LABORATORY SESSION 4

Study of the effect of temperature on the reaction rate

Material	1 shared methacrylate bucket, thermostat and refrigeration unit
1 x 500 mL volumetric flask	1 solids carrier for weighing / 1 stirring rod / 1 eyedropper/ 1 funnel
1 x 250 mL volumetric flask	1 x 250 mL amber bottle (for $Na_2S_2O_3$)
1 x 100 mL volumetric flask	1 washing bottle
1 x 25 mL volumetric flask	1 magnetic stirrer with magnet
1 x 1000 mL Erlenmeyer flask	
4 x 100 mL beakers	**Products**
1 x 100 mL graduated cylinder	Potassium iodide
1 x 5 mL graduated pipette	Sodium thiosulfate pentahydrate
1 x 2 mL graduated pipette	Hydrogen peroxide of 30% w/w.
1 micropipette, 1 dropping pipette	Starch indicator 1%
1 chronometer	Sulfuric acid

Objectives

1. To analyze how temperature affects the reaction rate.
2. To relate rate constants and partial reaction times.
3. To determine the activation energy of the reaction.
4. To determine the experimental rate law for the oxidation reaction of hydroiodic acid by hydrogen peroxide in acidic medium (pseudo-order of reaction and apparent rate constant).

Theoretical foundations

The rate of almost every chemical reaction generally increases with temperature (doubling or trebling with every 10ºC increase). One of the most common equations to represent how the rate constant changes with temperature is the empirical Arrhenius equation:

$$k = Ae^{-E_a/RT} \qquad (1)$$

where A is the frequency factor and E_a is the **activation energy**. Using logarithms in equation (1), we have:

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T} \qquad (2)$$

When applied at two temperatures (T_1 and T_2) and when both temperatures are divided, this becomes:

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (3)$$

This is a valid equation if we assume that A and E_a are constant in the studied temperature range. The activation energy of the reaction can therefore be determined from the relationship between the rate constants at two temperatures.

In this experiment we determine the relationship between the rate constants, and therefore the value of the activation energy, by:

a) determining the partial reaction time, and

b) using the integrated rate equations.

(a) The **partial reaction time**, t_p, is defined as the time required to consume a given amount of reagent under certain initial reaction conditions.

At two temperatures (T_1 and T_2), provided the initial concentration ($[A]_0$ at t=0) and instantaneous concentration ($[A]_t$ at t=t) of all the reagents are the same at both temperatures, the rate constants are inversely proportional to the partial reaction times t_{p_1} and t_{p_2}:

$$\frac{k_1}{k_2} = \frac{t_{p_2}}{t_{p_1}} \qquad (4)$$

The chosen **reaction** is the oxidation of the iodide ion by hydrogen peroxide in an acidic (sulfuric) medium:

$$\mathbf{H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2\,H_2O}$$

$$H_2O_2 + 2\,KI + H_2SO_4 \rightarrow I_2 + 2\,H_2O + K_2SO_4 \qquad (5)$$

with a **rate equation** that can be expressed as:

$$v = k[I^-]^a\,[H_2O_2]^b\,[H^+]^c \qquad (6)$$

where k is the absolute rate constant and *a*, *b* and *c* are the partial reaction orders with respect to I^-, H_2O_2 and H^+, respectively.

The rate equation is simplified because the acidic medium remains approximately constant (excess H^+ with respect to the other components) and the experimental design enables the concentration of I^- to remain constant throughout the reaction (as we will see). Then:

$$v = k_{ap}\,[H_2O_2]^b \quad \text{where} \quad k_{ap} = k[I^-]^a\,[H^+]^c \cong \text{cte} \qquad (7)$$

The amount of iodine produced (and therefore the amount of hydrogen peroxide that is reacted) is determined by adding to the reaction medium a predetermined amount of sodium thiosulfate, which, depending on the reaction, reduces the iodine as it is produced:

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \qquad (8)$$

Consequently, the number of moles (and the concentration) of I^- will remain roughly constant.

$$2NaI + 2H_2SO_4 \rightarrow 2HI + 2NaHSO_4 \qquad (9)$$

and the number of moles (and the concentration) of HI will also remain roughly constant.

According to the stoichiometry of the reaction (5), the moles of I_2 produced are equal to those of H_2O_2 consumed and, since I_2 reacts immediately with thiosulfate, we can determine the amount of hydrogen peroxide that has reacted from the amount of thiosulfate that is added to the reaction medium. The time needed to consume an added and prefixed amount of sodium thiosulfate for the iodine produced will be a measure of the partial reaction time. The presence of iodine is easily detected by adding a few drops of starch (due to the blue complex iodine forms with the starch).

(b) The rate constants can also be obtained from the slopes of the graph of the corresponding integrated equation, for which the order of the reaction must be determined in advance.

Given equations (5) and (7), the integrated equation of order one (b=1) is:

$$\ln[H_2O_2] = \ln[H_2O_2]_0 - k_{ap}t \qquad (10)$$

and that of order two is:

$$\frac{1}{[H_2O_2]} = \frac{1}{[H_2O_2]_0} + k_{ap}t \qquad (11)$$

The k_{ap} at each temperature (k_{ap1} and k_{ap2}) will be obtained from the slope of the best fit. Their quotient, according to equation (7) and since the starting concentrations of I^- and H^+ in each series are equal, is:

$$\frac{k_{ap1}}{k_{ap2}} = \frac{k_1}{k_2} \qquad (12)$$

Using this relationship and equation (3), we can determine the activation energy.

