

## CHEMICAL KINETICS: H<sub>2</sub>O<sub>2</sub> DECOMPOSITION, RATE, AND ACTIVATION ENERGY

### OBJECTIVE:

In this experiment, you will determine the order, rate constant, and activation energy for the reaction between hydrogen peroxide and the iodide ion in a basic solution.

### INTRODUCTION:

The reaction to be studied is the decomposition of hydrogen peroxide in the presence of the iodide ion, for which the form of the rate equation, the value of the rate constant, and the activation energy will be determined.



At the same time, it will be shown that the iodide ion is unchanged in the reaction and is thus a catalyst.

**Note:** There is another similar reaction possible in this system involving H<sup>+</sup> that also liberates O<sub>2</sub>. The solution will be slightly basic to reduce [H<sup>+</sup>] and to minimize this possible complication.

### PROCEDURE:

Two reaction mixtures are to be studied. Mixture A and Mixture B. Mixture A will consist of:

H <sub>2</sub> O <sub>2</sub>	4 mL
H <sub>2</sub> O	15 mL
NaOH (0.2 M)	1 mL
KI (0.8 M)	5 mL

Mixture A is to be studied at three temperatures:

T <sub>1</sub>	= approximately 25°C
T <sub>2</sub>	= approximately 35°C
T <sub>3</sub>	= approximately 45°C

Mixture B will consist of:

H <sub>2</sub> O <sub>2</sub>	4 mL
H <sub>2</sub> O	10 mL
NaOH (0.2 M)	1 mL
KI (0.8 M)	10 mL

Mixture B will be studied at one temperature: T<sub>1</sub> = approximately 25°C

For convenience, the four runs can be referred to as A-1, A-2, A-3, and B.

Set up the apparatus as shown in Figure 1, making sure that the buret leveling system is free of air bubbles and that the Erlenmeyer flask is centered over the magnetic stirrer and clamped in place so that good, constant stirring can be achieved by the stirring bar in the flask.

Transfer the reactants into the Erlenmeyer flask with a pipette in the order: (1)  $\text{H}_2\text{O}_2$ , (2)  $\text{H}_2\text{O}$ , (3)  $\text{NaOH}$ . Allow a minute or so for them to come to thermal equilibrium with the water bath. Add the  $\text{KI}$  with a pipette, quickly insert the stopper in the tube, close the pinch clamp, and start the stirrer. Start the stop watch when the water level in the burette reaches 2.00 mL. Record the times of evolution of successive 2.00 mL increments up to 20.00 mL. Let the reaction continue to completion and record the final volume of  $\text{O}_2$  evolved. Throughout the gas evolution and timing, maintain the water level in the leveling funnel at the same height as that in the burette to ensure that the volume of  $\text{O}_2$  is being measured at a constant pressure.

At the start of each test: (1) The Erlenmeyer flask should be clean, dry, and clamped in place in the water bath over the magnetic stirrer. (2) The stirring bar should be in place at the bottom of the flask with the stirrer off. (3) The water level in the buret should be at 0.00 to 1 mL from the top, and the value should be recorded. (4) The pinch clamp on the two-hole stopper should be open, with the stopper itself hanging just to the side of the flask (ready to be inserted when the  $\text{KI}$  is added.)

Do test runs A-1 and B (at  $T_1 \approx 25^\circ\text{C}$ ). Then heat the water bath slightly to do runs A-2 and A-3. In all cases record the temperature of the water bath before and after the kinetic reaction, taking the reaction temperature as the average.

