g T^2} \tag{2-16}$$

$$\frac{d(\ln k_1')}{dT} = \frac{\Delta H_1}{R_g T^2} \tag{2-17}$$

Integrating either equation and setting the integration constant equal to ln A gives a result of the form of the Arrhenius equation, Eq. (2-8):

$$k = A e^{-\Delta H/R_g T} \tag{2-18}$$

An alternate derivation is based on the concept of an intermediate state, often called a *transition* or *activated state*, which is a postulate of the transition-state theory (Sec. 2-5). Suppose that product C of the reaction

$$A + B \leftrightarrows C$$
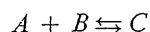
is formed only by decomposition of an activated form of reactants A and B, which will be designated $(AB)^*$. Then the reaction occurs by two elementary steps,

1. $A + B \rightleftarrows (AB)^*$

2. $(AB)^* \rightarrow C$

If the first step is comparatively rapid in both forward and reverse directions, $(AB)^*$ will be in equilibrium with A and B so that its concentration is given by

$$[(AB)^*] = K^*[A][B] \tag{2-19}$$

where K^* is the equilibrium constant for the formation of $(AB)^*$. The rate of reaction (rate of formation of C) is then given by the rate of the first-order decomposition step. With Eq. (2-19), this may be expressed as

$$r = k^*[(AB)^*] = k^* K^*[A][B] \tag{2-20}$$

If we integrate the van't Hoff equilibrium equation for K^*,

$$\frac{d(\ln K^*)}{dT} = \frac{\Delta H^*}{R_g T^2} \tag{2-21}$$

we obtain

$$K^* = Ie^{-\Delta H^*/R_g T} \qquad\qquad\qquad (2\text{-}22)$$

where I is the constant of integration. Combining Eqs. (2-20) and (2-22) gives

$$r = k^*\, Ie^{-\Delta H^*/R_g T}\, [A][B] \qquad\qquad (2\text{-}23)$$

Comparison with Eq. (2-6) shows that

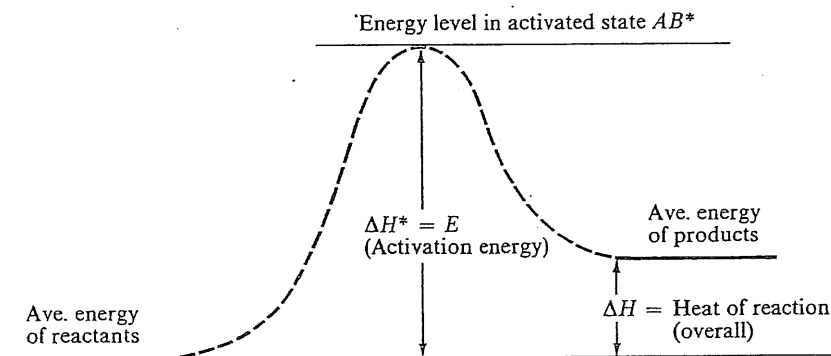$$k = Ae^{-\Delta H^*/R_g T} \qquad\qquad\qquad (2\text{-}24)$$

where $A = k^* I$. Equation (2-24) is also of the form of the Arrhenius equation.

Since ΔH^* is the energy required to form the activated state $(AB)^*$ from A and B, $e^{-\Delta H^*/R_g T}$ is the *Boltzmann expression* for the fraction of molecules having an energy ΔH^* in excess of the average energy. This gives some meaning to the activation energy E in the Arrhenius equation. The diagram in Fig. 2-1 shows that this value is the energy barrier that must be overcome to form $(AB)^*$, and ultimately product C.

The value of Eq. (2-8) rests substantially on the accuracy with which it represents experimental rate-temperature data (see Example 2-1). When measured rates do not agree with the theory it is usually found that the reaction is not an elementary step or that physical resistances are affecting the measurements. In other words, Eq. (2-8) correlates remarkably well the rate measurements for single reactions free of diffusion and thermal resistances. The Arrhenius equation provides no basis for discerning the value of E. However, Fig. 2-1 indicates that the activation energy must be greater than the heat of the overall reaction, ΔH, for an endothermic case.

In view of the success of the Arrhenius equation, there have been many attempts to develop theoretical interpretations for the frequency

Fig. 2-1   Energy levels of initial, activated, and final states

'Energy level in activated state AB^*

$\Delta H^* = E$
(Activation energy)

Ave. energy
of products

Ave. energy
of reactants

$\Delta H = $ Heat of reaction
(overall)

factor A and the activation energy E. The collision theory (see Sec. 2-4), in which the frequency factor is treated as a collision rate, was inspired by the kinetic theory of gases. Subsequently the more sophisticated activated-complex theory was developed to take advantage of the more detailed description of collisions made possible with statistical thermodynamics and quantum chemistry.

Example 2-1 Wynkoop and Wilhelm[1] studied the rate of hydrogenation of ethylene, using a copper–magnesium oxide catalyst, over restricted pressure and composition ranges. Their data may be interpreted with a first-order rate expression of the form

$$r = (k_1)_p \, p_{H_2} \tag{A}$$

where r is the rate of reaction, in g moles/(cm^3)(sec), and p_{H_2} is the partial pressure of hydrogen, in atmospheres. With this rate equation $(k_1)_p$ will be reported in g moles/(cm^3)(sec)(atm). The results for $(k_1)_p$ at various temperatures are given in Table 2-1. (a) What is the activation energy from rate equation (A)? (b) What would it be if the rate equation were expressed in terms of the concentration of hydrogen rather than the partial pressure?

Solution   (a) In the last column of Table 2-1 the reciprocal of the absolute temperature is shown for each run. Figure 2-2 is a plot of $(k_1)_p$ vs $1/T$ on semilogarithmic coordinates. It is apparent that the data describe a straight line, except for runs 8, 20, 21, and 22. It has been suggested that water vapor may have caused the low rates in these cases.[1] The line shown in the figure was located by fitting the data points by the least-mean-squares technique. This requires writing Eq. (2-8) in logarithmic form,

$$\ln (k_1)_p = \ln A - \frac{E_p}{R_g} \frac{1}{T} \tag{B}$$

This is a linear relation between $\ln (k_1)_p$ and $1/T$ with a slope of $-E_p/R_g$. If (T_i, k_i) represents one of n data points, the values of A and E_p/R_g which describe the least-mean-square fit are

$$-\frac{E_p}{R_g} = \frac{n \sum_{i=1}^{n} (\ln k_i)(1/T_i) - \left(\sum_{i=1}^{n} 1/T_i\right) \sum_{i=1}^{n} \ln k_i}{n \sum_{i=1}^{n} (1/T_i)^2 - \left(\sum_{i=1}^{n} 1/T_i\right)^2} \tag{C}$$

$$\ln A = \frac{\sum \ln k_i \sum (1/T_i)^2 - \sum 1/T_i \sum (1/T_i \ln k_i)}{n \sum (1/T_i)^2 - (\sum 1/T_i)^2} \tag{D}$$

Carrying out the summations indicated for all the data points, with the data in Table 2-1 for k_i and T_i, we find

$$-\frac{E_p}{R_g} = -6,460$$

$$E_p = 6,460 R_g = 12,800 \text{ cal/g mole}$$

[1] Raymond Wynkoop and R. H. Wilhelm, *Chem. Eng. Prog.*, **46**, 300 (1950).

