# KINETICS OF THE REACTION OF HYDROGEN PEROXIDE WITH POTASSIUM IODIDE IN ACID MEDIUM

## 1. PURPOSE OF THE WORK

Determination of reaction order and rate constant for the reaction of hydrogen peroxide with potassium iodide.

## 2. THEORETICAL NOTIONS

For the complex reaction:

$$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2 \quad (1)$$

the overall reaction rate is given by the relation:

$$-\frac{dC_{H_2O_2}}{dt} = k_1 \cdot C_{H_2O_2} \cdot C_{I^-} + k_2 \cdot C_{H_2O_2} \cdot C_{I^-} \cdot C_{H^+} \quad (2)$$

where $k_1$, $k_2$ are rate constants within the reaction mechanism.

When potassium iodide and acid are in excess, the relation (2) is simplified, because the concentrations of $I^-$ and $H^+$ ions remain practically constant. It turns out:

$$-\frac{d\,C_{H_2O_2}}{dt} = k \cdot C_{H_2O_2} \quad (3)$$

where $k$, the global rate constant, has the meaning:

$$k = k_1 \cdot C_{I^-} + k_2 \cdot C_{I^-} \cdot C_{H^+} \quad (4)$$

The development of the reaction respects the kinetic relation of the first order (linearity between $\ln C_{H_2O_2}$ and time):

$$\ln C_{H_2O_2} = \ln C^0_{H_2O_2} - k \cdot t \quad (5)$$

Towards the end of the reaction, when the consumption of $I^-$ and $H^+$ begins to become important, their concentrations decrease, observing a deviation from linearity. The variation of the $H_2O_2$ concentration during the reaction is followed by titration $I_2$ resulting from the reaction (1) with sodium thiosulfate in the presence of starch. The reaction that takes place is:

$$2\,S_2O_3^{2-} + I_2 \rightarrow 2\,I^- + S_4O_6^{2-} \quad (6)$$

Because reaction (6) is very fast, the iodine produced in reaction (1) is consumed as it is produced. Therefore, it cannot be traced by titrating samples at different times. The chronometric method using the time in which a certain amount of the titration reagent is

consumed is used.

To this end, a given amount of thiosulphate is introduced into the reaction vessel, prepared according to the working method, and the time from the addition to its total consumption is measured. The excess of unreacted iodine after consuming the whole amount of thiosulfate, according to reaction (6), forms a molecular complex with starch, present in the reaction mass, producing the blue coloration of the solution.

## 3. EXPERIMENTAL PART

### 3.1. APPARATUS AND SUBSTANCES

- 500 mL Erlenmayer beaker, 250 mL graduated cylinder, 25 mL Erlenmayer beaker, 2 x 25 mL pipettes and one 10 mL pipette, 3% hydrogen peroxide, stopwatch, distilled water, sulfuric acid solution 3M, potassium permanganate solution 0.02 M.

### 3.2. PROCEDURE

A solution of 0.05 mol / L $H_2O_2$ is prepared in an Erlenmayer vessel. To do this, add 3 mL of 3% $H_2O_2$ in 50 mL of distilled water. To determine the exact concentration of the prepared $H_2O_2$ solution, place in two Erlenmayer vessels 5 mL $H_2O_2$ (from the one previously prepared), add 3 mL $H_2SO_4$ and titrate with 0.02 mol / L $KMnO_4$ to pale pink (the color is due to a small excess of $KMnO_4$, do not put another indicator). The reaction is:

$$5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ \rightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,O_2 \qquad (7)$$

The exact concentration of the $H_2O_2$ solution is:

$$c_1^0 = c_{H_2O_2} = \frac{5}{2} \cdot \frac{V_{KMnO_4}}{V_{H_2O_2}} \cdot c_{KMnO_4} \qquad (8)$$

where 5/2 is the ratio between the stoechiometric coefficients of $H_2O_2$ and $KMnO_4$ in reaction (7).

