CHAPTER 8

CHEMICAL KINETICS

27. Hydrolysis of Methyl Acetate

The rate of a chemical reaction is measured and treated mathematically. The specific reaction-rate constants are calculated at two different temperatures, and from these the energy of activation is determined.

Theory. In predicting the behavior of physical-chemical systems, it is necessary to know the equilibrium conditions, but it is frequently necessary to know also the speed with which the equilibrium is attained. In most of the reactions of inorganic chemistry, equilibrium is attained in so short a period of time that the reaction appears to be instantaneous, but in many of the reactions of organic chemistry, the time variable is extremely important. Often it is more important than the equilibrium relationships.

A first-order reaction is one in which the rate of reaction is found by experiment to be directly proportional to the concentration of the reacting substance. Many reactions follow the first-order equation

$$-\frac{dc}{dt} = kc \tag{1}$$

which expresses mathematically the fact that the rate of decrease of concentration c with time t is proportional to the concentration. Integrating this equation,

$$-2.303 \log c = kt + \text{constant} \tag{2}$$

Integrating between limits c_1 at t_1 and c_2 at a later time t_2,

$$k = \frac{2.303}{t_2 - t_1} \log \frac{c_1}{c_2} \tag{3}$$

Also

$$k = \frac{2.303}{t} \log \frac{c_0}{c} \tag{4}$$

where c_0 = concentration at beginning of experiment
c = concentration after time t

The constant k is called the reaction-velocity constant or, better, the specific reaction rate. It is a number that expresses the fraction of the material that reacts in a unit of time. It may be expressed in reciprocal seconds or minutes.

Many reactions follow the first-order equation, when in reality there are two molecules involved in the reaction. If in a bimolecular reaction one reacting material is greatly in excess, its concentration does not appear to change; then the first-order equation applies. Sometimes a trace of catalyst is present, and its concentration does not change, although it takes part in the reaction.

Frequently there are complications of two or more reactions going on simultaneously. In some cases, near the end of the reaction, the reverse reaction must be considered.

The course of a reaction must be followed in such a way that the concentrations of the reacting materials are not disturbed. The best way is to determine the concentration of reacting material by measuring some physical property, such as volume, electrical conductance, optical rotation, or the quantity of gas evolved. If it is necessary to resort to chemical analyses, samples are drawn off and titrated. The reaction taking place in the sample may be stopped, if necessary, by cooling or by the addition of a suitable reagent.

Methyl acetate hydrolyzes in water to give methanol and acetic acid, according to the reaction

$$CH_3COOCH_3 + H_2O + H^+ \rightarrow CH_3COOH + CH_3OH + H^+$$

The reaction is catalyzed by hydrogen ions and, in fact, it does not proceed with measurable velocity in pure, neutral water. Although two molecules are involved in this reaction, the water is in such large excess that only the methyl acetate appears to change in concentration. The large excess of water prevents the reverse reaction.

A determination of the specific rate constant at two or more temperatures permits a determination of the activation energy ΔH_a defined by Eq. (5) where T refers to absolute temperature:

$$\frac{d \ln k}{dT} = \frac{\Delta H_a}{RT^2} \tag{5}$$

or in integrated form by Eq. (6):

$$\log \frac{k_2}{k_1} = \frac{\Delta H_a(T_2 - T_1)}{2.303RT_2T_1} \tag{6}$$

The energy of activation, ΔH_a, usually expressed in calories per mole, is the amount of energy the molecules must have in order to be able to react.

Apparatus. Thermostats at 35 and 25°; four 150-ml Erlenmeyer flasks; 5-ml pipette; watch or electric clock; methyl acetate; 2 liters 0.2N sodium hydroxide; 500 ml 2N hydrochloric acid; 1 liter distilled water.

Procedure. The concentration of methyl acetate at any time is determined by titration of samples with 0.2N sodium hydroxide.

The success of the experiment depends chiefly on the care used in pipetting and titrating.

The sodium hydroxide solution used is prepared from saturated sodium hydroxide to reduce the amount of carbonate present, because carbonates cause a fading end point with phenolphthalein. It is not necessary, however, to use carbon dioxide-free distilled water because the amount of carbonate introduced in this way is negligible.

One hundred milliliters of 1N hydrochloric acid is placed in a 150-ml flask clamped in a thermostat at 35°. Another solution is placed in a second flask for a check determination. Some methyl acetate in a test tube is also set into the thermostat. After allowing 10 to 15 min for the solutions to come to the temperature of the thermostat, exactly 5 ml of the methyl acetate is pipetted into one of the flasks. It is shaken to mix thoroughly, and a sample of exactly 5 ml is withdrawn immediately and run into 50 ml of water. The dilution with water arrests the reaction somewhat, but the solution should be titrated at once. The error can be further minimized by chilling the water in an ice bath. The time at which the pipette has been half emptied into the water of the titration flask is recorded accurately together with the titration.