Table 2-1   Data for hydrogenation of ethylene

Run	$(k_1)_p \times 10^5$, g moles/(sec)(atm)(cm^3)	T, °C	$1/T \times 10^3$, °K^{-1}
1	2.70	77	2.86
2	2.87	77	2.86
3	1.48	63.5	2.97
4	0.71	53.3	3.06
5	0.66	53.3	3.06
6	2.44	77.6	2.85
7	2.40	77.6	2.85
8	1.26	77.6	2.85
9	0.72	52.9	3.07
10	0.70	52.9	3.07
11	2.40	77.6	2.85
12	1.42	62.7	2.98
13	0.69	53.7	3.06
14	0.68	53.7	3.06
15	3.03	79.5	2.83
16	3.06	79.5	2.83
17	1.31	64.0	2.97
18	1.37	64.0	2.97
19	0.70	54.5	3.05
20	0.146	39.2	3.20
21	0.159	38.3	3.21
22	0.260	49.4	3.10
23	0.322	40.2	3.19
24	0.323	40.2	3.19
25	0.283	40.2	3.19
26	0.284	40.2	3.19
27	0.277	39.7	3.20
28	0.318	40.2	3.19
29	0.323	40.2	3.19
30	0.326	40.2	3.19
31	0.312	39.9	3.19
32	0.314	39.9	3.19
33	0.307	39.8	3.19

A quicker but less accurate method is to draw, visually, a straight line through the data plotted as ln $(k_1)_p$ vs $1/T$, measure its slope, and multiply by R_g to obtain the activation energy.

(b) For gaseous reactions the rate equation can be expressed in terms of concentrations or pressures. Equation (A) is the pressure form for this example. In terms of concentrations, the rate is
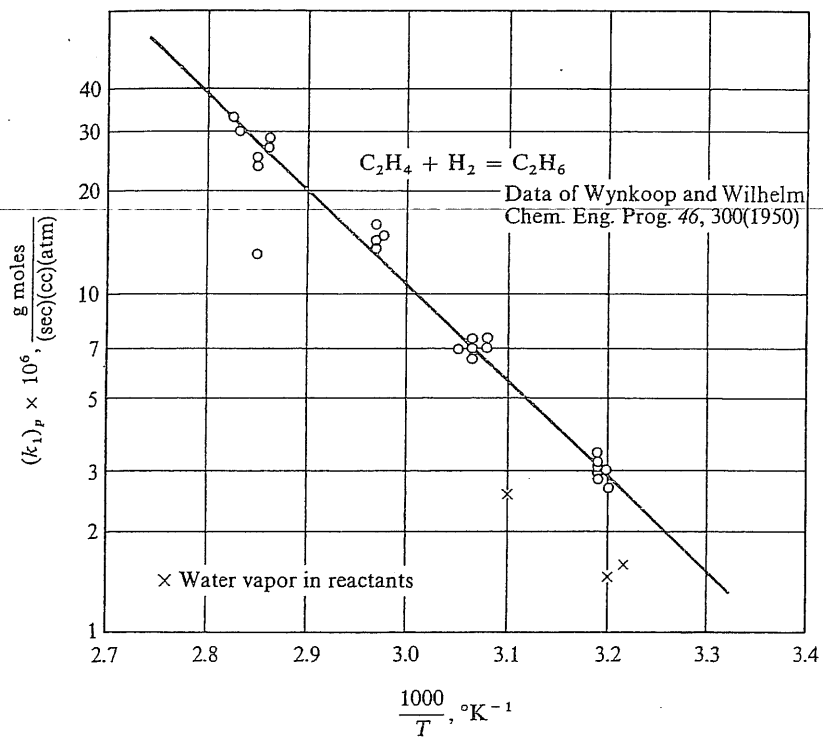
$$r = (k_1)_c \, [H_2]$$

Fig. 2-2   Plot of Arrhenius equation for hydrogenation of ethylene

Expressing $(k_1)_C$ in the Arrhenius form and then differentiating gives

$$(k_1)_C = A_C\, e^{-E_C/R_g T}$$

and

$$\frac{d[\ln (k_1)_C]}{d(1/T)} = -\frac{E_C}{R_g} \qquad\qquad\qquad (E)$$

This may be related to Eq. (A) by noting that for an ideal-gas mixture the concentration of H_2 is

$$[H_2] = \frac{p_{H_2}}{R_g T}$$

Then

$$r = \frac{(k_1)_C}{R_g T}\, p_{H_2} \qquad\qquad\qquad (F)$$

Comparison of Eqs. (A) and (F) gives the relationship between the two rate constants,

$$(k_1)_c = (k_1)_p \, R_g T \tag{G}$$

Differentiating the logarithmic form of Eq. (G) and using Eqs. (B) and (E), we obtain

$$\frac{d[\ln (k_1)_c]}{d(1/T)} = \frac{d[\ln (k_1)_p]}{d(1/T)} + \frac{d(\ln T)}{d(1/T)}$$

$$-\frac{E_c}{R_g} = -\frac{E_p}{R_g} - T$$

or
$$E_c = E_p + R_g T \tag{H}$$

Thus the activation energy, in principle, depends on whether the rate equation is expressed in terms of concentrations or partial pressures. Also, the difference between E_c and E_p depends on the temperature. In practice this difference is not significant. In this example, at a temperature of 77°C,

$$E_c - E_p = 2(350°K) = 700 \text{ cal/g mole}$$

This difference of 6% is too small to be discerned from rate measurements of the usual precision. Hence it generally makes little difference whether E is evaluated from a rate equation expressed in terms of pressures or in terms of concentrations.