<u>**Note:**</u> To deduce equation (4) it is taken into account that the integrated rate equation, in simple mechanism reactions, can always be written as:

$$f([A],[A]_0) = kt \qquad (a)$$

where $[A]_0$ and $[A]$ are the concentrations of reagent A at t=0 and at time t, respectively. This equation is valid for any temperature provided there are no changes in the mechanism. Therefore, at two temperatures (T_1 and T_2):

$$f([A],[A]_0) = k_1t_1 \quad \text{and} \quad f([A],[A]_0) = k_2t_2 \qquad (b)$$

If f ($[A]_0$, $[A]$) is the same at both temperatures, then: $k_1t_1 = k_2t_2$ (c)

Also, if the reaction times correspond to the partial times in which a certain fraction of reagent has been consumed, the above equality leads us to equation (4).

Solutions

1. 250 mL of 0.1 M $Na_2S_2O_3$ solution (to be stored in a topaz-colored bottle or light shelter).
2. 100 mL of 0.2 M hydrogen peroxide (H_2O_2) from 30% w/w (M=34.01, d= 1.11 g/cm^3) (in the fume cupboard).

For **each series** (temperature), the following must be prepared:

3. 500 mL of KI of 0.12% by weight (0.6 g in 500 mL of water).
4. **10 mL of concentrated sulfuric acid** (in the fume cupboard). The **procedure** is as follows: add the prepared KI dissolution (500 mL) to a 1000 mL Erlenmeyer flask; then (**in the fume cupboard!!!**) add 10 mL of concentrated sulfuric acid **VERY SLOWLY** to the Erlenmeyer flask using the dispenser (or pipette).

Experimental procedure

The study is performed at two temperatures (two series), which must be noted down:

Series 1 is performed at a temperature of 10°C in a thermostatic bath with cryostat.

Series 2 is performed at a temperature of 22°C in a thermostatic bath (if necessary, use the cryostat).

For **each series** the procedure is as follows:

1. In the bath and on the magnetic stirrer (so that they reach the experimental temperature), place:
   - the 1000 mL Erlenmeyer flask with the KI solution, the 10 mL sulfuric acid (prepared in the fume cupboard) and the magnet. The agitator starts and must not be stopped throughout the experiment.
   - an Erlenmeyer flask covered with 25 mL of the H_2O_2 solution.
2. When the thermal equilibrium has been reached (after roughly 10 minutes), add 1 mL of starch indicator (measured with a pipette) to the reaction flask. Then add the 25 mL of H_2O_2 to the reaction Erlenmeyer flask and start the timer **(t=0).**
3. When the solution changes color, immediately add 3 mL of sodium thiosulfate solution using the micropipette. The blue color will disappear (because of the complex that forms between the iodine that is produced and the starch indicator). When the color reappears (which indicates that the thiosulfate is no longer in the solution), record the time without stopping the timer and add another 3 mL aliquot of sodium thiosulfate.
4. Repeat step 3 until you complete a 12-part time series. **Note**: The time it takes for the blue color to appear is the time it takes for the added thiosulfate to be consumed and will be the partial reaction time.
5. Prepare solutions 3 and 4 again, making sure that the mass of KI is as close as possible to that of series 1.
6. Repeat the experiment at a temperature of 22°C.

Note: Remember that containers are available to dispose of waste after you finish the experiment.

Experimental results: presentation of the data

1. Tabulate the calculated theoretical masses or volumes, the masses or volumes actually used, and the concentrations of thiosulfate and hydrogen peroxide solutions actually used.

2. In another table present the experimental data: for both temperatures, the volume of thiosulphate added and the times at which each aliquot was consumed.

Treatment and discussion of results

1. Determine the concentration of hydrogen peroxide based on the volume of thiosulfate added and record it in Table 2 (use the actual thiosulfate and hydrogen peroxide concentrations).
2. Determine the partial reaction times for both series and complete Table 2.
3. Discuss the values and trends for t_p at each temperature and their possible relationship to the reaction order.
4. Use equation (4) to calculate the average value of k_1/k_2 from the part-time quotients. Also calculate the random error.
5. Use equation (3) to calculate the activation energy with the appropriate number of significant figures.
6. Construct Table 3 with $[H_2O_2]$, $\ln[H_2O_2]$ and $1/[H_2O_2]$ as a function of time for both temperatures.
7. Plot the integrated rate equations for orders one and two (plot the data for both temperatures on each graph). Determine the order of reaction with respect to hydrogen peroxide.
8. Use the slope of the lines in the above graph to determine the apparent rate constants at each temperature and the activation energy using the Arrhenius equation. Compare the activation energy with the value obtained from the partial reaction times.
9. The concentration of hydrogen peroxide is usually expressed in "volumes". In fact, the hydrogen peroxide from the pharmacy is 10 volumes. Calculate the concentration of hydrogen peroxide that you have used in this practice, 0.2 M, in "volumes".