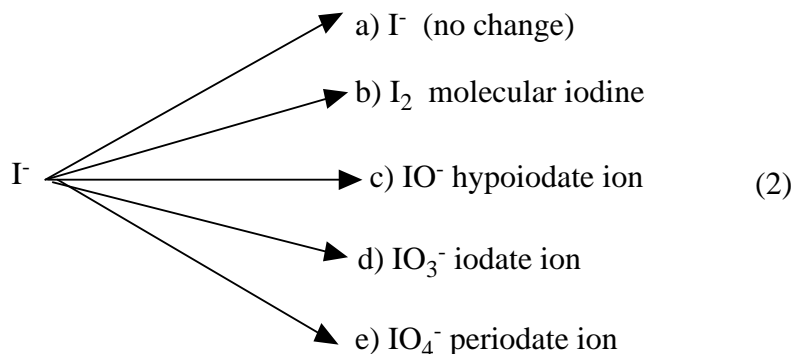
To prove that the  $\text{I}^-$  is a true catalyst, i.e., that it is unchanged in the reaction (though it may appear in the kinetic equation), three simple tests are all that are required.

1. To a 2-mL portion of the finished reaction mixture, add 10 drops of starch solution. Shake well and record your observations.
2. To a second 1-mL portion of the finished reaction mixture add 10 drops of 0.2 M  $\text{BaCl}_2$  solution (acidify with  $\text{HCl}$  if a precipitate forms). Record your observations.
3. To a third 1-mL portion, add 10 drops of mercuric nitrate solution and again record your observations.

## DATA TREATMENT:

### Qualitative Tests

What happens to the iodide ion? The original  $\text{I}^-$  in the presence of an oxidizing agent, could theoretically react in one of these five ways:



The following information will help you make the correct interpretation.

- $\text{HgI}_2$ , has two forms, yellow and red, both insoluble in water.
- Molecular iodine forms a characteristic blue colored complex with starch indicator.
- The hypoiodate ion is unstable in aqueous solution, disproportionating into iodate and iodide ions.
- $\text{Ba}(\text{IO}_3)_2$  is white and insoluble in aqueous solutions.
- $\text{BaI}_2$  is quite soluble in water.
- The periodate ion would require a stronger oxidizing agent than hydrogen peroxide for its formation and even if formed, would be removed by the reaction with  $\text{I}^-$



With the above information applied to the results of the three qualitative tests, it is possible to establish the fate of the original  $\text{I}^-$ . Enter this data in your report as "test", "observation", "inference" and state your conclusion.

### **Kinetic data treatment**

Assume that the kinetic equation for the reaction is

$$-d[\text{H}_2\text{O}_2]/dt = k[\text{H}_2\text{O}_2][\text{I}^-] \quad (4)$$

that is, the reaction is second order overall, first order in each of the reagents hydrogen peroxide and iodide ion. Enough information is available from the experiment to establish this relationship, however it is sufficient to simply assume the equation is valid as long as the assumption is justified in the treatment and interpretation of this data.

In the experimental procedure the volume of  $\text{O}_2$  evolved is measured as a function of time. The amount of oxygen gas evolved bears a simple relationship to the amount of  $\text{H}_2\text{O}_2$  decomposed (1 mole of  $\text{O}_2$  is evolved from the decomposition of two moles of hydrogen peroxide); thus, a measure of the rate of decomposition of hydrogen peroxide is available.

At the start of the reaction:

$$\text{time } t = 0, [\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0, V(\text{O}_2) = 0,$$

at the end of the reaction:

$$\text{time } t = \infty, [\text{H}_2\text{O}_2] = 0, V(\text{O}_2) = V_\infty,$$

at any intermediate time:

$$\text{time } t = t, [\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_t, V(\text{O}_2) = V_t,$$

It is easily seen that  $[\text{H}_2\text{O}_2]_t$ , the concentration remaining at any time  $t$ , is proportional to the total possible amount of  $\text{O}_2$  minus that already evolved, that is  $(V_\infty - V_t) = \Delta V_t$ ; in other words,

$$[\text{H}_2\text{O}_2]_t = C(V_\infty - V_t) = C\Delta V_t \quad (5)$$

The proportionality constant, C, can be evaluated from  $P, V, T$ , data on the  $O_2$  and the solution volume containing the hydrogen peroxide (see Appendix); however, the exact value of C is not important, as the C cancels in the kinetic expression when  $(C\Delta V_t)$  is substituted for  $[H_2O_2]_t$ .