RATE THEORIES

2-4 Collision Theory

The Arrhenius concept as pictured in Fig. 2-1 requires that the molecules of reactants have an energy E above their normal, or average, energy. There is a possibility that some molecules will possess this excess because of the wide range over which the energy is distributed and the large number of molecules that make up the system. According to classical kinetic theory, some gaseous molecules will possess much larger amounts of translational energy than others because of variations in their molecular velocities. It is logical to suppose that collisions between these reactant molecules would provide the activation energy necessary for the reaction to occur. By assuming that the molecules behave as hard spheres, it is possible to develop simple expressions for the rate. This approach, originally advanced by Lewis[1] and Polanyi,[2] has become known as the collision theory.

The theory has a number of weaknesses and has been extended and supplemented by later developments. However, it offers a simple picture

[1]W. C. McC. Lewis, J. Chem. Soc. (London), 113, 471 (1918).

[2]M. Polanyi, Z. Elektrochem., 26, 48 (1920).

of the mechanism of reactions. According to the collision theory, the number of molecules of product formed per unit time per unit volume—i.e., the rate—is equal to the number of collisions multiplied by a factor f. This factor takes into account the fact that only a fraction of the collisions involve molecules that possess the excess energy (activation energy) necessary for reaction. For a gaseous reaction, such as $A + B \rightarrow C + D$, this may be stated mathematically as

$$\mathbf{r} = zf \tag{2-25}$$

where z is the number of collisions between molecules A and B in 1 cm^3 of reaction mixture per second. From kinetic theory (with the assumption that molecules are hard spheres), the number of collisions is given by

$$z = [A][B]\sigma_{AB}^2 \left(8\pi R_g T \frac{M_A + M_B}{M_A M_B} \right)^{1/2} \tag{2-26}$$

where the concentration is in molecules (not moles) per cubic centimeter, and

σ_{AB} = effective diameter of A plus B upon collision
M = molecular weight
R_g = gas constant = $k_B N_0$, the product of Boltzmann's constant and Avogadro's number, ergs/(°K)(g mole)

Then the rate equation (2-25) may be written

$$\mathbf{r} = f[A][B]\sigma_{AB}^2 \left(8\pi R_g T \frac{M_A + M_B}{M_A M_B} \right)^{1/2} \tag{2-27}$$

The rate may also be expressed in terms of the specific rate constant,

$$\mathbf{r} = k[A][B] \tag{2-28}$$

Using the Arrhenius equation (2-8) for k, we may write this as

$$\mathbf{r} = Ae^{-E/R_g T}[A][B] \tag{2-29}$$

Combining Eqs. (2-27) and (2-29) gives the following result for the frequency factor A:

$$Ae^{-E/R_g T} = f\sigma_{AB}^2 \left(8\pi R_g T \frac{M_A + M_B}{M_A M_B} \right)^{1/2}$$

The fraction of the molecules that possess the required excess energy for reaction should not depend on the number of collisions but on the magnitude of the energy itself. If a Maxwellian distribution is assumed, the fraction of the total molecules having an energy at least equal to E

can be shown to be e^{-E/R_gT}. Hence f may be taken as e^{-E/R_gT}, and then the frequency factor is given by

$$A = \sigma_{AB}^2 \left(8\pi R_g T \frac{M_A + M_B}{M_A M_B}\right)^{\frac{1}{2}} \tag{2-30}$$

Finally, substitution of this value of frequency factor A in Eq. (2-8) gives the collision-theory expression for the specific reaction rate,

$$k = \sigma_{AB}^2 \left(8\pi R_g T \frac{M_A + M_B}{M_A M_B}\right)^{\frac{1}{2}} e^{-E/R_gT} \qquad \text{cm}^3/(\text{molecule})(\text{sec}) \tag{2-31}$$

The first part of the equation represents the number of collisions per unit time per unit volume (when $[A] = [B] = 1$), and e^{-E/R_gT} represents the fraction of the collisions that involve molecules with the necessary activation energy.

Example 2-2 Use the collision theory to estimate the specific reaction rate for the decomposition of hydrogen iodide, $2HI \rightarrow I_2 + H_2$. Assume that the collision diameter σ is $3.5A$ (3.5×10^{-8} cm), and employ the activation energy of 44,000 cal/g mole determined experimentally by Bodenstein.[1] Also evaluate the frequency factor.

Solution According to the collision theory, the specific reaction rate is given by Eq. (2-31) in units of cm^3/(molecule) (sec). For the reaction $2HI \rightarrow H_2 + I_2$

$$M_A = M_B = M_{HI} = 128$$

The other numerical quantities required are

$$R_g = k_B n = (1.38 \times 10^{-16})(6.02 \times 10^{23})$$

$$= 8.30 \times 10^7 \text{ ergs}/(°K)(\text{g mole}) \qquad \text{or } 1.98 \text{ cal}/(\text{g mole}) (°K)$$

$$\sigma_{AB} = 3.5 \times 10^{-8} \text{ cm}$$

$$E = 44,000 \text{ cal/g mole}$$

$$T = 273 + 321.4 = 594.6°K$$

Substituting these values in Eq. (2-31) yields

$$k = (3.5 \times 10^{-8})^2 \left[8\pi(8.30 \times 10^7) \, 594.6 \left(\frac{2}{128}\right)\right]^{\frac{1}{2}} e^{-44,000/R_gT}$$

$$= 1.70 \times 10^{-10} e^{-37.4} \qquad \text{cm}^3/(\text{molecule})(\text{sec})$$

To convert this result to the usual units of liters/(g mole)(sec) it should be multi-

[1]M. Bodenstein, *Z. Physik Chem.*, **100**, 68 (1922).

plied by Avogadro's number, 6.02×10^{23} molecules/mole, and divided by 1,000 cm^3/liter:

$$k = \frac{6.02 \times 10^{23}}{1,000} \, 1.70 \times 10^{-10} \, e^{-37.4}$$

$$= 1.02 \times 10^{11} \, e^{-37.4} = 5.7 \times 10^{-6} \text{ liter/(g mole)(sec)} \qquad (A)$$

As we shall see in Example 2-6, the rate constant from Kistiakowsky's data is found to be 2.0×10^{-6} liter/(g mole)(sec). For reactions involving more complex molecules the experimental rates are usually much less than the theory predicts.

