solvents may be used, and methyl acetate may be replaced by other esters, 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 $k$.^3

References


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:

$$k = \frac{g^c}{e^{-\Delta H_a/R}}$$

where $e$ = base of natural logarithms

$\Delta H_a$ = energy per mole required for activation

$R$ = gas constant

$T$ = absolute temperature

The expression $e^{-\Delta H_a/R}$ 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

$$\frac{dx}{dt} = k(a - x)(b - x)$$
where \( x \) = number of moles reacting in time \( t \)

\( a = \) initial concentration of one reacting material

\( b = \) initial concentration of the other

\( k = \) specific reaction rate

The bimolecular reaction studied in this experiment is the saponification of an ester by sodium hydroxide.

\[
\text{CH}_3\text{COOC}_2\text{H}_5 + \text{Na}^+ + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{Na}^+ + \text{C}_2\text{H}_5\text{OH}
\]

The hydroxyl ion and ethyl acetate are the reacting materials, the sodium ion being incidental.

A solution containing sodium hydroxide and ethyl acetate undergoes a marked decrease in conductance with time because the highly conducting hydroxyl ion is replaced by the poorly conducting acetate ion during the reaction. Accordingly, a conductance bridge can be used to study the progress of the reaction. An alternative but more tedious procedure is to withdraw samples from the reaction mixture at definite intervals, discharge them into excess standard HCl solution, and back-titrate with standard NaOH.

**Apparatus.** Two 250-ml glass-stoppered volumetric flasks; two 250-ml Erlenmeyer flasks; bottle-type conductance cell, conductance bridge; tall glass-stoppered weighing bottle; ethyl acetate; standardized sodium hydroxide; 25-ml burette; 1-ml graduated pipette; 25-ml pipette; 50-ml pipette; thermostats at 25 and 35°; stop watch or timer.

**Procedure.** Standard solutions of ethyl acetate and sodium hydroxide having exactly the same normality are to be prepared. This requires careful technique.

Enough pure ethyl acetate is pipetted into a weighed weighing bottle containing about 5 ml of water to prepare 250 ml of 0.02M solution. The bottle is reweighed, the solution transferred quantitatively to a volumetric flask, and distilled water is added to the mark. The exact normality is calculated.

The same volume of NaOH whose normality is exactly equal to that of the ethyl acetate is prepared by quantitative dilution of standardized 0.5N stock reagent.

The flasks containing these solutions and a 250-ml flask containing distilled water are clamped in the 25° thermostat and allowed to come to temperature equilibrium before use.

The conductance bridges described on pages 163 and 454 are satisfactory for this experiment. A compact bridge utilizing an electron-ray tube or “magic eye” as a null indicator is available on the market.
and can be highly recommended. The student is referred to Exp. 34 and Chap. 21 for information on the theory and practice of conductance measurements. The Freas-type conductance cell shown in Fig. 39 is recommended.

The conductance bridge is set up by the thermostat, and a cell which has been rinsed with distilled water is brought to thermostat temperature.

Into another 250-ml flask is pipetted exactly 25 ml of ester solution, 25 ml water, and 50 ml NaOH solution in that order. The flask is swirled rapidly in the thermostat as the NaOH is introduced, and the stop watch started after about half has been added. The conductance cell is quickly rinsed with a few milliliters of the mixture and then filled about two-thirds full. Conductance readings are begun as soon as the cell can be returned to the thermostat. Readings are taken up to an hour or so every minute or two at first, with intervals lengthened as time goes on. The solution is then returned to the mixing flask, which is stoppered and set aside for conductance readings after at least 24 hr has elapsed, when the reaction will have reached equilibrium.

For the next run, the proportions of ester and base are reversed, and the experiment is repeated.

Next, equal volumes of the base and ester solutions are mixed, and readings are taken for about an hour at 25°C. With solution and apparatus transferred to the 35°C thermostat, the experiment is repeated. It is not necessary to measure a final conductance for these two experiments.

Calculations. Appropriate plots are made, and rate constants are determined for each of the experiments performed. The equation

\[ k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)} \]

is used where unequal concentrations of ester and base were present. To obtain \( x \) at time \( t \), the quantity \( (y_b - y) / (y_a - y) \) is multiplied by \( a \) or \( b \), whichever was originally present in smaller amount. In this equation \( y_b \) is the conductance at time \( t \), \( y_b \) is the conductance at time 0, and \( y_a \) is the conductance at completion of the reaction. The
conductance at time 0 is obtained by extrapolation of the first few points on a plot of conductance versus time to zero time.

When the concentrations of the two reactants are the same, the equation

\[ k = \frac{1}{t a} \frac{x}{(a - x)} = \frac{1}{t a} \frac{y_0 - y_t}{y_t - y_\infty} \]

is applicable. It may be rearranged to yield

\[ y_t = \frac{1}{ka} \frac{y_0 - y_t}{t} + y_\infty \]

This is the equation of a straight line with \( y_t \) and \( (y_0 - y_t)/t \) as variables. When \( y_t \) is plotted against \( (y_0 - y_t)/t \), the slope of the line is equal to \( 1/ka \).

From the temperature coefficient of \( k \) obtained from the last two experiments the energy of activation is calculated.

Practical Applications. The calculations in this experiment are typical for a second-order reaction, and the influence of concentration of either reacting material on the velocity of the reaction may be calculated quantitatively.

Suggestions for Further Work. The rates of saponification of other esters may be determined. Methyl acetate saponifies rapidly; consequently it should be studied at lower temperatures. The more complicated esters saponify more slowly, and they may be studied conveniently at higher temperatures. The saponification rate is the same with all strong bases, but with weak bases the reaction is complicated and depends on the degree of dissociation of the base.

References


29. The Decomposition of Silver Oxide. An Autocatalytic Reaction

The rate of an autocatalytic reaction is measured at two temperatures by determining the volume of gas evolved as a function of time. The results are treated mathematically and graphically.

Theory. In most reactions the rate decreases as the reaction proceeds, owing to the fact that reactant materials are being used up. Occasionally a reaction is found whose rate is very slow at first, builds up to a maximum, and then decreases. An autocatalytic reaction is