In any given reaction,  $[I^-]$  remains constant since the qualitative tests show it to be unchanged chemically in the reaction; thus

$$-d[H_2O_2]/dt = k[H_2O_2][I^-] = k'[H_2O_2] \quad (6)$$

where the constant  $[I^-]$  has been included in the new rate constant ( $k'$ ), that is

$$k' = k[I^-] \quad (7)$$

Rearranging and integrating Equation 6,

$$-\int_{[H_2O_2]_0}^{[H_2O_2]_t} \frac{d[H_2O_2]}{[H_2O_2]} = \int_0^t k' dt \quad (8)$$

one obtains,  $\ln[H_2O_2]_t - \ln[H_2O_2]_0 = -k't$  (9)

Substituting  $V_\infty, V_0, \Delta V_t$  and so forth into Eq.(9) gives

$$\ln C\Delta V_t = -k't + \ln C(V_\infty - V_0) \quad (10)$$

The proportionality constant, C can now be cancelled out and since  $V_0 = 0$

$$\ln \Delta V_t = -k't + \ln V_\infty \quad (11)$$

Equation (11) has the form  $y = mx + b$  and thus we obtain a straight line by plotting  $\ln \Delta V_t$  vs. time if the reaction is indeed first order with respect to  $H_2O_2$ , where  $[H_2O_2] \propto V_t$  and if  $I^-$  is a catalyst. The intercept would then correspond to  $\ln V_\infty$  and the slope =  $-k'$ , from which the value of  $k' = k[I^-]$  can be calculated.

Do this plot and calculation for Mixtures A and B at  $T_1 (\approx 25^\circ C)$ , both to justify the assumptions and to find  $k'_A$  and  $k'_B$ ; for the two runs. The value of  $k'_B$  will differ from that calculated for  $k'_A$  since  $[I^-]$  differed between the two runs:  $[I^-]_B = 2[I^-]_A$ . If the reaction is indeed first order with respect to the iodide ion, as has been assumed, then

$$\frac{k'_B}{k'_A} = \frac{k[I^-]_B}{k[I^-]_A} = 2 \quad (\text{For runs A-1 and B})$$

Check this relationship to verify the first order dependence of the reaction rate on  $[I^-]$ .

Finally, the rate constant,  $k_A$ , of the reaction can be calculated from  $k' = k[I^-]$ , using the value of  $[I^-]$  for the particular mixture under study.

From the three runs of Mixture A at various temperatures (A-1,2,3), the temperature dependence of the rate constant can be determined, since  $k_{A-1}$  has already been obtained. Similarly determine  $k_{A-2}$  and  $k_{A-3}$  from plots of  $\ln \Delta V_t$  vs. time and their known, common iodide ion concentration.

Using the Arrhenius expression for the rate constant,

$$k = Ae^{-(E_a/RT)} \quad (12)$$

$$\ln k = \ln A - E_a/RT \quad (13)$$

where  $k$  is the rate constant for the reaction,  $E_a$  is the activation energy for the reaction (in J/mole),  $R$  is the gas constant (8.314 J/mol-K),  $T$  is the absolute temperature at which  $k$  was obtained and  $A$  is the pre-exponential factor which contains various parameters of the kinetic theory such as the collision diameter.

Therefore a plot of  $\ln k$  versus  $1/T$  should yield a straight line with slope of  $-E_a/R$ , from which we can determine the activation energy,  $E_a$ .

Plot the results in your report and make the calculations for the three temperatures.

### REPORT:

Your report should include the following:

(a) Plot of  $\ln \Delta V_t$  versus time for:

(A-1) to justify the assumption of  $[H_2O_2]$ , that is, first order with respect to hydrogen peroxide, by a straight line plot, and to determine  $k'_{A-1}$  and  $k_{A-1}$ .