Comparison of the form of Eq. (A) and the Arrhenius expression shows that the frequency factor is

$$A = 1.0 \times 10^{11} \text{ liters/(g mole)(sec)}$$

2-5 Activated-complex (Transition-state) Theory

The collision theory has been found to give results in good agreement with experimental data for a number of bimolecular gas reactions. The decomposition of hydrogen iodide considered in Example 2-2 is an illustration. The theory has also been satisfactory for several reactions in solution involving simple ions. However, for many other reactions the predicted rates are much too large. Predicted frequency factors lie in the rather narrow range of 10^9 to 10^{11}, while measured values may be several orders of magnitude less. The deviation appears to increase with the complexity of the reactant molecules. (Moreover, unimolecular decompositions are difficult to rationalize by the collision theory.) As a means of correcting for this disagreement it has been customary to introduce a probability, or steric, factor (having a value less than unity) in Eq. (2-31). To retain the hard-sphere concept we must then explain why all the collisions supplying the necessary energy do not result in reaction.[1]

Beginning in about 1930 the principles of quantum mechanics were applied to this problem by Eyring, Polanyi, and their coworkers, and the result is known as the activated-complex theory.[2] In this theory reaction is still presumed to occur as a result of collisions between reacting molecules, but what happens after collision is examined in more detail. This examination is based on the concept that molecules possess vibrational and rotational, as well as translational, energy levels.

[1] For a more detailed and complete description of the collision theory and its limitations see E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, New York, 1946.

[2] Samuel Glasstone, K. J. Laidler, and Henry Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, New York, 1941.

The essential postulate is that an activated complex (or transition state) is formed from the reactant, and that this subsequently decomposes to the products. The activated complex is assumed to be in thermodynamic equilibrium with the reactants. Then the rate-controlling step is the decomposition of the activated complex. The concept of an equilibrium activation step followed by slow decomposition is equivalent to assuming a time lag between activation and decomposition into the reaction products. It is the answer proposed by the theory to the question of why all collisions are not effective in producing a reaction.

These ideas may be illustrated by a simple reaction between A and B to form a product C. If the activated complex is designated by $(AB)^*$, the overall process can be written as

$$A + B \rightleftharpoons (AB)^* \rightarrow C$$
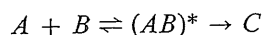
Since equilibrium is assumed for the first step, the concentration of $(AB)^*$ is that determined by the equilibrium constant. Then the rate of the overall reaction is equal to the product of the frequency of decomposition of the complex and its equilibrium concentration, or

$$r = v[(AB)^*] \qquad \text{molecules/(sec)(cm}^3) \tag{2-32}$$

where v is in units per second and the concentration $[(AB)^*]$ is in molecules per cubic centimeter. If the equilibrium constant for the formation of AB is K^*, then in terms of activity a,

$$K^* = \frac{a_{(AB)^*}}{a_A a_B} = \frac{\gamma_{AB}[(AB)^*]}{(\gamma_A[A])(\gamma_B[B])} \tag{2-33}$$

where γ is the activity coefficient. The concentration of the activated complex can be substituted in Eq. (2-32) to give

$$r = v \frac{\gamma_A \gamma_B}{\gamma_{AB}} K^*[A][B] \tag{2-34}$$

The equilibrium constant is related to the standard free-energy change for the formation of the activated complex. From Eq. (1-4), this relationship is

$$K^* = e^{-\Delta F^*/R_g T} \tag{2-35}$$

It can be shown[1] that the decomposition frequency is

$$v = \frac{k_B T}{h} \tag{2-36}$$

[1] Samuel Glasstone, K. J. Laidler, and Henry Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, New York, 1941.

where k_B = Boltzmann's constant, 1.380×10^{-16} erg/°K, and h = Planck's constant, 6.624×10^{-27} ergs(sec).

Substituting Eqs. (2-35) and (2-36) in Eq. (2-34) gives

$$\mathbf{r} = \frac{k_B T}{h} \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}} \right) e^{-\Delta F^*/R_g T} [A][B] \tag{2-37}$$

Hence the specific reaction rate is

$$k = \frac{k_B T}{h} \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}} \right) e^{-\Delta F^*/R_g T} = \frac{k_B T}{h} \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}} \right) e^{\Delta S^*/R_g - \Delta H^*/R_g T} \tag{2-38}$$

The latter form follows from the thermodynamic relation $\Delta F = \Delta H - T \Delta S$.

Comparison of Eq. (2-38) with the Arrhenius equation shows that

$$A = \frac{k_B T}{h} \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}} \right) e^{\Delta S^*/R_g} \tag{2-39}$$

$$E = \Delta H^* \tag{2-40}$$

These two relations are the predictions of the activated-complex theory for the frequency factor and the energy of activation.

The collision theory [Eq. (2-31)] does not offer a method for calculating the activation energy. The activated-complex theory suggests that E is the enthalpy change for formation of the activated complex from the reactants [Eq. (2-40)]. To predict this enthalpy we must know exactly what the activated complex is; i.e., we must know its structure. Even then the prediction of enthalpy from molecular-structure data by statistical mechanics is an uncertain operation for any but the simplest molecule. Eckert and Boudart[1] have illustrated the calculation procedures with the hydrogen iodide decomposition reaction. If an activation energy is available from experimental measurements, the theory need be used only for estimating the frequency factor from Eq. (2-39). Again the structure of the activated complex is necessary, this time to calculate the entropy of activation, ΔS^*.

Uncertainties about the structure of the activated complex and the assumptions involved in computing its thermodynamic properties seriously limit the practical value of the theory. However, it does provide qualitative interpretation of how molecules react and a reassuring foundation for the empirical rate expressions inferred from experimental data. The effect of temperature on the frequency factor is extremely difficult to evaluate from rate measurements. This is because the strong exponential function in the Arrhenius equation effectively masks the temperature dependency of A.

[1] C. A. Eckert and M. Boudart, *Chem. Eng. Sci.*, **18**, 144 (1963).

Equation (2-39) suggests that A is proportional to T, the collision theory indicates a $T^{1/2}$ dependency [Eq. (2-30)], and the Arrhenius relationship [Eq. (2-8)] implies that A is unaffected by temperature. It is normally impossible to measure rates of reaction with sufficient sensitivity to evaluate these differences.

In Eq. (2-32) it is supposed that the rate is proportional to the *concentration* of the activated complex. Similarly, in the collision theory, Eq. (2-25), it is tacitly assumed that the concentration determines the collision frequency and the rate. However, if the results of thermodynamics were followed, the rate might be assumed proportional to activity. If the activity replaced concentration in Eq. (2-32), the activity coefficient of the activated complex would not be needed in Eq. (2-34). The final expression for the rate constant would then be

$$k = \frac{k_B T}{h} \gamma_A \gamma_B \, e^{\Delta S^*/R_g - \Delta H^*/R_g T} \qquad (2\text{-}41)$$

instead of Eq. (2-38). Since the activity coefficient is a function of pressure, k values predicted from the two equations would vary differently with pressure.

