Experiment 4

Second Order Reaction : Effect of Temperature on Rate

Purpose :

To determine the rate constant for a reaction of second order and calculate the activation energy.

Principle :

In the bimolecular reaction, the saponification of ethyl acetate,

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH \qquad (1)$$

the progress of the reaction may be followed by titrating the quantities of sodium hydroxide present from time to time with standard acid; or it may be followed by observing the change in electrical conductance as sodium hydroxide is consumed and sodium acetate formed.

The above reaction follows the second-order equation,

$$\frac{dx}{dt} = k(a - x)(b - x) \qquad (2)$$

where t = time elapsed from initiation of reaction,

x = number of moles per liter reacted or decrease in concentration of reactants at time t,

a = initial molar concentration of ethyl acetate,

b = initial molar concentration of sodium hydroxide,

k = second order rate constant.

Integration of Eq. (2) for the case $a \neq b$ leads to the result

$$\frac{1}{(a - b)} \ln \frac{b(a - x)}{a(b - x)} = kt \qquad (3)$$

For the case $a = b$ one obtains

$$\frac{x}{a(a - x)} = kt \qquad (4)$$

In this experiment, we use equal initial concentration of the reacting substances. The concentration of reaction that has occurred, x, and the concentration of the reactants remaining at time t, $(a - x)$, can be deduced from the conductance, G. The total amount of reaction possible is proportional to the total change of conductance, i.e., $a \propto (G_o - G_\infty)$. Therefore the amount of reaction after time t, x, is proportional to $(G_o - G_t)$. Substituting the above expression into Eq. (4) and rearranging, one finds

$$k = \frac{1}{at} \times \frac{G_o - G_t}{G_t - G_\infty} = \frac{1}{at} \times \frac{\kappa_o - \kappa_t}{\kappa_t - \kappa_\infty} \qquad (5)$$

where $G_\circ$ represents the observed conductance at the start of the reaction (due to NaOH), G_t that at time t, and G_∞ that after *100* percent reaction (due to sodium acetate). κ is the specific conductance (conductivity) and equal to the product of conductance and cell constant, K_{cell} .

The rate constant k is related to the temperature by the expression

$$\frac{d \ln k}{d T} = \frac{E_a}{RT^2} \tag{6}$$

where E_a is the activation energy, R is the gas constant, and T is the absolute temperature. If E_a is assumed independent of temperature, integrate Eq. (6) and obtain the following equation

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1}) \tag{7}$$

Eq. (7) shows that a low activation energy means a fast reaction and a high activation energy means a slow reaction. It is found that many reactions whose rate constants at room temperature are always doubled by a ten-degree increase in temperature. The rapid increase in rate constant as temperature increase is due mainly to the increase in the number of collisions whose energy exceeds the activation energy.

Apparatus and Chemicals :

Conductivity meter; thermostat; three *250-ml* beakers; *400-ml* beaker; six *250-ml* Erlenmeyer flasks; glass bar; *100-ml* graduated cylinder; two *25-ml* pipettes; *100°C* thermometer; two safety bulbs.

0.02 M Ethyl acetate; *0.01 M* NaOAc; *0.02 M* NaOH.

Procedure :

(1) The reaction is investigated at room temperature, *35°C* , and *45°C* by using a thermostat.

(2) Measure the specific conductance of *0.01 M* NaOH ($\kappa_\circ$) at each temperature.

(3) Measure the specific conductance of *0.01 M* NaOAc (κ_∞) at each temperature.

(4) Among six Erlenmeyer flasks, three flasks contain *100 ml* of *0.02 M* NaOH and another three flasks contain *100 ml* of *0.02 M* Ethyl acetate.

(5) Put each pair of the above solutions into the thermostat and adjust the temperature to room temperature, *35°C* , and *45°C* .

(6) While the temperature of the solutions is reached and unchanged, mix the two solutions thoroughly and quickly. Start the stopwatch.

(7) Put the conductivity cell into the mixture and take the specific conductance readings at 3 minutes intervals for half-hour.

(8) The readings you got from the instrument are specific conductance.

(9) The conductivity cell can't be used as a stirring rod.

Calculations :

(1) Plot $(G_{\circ} - G_t)/(G_t - G_{\infty})$ or $(\kappa_{\circ} - \kappa_t)/(\kappa_t - \kappa_{\infty})$ versus t.

(2) Calculate the rate constants k for each temperature.

(3) Plot ln k versus $1/T$ and calculate the activation energy E_a from the slope.

(4) Calculate the half-life $t_{1/2}$ from the observed rate constant for each temperature.

References :

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