Two more samples are titrated in a similar manner after 5-min intervals; two additional samples are taken at 10-min intervals; and then a few at 20-min intervals. About half an hour after starting the first reaction, the check determination is started, and the two are carried along together. The remaining solutions (at least 25 ml in volume) are stoppered and allowed to stand in the desk for a couple of days in order to permit a final titration when the reaction mixture has reached equilibrium.

Additional determinations are carried out at 25° in the manner just described for 35°. The reaction goes less than half as fast, and samples are taken at 15-min intervals for an hour and then at 30-min intervals for 2 or 3 hr more. The second determination may be started shortly after the first one, as titrations are not required so frequently. Again, a sample of the remaining solutions is retained for a final titration after standing at least 2 days.

Calculations. The difference between the titration at any time t and the titration at the end of 2 days, when the reaction is completed, is a measure of the concentration of methyl acetate remaining unhydrolyzed at time t. Each molecule of methyl acetate that hydrolyzes produces one molecule of acetic acid, and the increase in acidity is a direct measure of the amount of methyl acetate that has reacted. The amount of hydrochloric acid remains unchanged throughout the experiment.

The concentrations of methyl acetate calculated from the differences between the titration values and the final titration are arranged in tabular form. They are plotted against time, and as time is the independent variable, it is plotted along the X-axis. One set of determinations is represented by circles and the other by crosses. A smooth curve is drawn through the points.

A second graph is drawn, in which $\log c$ is plotted against time for both determinations, and the best straight line is drawn through these points. Two lines are graphed, one for 25° and one for 35°. The specific reaction rates k are calculated from the slopes of the lines, using Eq. (2).

A table is prepared; the values of k over the different time intervals are calculated by Eq. (3). These are compared in a general way with the values of k determined graphically, but it is not significant[6] to average the constants obtained by Eq. (3). It is noted that in the case of a first-order reaction the specific reaction rate may be determined without information as to the initial concentration or even as to the absolute concentrations at various times, provided that a quantity directly proportional to the concentration can be determined experimentally. The activation energy ΔH_a is calculated from the values of k at the two temperatures by using Eq. (6).

Practical Applications. The speed of a chemical reaction is important in determining the efficiency of many industrial chemical reactions. In organic reactions particularly, where there is the possibility of several reactions going on simultaneously, that reaction which is fastest is the one that predominates.

The rate of hydrolysis of methyl acetate is useful in calculating the activity of hydrogen ions in a solution.

Suggestions for Further Work. The reaction rates may be determined at other temperatures, and the energy of activation checked by determinations over other temperature intervals.

Different acid concentrations and other acids may be used,[3] and the influence of neutral salts, inorganic bases, or organic materials may be studied. Nonaqueous solvents may be used,[1] and methyl acetate may be replaced by other esters,[4] higher temperatures being used if necessary.

The extent of hydrolysis of a salt may be determined by measuring the rate at which methyl acetate is hydrolyzed when added to the salt solution.

Instead of estimating by eye the best straight line passing through the graph of log c versus time, the equation for the line may be determined by the method of least squares (page 370).

Other statistical methods may be used in the closer estimation of k.[6]

References

1. Friedman and Almore, *J. Am. Chem. Soc.*, **63**, 864 (1941).
2. Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York (1941).
3. Griffith and Lewis, *J. Chem. Soc.*, **109**, 67 (1916).
4. Harned and Pfansteil, *J. Am. Chem. Soc.*, **44**, 2193 (1922).
5. Hinshelwood, "Kinetics of Chemical Change," Oxford University Press, New York (1940).
6. Roseveare, *J. Am. Chem. Soc.*, **53**, 1651 (1931).
7. Taylor, "Treatise on Physical Chemistry," Chap. XIV, D. Van Nostrand Company, Inc., New York (1931).

28. Saponification of Ethyl Acetate

This experiment illustrates a bimolecular reaction for which a second-order constant may be calculated. A conductometric method is used for following the course of the reaction.

Theory. The rate constant k for chemical reactions is given by the Arrhenius equation:

$$k = se^{-\Delta H_a/RT}$$

where e = base of natural logarithms
ΔH_a = energy per mole required for activation
R = gas constant
T = absolute temperature

The expression $e^{-\Delta H_a/RT}$ represents the fraction of molecules having an energy equal to or greater than the energy required for activation. For bimolecular gas reactions, the constant s is probably about equal to the number of molecules colliding. Reactions in solution have not been worked out so completely as yet.

The rate of a second-order reaction, dx/dt, is proportional to the concentration of each of the two reacting materials, as expressed in the equation

$$\frac{dx}{dt} = k(a - x)(b - x)$$