Eckert and Boudart analyzed rate data for the decomposition of HI in this way. Their results were more compatible with Eq. (2-38), suggesting that the rate is proportional to the *concentration* of the activated complex. In this text the rate equation will be written in terms of concentrations.

2-6 Unimolecular Reactions

The activated-complex theory provides a plausible explanation of the first-order rate of unimolecular gaseous reactions. In such a reaction the reacting molecules gain the energy of activation by collision with other molecules. This might be thought of as a second-order process, since the number of collisions is proportional to the square of the concentration. However, Lindemann[1] showed in 1922 that activation by collision could result in first-order rates. If A^* is an activated molecule of reactant, the equilibrium between A and A^* and reaction to products B can be represented as

$$A + A \underset{}{\overset{K_1}{\rightleftharpoons}} A^* + A \qquad (2\text{-}42)$$

$$A^* \overset{k_2}{\rightarrow} B \qquad (2\text{-}43)$$
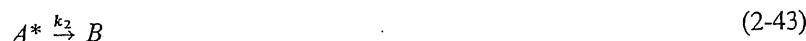
If the pressure (e.g., concentration) in the reaction mixture is high enough,

[1] F. A. Lindemann, *Trans. Faraday Soc.*, 17, 598 (1922).

the number of collisions between A and A^* will be so large that equilibrium exists between A and A^*, according to Eq. (2-42). If the equilibrium constant is K_1, the concentration of A^* is given by

$$K_1 = \frac{[A^*][A]}{[A]^2}$$

$$[A^*] = K_1[A] \qquad (2\text{-}44)$$

The rate of formation of products is determined by the second reaction, the decomposition of activated molecules. No collisions are needed for reaction, so the rate is first order in A^*, that is,

$$r = k_2[A^*] \qquad (2\text{-}45)$$

Substituting $[A^*]$ from Eq. (2-44), the rate is seen to be first order in A,

$$r = k_2 K_1[A] \qquad (2\text{-}46)$$

At low pressures the collision rate is low and equilibrium is not attained between A and A^*, so that Eq. (2-42) should be written

$$A + A \xrightarrow{k_1} A^* + A \qquad (2\text{-}47)$$

If the A^* has a short lifetime, its concentration will be low with respect to that of A or products. Then $[A^*]$ will rapidly reach a constant, low value after which $d[A^*]/dt = 0$.[1] Summing the rates of formation and destruction of A^* by reactions (2-47) and (2-43) yields

$$\frac{d[A^*]}{dt} = 0 = k_1[A]^2 - k_2[A^*]$$

or

$$[A^*] = \frac{k_1}{k_2}[A]^2 \qquad (2\text{-}48)$$

Substituting this result into Eq. (2-45) gives a second-order rate

$$r = k_1[A]^2 \qquad (2\text{-}49)$$

This changeover from first-order to second-order kinetics at low pressures has been observed experimentally for a number of unimolecular reactions.

[1] This statement is termed the stationary-state hypothesis—a concept widely used for reactions involving species of a transitory nature, such as free radicals and atoms. See Sec. 2-11 for a discussion of its use in photochemical kinetics. It is equally applicable here to the high-pressure case and also leads to Eq. (2-46), but by a more complicated route.
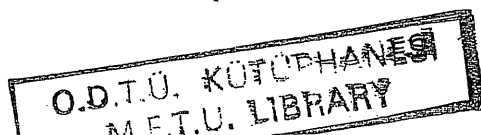
ANALYSIS OF RATE EQUATIONS

The most common experimental procedure for establishing rate equations is to measure the composition of the reaction mixture at various stages during the course of reaction.[1] In a batch system this means analysis at various times after the reaction begins.[2] Then the data are compared with various types of rate equations to find the one giving the best agreement. The comparison can be made in two ways:

1. The *integration* method, comparison of predicted and observed compositions. For this approach it is necessary to integrate the rate expression [for example, Eq. (2-6)] to give concentration as a function of time.
2. The *differential* method, comparison of predicted and observed rates. The latter are obtained by differentiating the experimental data.

In this chapter we are concerned only with the rate equation for the chemical step (no physical resistances). Also, it will be supposed that the temperature is constant, both during the course of the reaction and in all parts of the reactor volume. These ideal conditions are often met in the stirred-tank reactor (see Sec. 1-6). Data are invariably obtained with this objective, because it is extremely hazardous to try to establish a rate equation from nonisothermal data or data obtained in inadequately mixed systems. Under these restrictions the integration and differential methods can be used with Eqs. (2-1) and (2-5) or, if the density is constant, with Eq. (2-6). Even with these restrictions, evaluating a rate equation from data may be an involved problem. Reactions may be simple or complex, or reversible or irreversible, or the density may change even at constant temperature (for example, if there is a change in number of moles in a gaseous reaction). These several types of reactions are analyzed in Secs. 2-7 to 2-11 under the categories of simple and complex systems.

2-7 Integrated Rate Equations for Irreversible Reactions

If all the reactants and products can be explained by a single reaction, the reaction system is *simple*. Within this category the reaction may be of any order and may be reversible or irreversible.

[1] Many other methods are used for studying kinetics, particularly for fast reactions. For a description of various methods see F. J. W. Roughton and B. Chance, in S. L. Friess and A. Weissberger (eds.), "Rates and Mechanisms of Reactions," chap. 10, Interscience Publishers, New York, 1953.

[2] In continuous reactors the course of the reaction is measured at different flow rates, or reactor volumes. The analysis is different from that for batch reactors and involves Eq. (2-2). Analysis of such systems is discussed in Chaps. 4 and 8.

Zero Order   Zero order, meaning that the rate is independent of the concentration, may occur in two situations: when the rate is intrinsically independent of concentration and when the species is in such abundant supply that its concentration is nearly constant during reaction. In the latter case the dependency of the rate on concentration cannot be detected, and apparent zero order prevails. Thus in the oxidation of NO to NO_2 in the presence of a large excess of O_2, the rate is zero order in O_2.