Next, prepare the following mixture: 150 mL of distilled water with a graduated cylinder are placed in a 500 mL beaker, then using right pipette 20 mL KI 0.1 M, 10 mL $H_2SO_4$ 3M, 5 mL of starch and 2 mL thiosulphate from the burette. Place the flask on the magnetic stirrer, or stir it manually. In case of manual stirring, a 500 mL Erlenmayer beaker is preferred. To start the reaction, measure 20 mL of $H_2O_2$ from the previously prepared solution, which is placed in a 50 mL Berzelius beaker to be poured into the reaction vessel. Prepare the stopwatch. Then, pour the prepared $H_2O_2$ solution into the reaction vessel so that the mixing is abrupt. Start the stopwatch

**Caution: When the hydrogen peroxide is poured into the reaction vessel, the stopwatch is triggered, read the time of appearance of the blue color <u>without stopping</u> the stopwatch.**

Next, the following operations must be done quickly. When the blue color appears, after reading the time, 2 mL of thiosulfate is added quickly (from the burette or with a pipette). The solution discolors as iodine is consumed by thiosulphate. It is necessary that the interval between staining and discoloration be as short as possible. Note the time of onset of the blue color, then add another 2 mL of thiosulphate rapidly. In total, 10-12 additions are made, namely: 4-5 with 2 mL of thiosulfate and if the time between discolorations increases to over 4 minutes, continue with 5-7 additions of 1 mL of thiosulfate; if the time is less than 3 minutes only 2 mL are used. Towards the end of the reaction the coloration is much weaker, because hydrogen peroxide is consumed. The times are read when the first color tint appears.

## 4. PROCESSING OF EXPERIMENTAL DATA

4.1. The experimental results are listed in a table of the form:

| ***t*, s** | $V_{Na_2S_2O_3}$ **, mL** | $V_{all}$ **, mL** | $\Sigma V_2$**, mL** | $c_t$ **, mol/L** | $\ln c_t$ | **k, $s^{-1}$** |
|---|---|---|---|---|---|---|
| 0 | 0 | 205 | 0 | | | |
| | 2 | 207 | 2 | | | |
| | | | | | | |
| … | | | | | | |

$V_{Na_2S_2O_3}$ - the volume of thiosulfate added , mL

$V_{all}$ - the total volume of the reaction vessel at the time t , mL

$\Sigma V_2$ - the total volume of thiosulfate added , mL

4.2. From the volume of thiosulphate added, the unreacted $H_2O_2$ concentration is calculated up to the time read on stopwatch. Will be drawn the graph of $\ln c_t$ as a function of time. It should be a straight line. In conclusion, the studied reaction is of order 1. The initial concentration is that obtained by titrating the hydrogen peroxide (see relation 8), and the $H_2O_2$ concentration at time *t,* is calculated with the relation:

$$c_t = \frac{V_1^0 c_1^0 - 0.5\, c_2^0 \sum V_2}{V_{all}} \qquad (9)$$

where: $c_t$ - $H_2O_2$ concentration in the reaction vessel at time $t$, mol / L

$V_1^0$ - volume of $H_2O_2$ solution initially introduced, mL

$c_1^0$ - initial concentration of $H_2O_2$, mol / L

$V_{all}$ - the total volume of solution in the reaction vessel , mL

$c_2^0$ - concentration of the added thiosulfate solution , mol/L

$\Sigma V_2$ - the volume of thiosulfate added , mL

The data obtained are represented graphically $\ln c_t$ as a function of time. At the end of the reaction, the points deviate from linearity for the reasons shown above.

Calculate the rate constant with the relation

$$k = \frac{1}{t}(\ln c_0 - \ln c_t)$$

where the concentration at the initial moment is: $c_0 = \frac{V_1^0 c_1^0}{V_{all}}$

The speed constant will also be calculated from the slope of the graph $\ln c_t = f(t)$

**5. QUESTIONS**

5.1. Give examples of other 1st order reactions.

5.2. Evaluate the initial concentration $c_0$ using the graphical representation $\ln c_t = f(t)$ .