For a zero-order reaction at constant density Eq. (2-6) becomes

$$-\frac{d[A]}{dt} = k_0 \qquad\qquad (2\text{-}50)$$

Integrating from an initial condition of $[A] = [A]_0$ yields

$$[A] = [A]_0 - k_0 t \qquad\qquad (2\text{-}51)$$

This result shows that the distinguishing feature of a zero-order reaction is that the concentration of reactant decreases linearly with time. It is difficult to cite a homogeneous reaction that is intrinsically zero order, although many reactions have apparent zero-order characteristics when the concentration of the species is large. However, in some heterogeneous reactions where the solid phase acts as a catalyst the rate is zero order. An example is the decomposition of NH_3 on platinum and tungsten surfaces.[1]

Equation (2-51) can be used with measurements of concentration vs time to determine if a reaction is zero order and to evaluate k. If two reactants, A and B, are involved, experiments can be carried out with A in large excess, so that the rate equation is independent of $[A]$. Then the concentration of B can be varied and its order determined. In this way the concentration of one reactant can be rendered ineffective in order to study the effect of another.

It may be simpler to measure the time when a certain fraction of reactant has disappeared than to obtain concentration-vs-time data. Common practice is to obtain the time required for one-half of the reactant to disappear. Defining this half-life as $t_{1/2}$, we have from Eq. (2-51)

$$\tfrac{1}{2}[A]_0 = [A]_0 - k_0 t_{1/2}$$

or

$$t_{1/2} = \frac{[A]_0}{2k_0} \qquad\qquad (2\text{-}52)$$

Half-life data can be used with Eq. (2-52) to evaluate k_0 as an alternate to Eq. (2-51).

[1]C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, 127, 1051, 1114 (1925).

First Order   Equation (2-6) for a first-order rate is

$$-\frac{d[A]}{dt} = k_1[A]$$ (2-53)

If the initial condition is $[A] = [A]_0$, integration yields

$$\ln\frac{[A]}{[A]_0} = -k_1 t$$ (2-54)

A plot of $\ln [A]/[A]_0$ vs t should be a straight line of slope equal to $-k_1$.
The half-life is given by

$$-k_1 t_{1/2} = \ln \tfrac{1}{2}$$ (2-55)

or

$$t_{1/2} = \frac{1}{k_1}\ln 2$$ (2-56)

Equations (2-54) and (2-56) show that the half-life and fraction of reactant
remaining are independent of initial concentration for a first-order reaction.

Among the numerous examples of homogeneous first-order reactions
are the rearrangement of cyclopropane to propylene,[1] certain cis-trans-
isomerizations, and the inversion of sucrose.

Second Order   Two types of second-order reactions are of interest:

TYPE I $A + A \to P$

$$-\frac{d[A]}{dt} = k_2[A]^2$$ (2-57)

TYPE II $A + B \to P$

$$-\frac{d[A]}{dt} = k_2[A][B]$$ (2-58)

For type I reactions integration of Eq. (2-57) yields

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k_2 t$$ (2-59)

In terms of the half-life, this becomes

$$t_{1/2} = \frac{1}{k_2[A]_0}$$ (2-60)

Note that for a zero-order reaction $t_{1/2}$ is directly proportional to $[A]_0$; for

[1]T. S. Chambers and G. B. Kistiokowsky, *J. Am. Chem. Soc.*, 56, 399 (1934).

a first-order reaction it is independent of $[A]_0$, and for a second-order reaction inversely proportional to $[A]_0$. Two well-known examples of type I reactions are the decomposition of HI in the gas phase and dimerization of cyclopentadiene in either gas or liquid phase.

When order and stoichiometry of type II reactions do not agree, the analysis is somewhat different. Suppose the stoichiometry may be represented as

$$aA + bB \to P$$
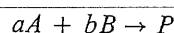
and the rate expression is Eq. (2-58). Initially $[A] = [A]_0$ and $[B] = [B]_0$; let $[X]$ be the amount of A that has reacted, expressed as a concentration. Then at any time

$$[A] = [A]_0 - [X] \tag{2-61}$$

$$[B] = [B]_0 - \frac{b}{a}[X] \tag{2-62}$$

$$-\frac{d[A]}{dt} = \frac{d[X]}{dt} \tag{2-63}$$

Substituting Eqs. (2-61) to (2-63) in (2-58) gives

$$-\frac{d[A]}{dt} = \frac{d[X]}{dt} = k_2([A]_0 - [X])\left([B]_0 - \frac{b}{a}[X]\right) \tag{2-64}$$

Integration from $t = 0$ gives the concentration of X, or A and B, at any time:

$$\ln\frac{[A]_0 - [X]}{[B]_0 - (b/a)[X]} = \ln\frac{[A]}{[B]} = \frac{b[A_0] - a[B_0]}{a}k_2 t + \ln\frac{[A]_0}{[B]_0} \tag{2-65}$$

In terms of A, $t_{1/2}$ corresponds to $[A]/[A]_0 = \frac{1}{2}$, and Eq. (2-65) can be solved to yield

$$t_{1/2} = \frac{a}{k_2(b[A]_0 - a[B]_0)} \ln \frac{a[B]_0}{2a[B]_0 - b[A]_0}. \tag{2-66}$$

If initial concentrations are stoichiometric, then

$$[B]_0 = \frac{b}{a}[A]_0$$

and Eq. (2-64) becomes

$$-\frac{d[A]}{dt} = k_2 \frac{b}{a}([A]_0 - [X])^2 = k_2 \frac{b}{a}[A]^2 \tag{2-67}$$

This is the same as Eq. (2-57), with k_2 multiplied by b/a. Numerous reactions of type II have been observed: for example, HI formation from gaseous H_2 and I_2,[1] dimerization of cyclopentadiene in benzene solution, and certain esterification reactions in aqueous solution.

Concentration-time data can easily be analyzed to test second-order kinetics. For type I (or type II with stoichiometric proportions of A and B initially), Eq. (2-59) indicates that the data should give a straight line if $1/[A]$ is plotted against t. For type II, Eq. (2-65) shows that a plot of log $[A]/[B]$ vs t should be linear. In this case the slope $(b[A]_0 - a[B]_0)k_2/a$ will be positive or negative, depending on the stoichiometric coefficients a and b and the initial concentrations.

In the following example first- and second-order rate equations are used to interpret data for an isothermal, constant-density, liquid system.

Example 2-3 The liquid-phase reaction between trimethylamine and n-propyl bromide was studied by Winkler and Hinshelwood[2] by immersing sealed glass tubes containing the reactants in a constant-temperature bath. The results at 139.4°C are shown in Table 2-2. Initial solutions of trimethylamine and n-propyl bromide in benzene, 0.2-molal, are mixed, sealed in glass tubes, and placed in the constant-temperature bath. After various time intervals the tubes are removed and cooled to stop the reaction, and the contents are analyzed. The analysis depends on the fact that the product, a quaternary ammonium salt, is completely ionized. Hence the concentration of bromide ions can be estimated by titration.

Table 2-2

Run	t, min	Conversion, %
1	13	11.2
2	34	25.7
3	59	36.7
4	120	55.2

From this information determine the first-order and second-order specific rates, k_1 and k_2, assuming that the reaction is irreversible over the conversion range covered by the data. Use both the integration and the differential method, and compare the results. Which rate equation best fits the experimental data?

Solution The reaction may be written

$$N(CH_3)_3 + CH_3CH_2CH_2Br \rightarrow (CH_3)_3(CH_2CH_2CH_3)N^+ + Br^-$$
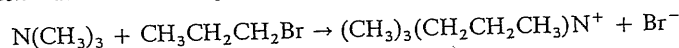
[1] M. Bodenstein, *Z. Physik Chem.*, 13, 56 (1894); *Z. Physik Chem.*, 22, 1 (1897); *Z. Physik Chem.*, 29, 295 (1899).
[2] C. A. Winkler and C. N. Hinshelwood, *J. Chem. Soc.*, 1147 (1935).

Since the concentrations of reactants and products are small and the temperature is constant, the density may be assumed constant without serious error. Then the rate equations (2-53) and (2-58) are applicable for the first- and second-order possibilities. If T denotes trimethylamine and P n-propyl bromide, the rate expressions are

$$r = -\frac{d[T]}{dt} = k_1[T] \tag{A}$$

$$r = -\frac{d[T]}{dt} = k_2[T][P] \tag{B}$$

INTEGRATION METHOD For the first-order case, the integrated form of Eq. (A) is Eq. (2-54); that is,

$$\ln \frac{[T]_0}{[T]} = k_1 t \tag{C}$$

In the second-order case it is noted that $a = b$ and $[T]_0 = [P]_0 = 0.1$ molal. Hence $[T] = [P]$, and Eq. (B) reduces to a type I second-order equation,

$$-\frac{d[T]}{dt} = k_2[T]^2 \tag{D}$$

The solution is Eq. (2-59), which may be solved for k_2 to give

$$k_2 = \frac{1}{t}\left(\frac{1}{[T]} - \frac{1}{[T]_0}\right) \tag{E}$$

The conversion x is the fraction of the reactant that has been consumed. In this problem

$$x = \frac{[T]_0 - [T]}{[T]_0}$$

or

$$[T] = [T]_0 (1 - x) \tag{F}$$

The calculation of k_1 and k_2 will be illustrated for the first run. From Eq. (F),

$$[T] = [T]_0 (1 - 0.112) = 0.1(0.888)$$

Substituting in Eq. (C), we find

$$k_1 = \frac{1}{t} \ln \frac{[T]_0}{[T]} = \frac{1}{13(60)} \ln \frac{0.1}{0.0888} = 1.54 \times 10^{-4} \text{ sec}^{-1}$$

Then, using Eq. (E) for the second-order possibility, we obtain

$$k_2 = \frac{1}{t[T]_0}\left(\frac{1}{1 - x} - 1\right) = \frac{0.112}{60(13)(0.1)(1 - 0.112)}$$

$$= 1.63 \times 10^{-3} \text{ liters/(g mole)(sec)}$$

Table 2-3 shows the results obtained in a similar way for the four runs. The k_1 values show a definite trend with time, and therefore the first-order mechanism does not

Table 2-3 Specific reaction rates for trimethylamine and n-propyl bromide reaction

Run	t, sec	$k_1 \times 10^4$, sec^{-1}	$k_2 \times 10^3$, liters/(g mole)(sec)	$[B]$, g mole/liter
1	780	1.54	1.63	0.0112
2	2,040	1.46	1.70	0.0257
3	3,540	1.30	1.64	0.0367
4	7,200	1.12	1.71	0.0552
			(1.67 av)	

satisfactorily explain the kinetic data. The k_2 values not only are more nearly identical, but the variations show no definite trend.

DIFFERENTIAL METHOD   The moles of bromide ions B produced are equal to the tri-methylamine reacted. Hence

$$[B] = [T]_0 - [T]$$

and from Eq. (F)

$$[B] = [T]_0 - [T]_0 (1 - x) = x[T]_0$$

Thus $[B]$ can be calculated from the conversion data. A plot of $[B]$ vs time of reaction is shown in Fig. 2-3. The slope of this curve at any point is equal to the rate of reaction, since

$$r = -\frac{d[T]}{dt} = \frac{d[B]}{dt}$$

Slopes determined from the curve are given in Table 2-4.

Fig. 2-3 Concentration vs time for reaction between $(CH_3)_3N$ *and* $CH_3CH_2 CH_2Br$
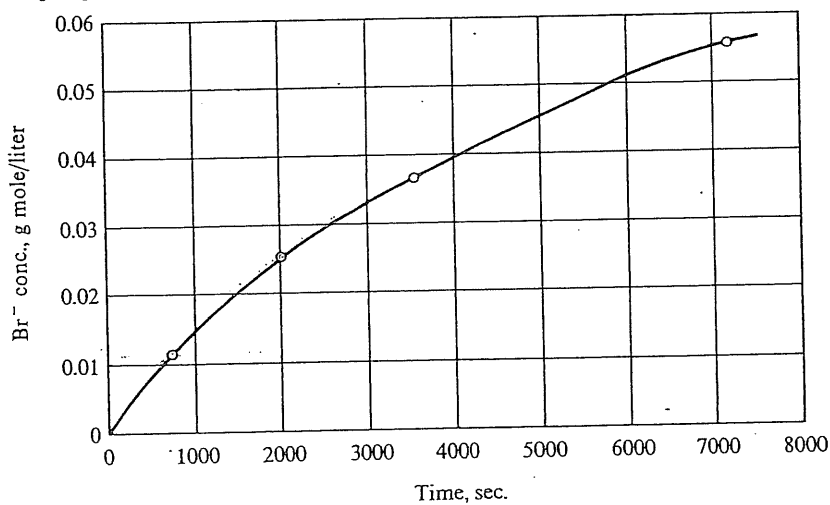
Table 2-4

Concentration, g mole/liter		$r = -d[T]/dt,$
[B]	[T]	g mole/(liter)(sec)
0.0	0.10	1.58×10^{-5}
0.01	0.09	1.38×10^{-5}
0.02	0.08	1.14×10^{-5}
0.03	0.07	0.79×10^{-5}
0.04	0.06	0.64×10^{-5}
0.05	0.05	0.45×10^{-5}

If the reaction is first order, the rate is given by Eq. (A), which may be written

$$\log r = \log k_1 + \log [T] \tag{G}$$

Similarly, if the reaction is second order, from Eq. (D) we have

$$\log r = \log k_2 + \log [T]^2 = \log k_2 + 2 \log [T] \tag{H}$$

For the first-order case log r plotted against log [T] should yield a straight line with a slope of 1.0. For the second-order case the result should be a straight line of slope of 2.0, in accordance with Eq. (H). A plot of the data in Table 2-4 is shown in Fig. 2-4. While there is some scattering, the points do suggest a straight line of a slope approximately equal to 2.0. For comparison purposes lines with slopes of both 2.0 and 1.0 have been included on the plot. The equation of the solid line (slope 2.0) is

$$\log r = -2.76 + 2.0 \log [T]$$

*Fig. 2-4 Rate vs concentration of trimethylamine*
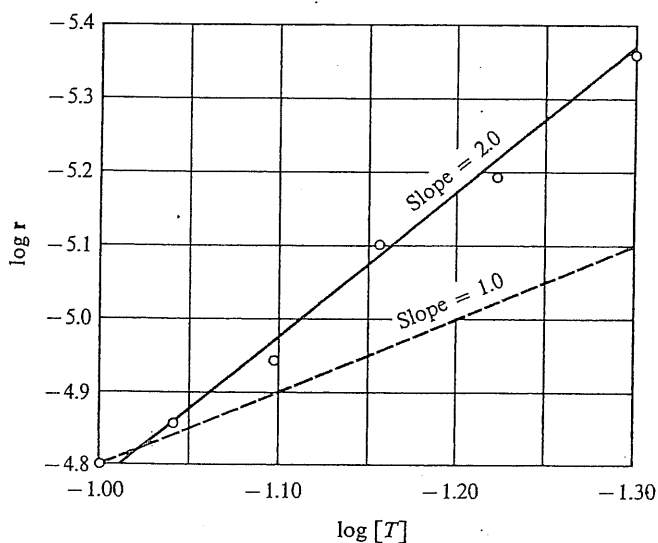
By comparison with Eq. (H),

$$\log k_2 = -2.76$$

$$k_2 = 1.73 \times 10^{-3} \text{ liter/(g mole)(sec)}$$

This value agrees well with the average result 1.67×10^{-3} obtained by the integration method.

Both methods show that the second-order mechanism is preferable. However, the failure of the first-order assumption is perhaps more clearly shown by the differential method than the integration approach. The data in Fig. 2-4 do not approach a slope of 1.0 at all closely, but the k_1 values in Table 2-3 are of the same magnitude, differing from an average value by not more than 17%. This is because the integration process tends to mask small variations.

Third-order reactions are uncommon. Fractional orders exist when the reaction represents a sequence of several elementary steps. Procedures for establishing the order and rate constants for these cases are similar to those given above. Experimental data that suggest fractional-order rate equations should be examined carefully for effects of physical resistances. Sometimes these effects, rather than a sequence of elementary processes, can be responsible for the fractional order. An example is the study of the hydrochlorination of lauryl alcohol with zinc chloride as a homogeneous catalyst:[1]

$$CH_3(CH_2)_{10}\, CH_2OH(l) + HCl(g) \rightarrow CH_3(CH_2)_{10}\, CH_2Cl(l)$$

$$+ H_2O(l)$$
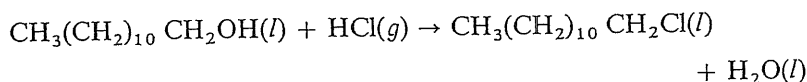
The reaction was carried out by dissolving gaseous HCl in a stirred vessel containing the alcohol. The resulting concentration-time data could be correlated with a rate equation half-order in alcohol concentration. However, the rate constant was found to vary with the gas (HCl) flow rate into the reactor, suggesting that the observed rate was influenced by the resistance to diffusion of dissolved HCl in the liquid phase. A method of analysis which took into account the diffusion resistance indicated that the chemical step was probably first order in dissolved HCl and zero order with respect to lauryl alcohol.

2-8 Reversible Reactions

For an *elementary* process the ratio[2] of the forward- and reverse-rate constants is equal to the equilibrium constant, Eq. (2-13). Hence the net rate of reaction can be expressed in terms of one k and the equilibrium constant. Then the integrated form of this rate expression can be used with

[1] H. A. Kingsley and H. Bliss, *Ind. Eng. Chem.*, 44, 2479 (1952).
[2] See Sec. 2-12 for a discussion of this ratio for nonelementary reactions.

concentration-time data to evaluate k, just as for irreversible reactions. However, the evaluation procedure is more complex.

First Order If k_1 and k'_1 are the forward- and reverse-rate constants for the elementary process

$A \rightleftharpoons B$

then

$$-\frac{d[A]}{dt} = k_1[A] - k'_1[B] \tag{2-68}$$

The concentration of B can be expressed in terms of $[A]$ by a simple mass balance. At constant density, and since the number of moles is constant, the concentration of B is its initial concentration $[B]_0$ plus the concentration of A that has reacted; that is,

$$[B] = [B]_0 + ([A]_0 - [A]) \tag{2-69}$$

Combining this result with Eq. (2-68) gives

$$-\frac{d[A]}{dt} = (k_1 + k'_1)[A] - k'_1([A]_0 + [B]_0) \tag{2-70}$$

At equilibrium the forward and reverse reaction rates are equal, and Eq. (2-68) becomes

$$k_1[A]_{eq} = k'_1[B]_{eq}$$

or

$$\frac{[B]_{eq}}{[A]_{eq}} = K = \frac{k_1}{k'_1} \tag{2-71}$$

where K is the equilibrium constant. Eliminating k'_1 from Eq. (2-70) by using Eq. (2-71) yields

$$-\frac{d[A]}{dt} = k_1 \left\{ \frac{K+1}{K}[A] - \frac{1}{K}([A]_0 + [B]_0) \right\} \tag{2-72}$$

Now, applying Eq. (2-69) at equilibrium conditions to find $[B]_{eq}$ and substituting this result in Eq. (2-71), we have

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{[B]_0 + [A]_0 - [A]_{eq}}{[A]_{eq}}$$

or

$$[A]_{eq}(K+1) = [B]_0 + [A]_0 \tag{2-73}$$