(B) to determine  $k'_B$  and  $k_B$  and to justify the assumption of first order dependence with respect to  $[I^-]$  by comparison with  $k'_{A-1}$

(A-2 and A-3) to determine  $k_{A-2}$ ,  $k_{A-3}$  in order to find  $E_a$ .

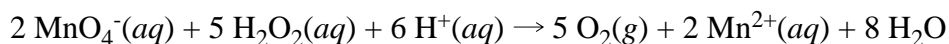
These four plots may be done on a single, clearly labeled graph.

(b) From  $k'_{A-1}$  and  $k'_B$  verify  $[I^-]$  dependence.

(c) Plot  $\ln k_{A-n}$ , vs.  $1/T$  and determine the  $E_a$  for the reaction, where the subscript  $n$  equals 1,2 or 3 and refers to the data obtained at each of the three temperatures listed as  $T_1, T_2$  and  $T_3$ .

### APPENDIX:

It may be advantageous to calculate  $V_\infty$  from an exact knowledge of the molar concentration of the initial  $H_2O_2$  solution. This can be done by titrating 5.00 mL of the hydrogen peroxide solution to which has been added a few mL of dilute  $H_2SO_4$ , with some standardized 0.500 N  $KMnO_4$ . The end point is the persistence of the pink permanganate color. The reaction is



Thus the 1 M H<sub>2</sub>O<sub>2</sub> solution is 2 N in this reaction.

The final volume, V<sub>∞</sub> of O<sub>2</sub> evolved when V mL of H<sub>2</sub>O<sub>2</sub> solution (of molarity M) is reacted and the gas measured at the temperature T and pressure P over water at the same temperature T is given by

$$V_{\infty} = (0.50 \times M \times RTV)/1000P$$

where  $P = P_{atm} - P_{water}$

Derivation of V~[H<sub>2</sub>O<sub>2</sub>] relationship.

A complete run produces V<sub>∞</sub> mL of oxygen gas collected over water at P = P<sub>atm</sub>, at T.

$$n = PV/RT = (P_{atm} - P_{water})V_{\infty}/RT$$

This is evolved from the decomposition of 2n moles of H<sub>2</sub>O<sub>2</sub> in 26 mL of solution. That is

$$[\text{H}_2\text{O}_2]_o = \frac{2n \text{ moles}}{26 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = \frac{1000}{26} \times \frac{2(P_{atm} - P_{water})V_{\infty}}{RT} = CV_{\infty}$$

For some intermediate extent of the reaction

$$[\text{H}_2\text{O}_2]_t = [\text{H}_2\text{O}_2]_o - [\text{H}_2\text{O}_2]_{\text{used}} = CV_{\infty} - CV_t = C\Delta V_t$$

## REFERENCES:

1. H.S. Harned, "Neutral Salt Catalysis. I. Role of the solvent in Neutral Salt Catalysis in Aqueous Solutions", J. Am. Chem. Soc., 40, 1461 (1918)
2. H.A. Liebhafsky, J. Am. Chem. Soc., 54, 1792 (1932).
3. H.A. Liebhafsky, J. Am. Chem. Soc., 54, 3499 (1932).

ALTERNATE PROCEDURE FOR CHEMICAL KINETICS: DECOMPOSITION OF HYDROGEN PEROXIDE

In this alternate procedure you will follow the rate of decomposition of  $\text{H}_2\text{O}_2$  by measuring the changing in pressure as the hydrogen peroxide is decomposed instead of measuring the change in volume.

The procedure is the same as previously described for the change in volume measurement except for the following:

- Use 4.00 mL of 7.5%  $\text{H}_2\text{O}_2$
- Set up apparatus connected to the mercury manometer to measure pressure changes as the reaction proceeds.
- Record the time every 1 cm increment on one side of the Hg manometer. This corresponds to a pressure change of 2 cm Hg.
- Allow at least 20 minutes for determination of  $h_\infty$ , (complete reaction).

**CALCULATIONS**

The calculations are the same as for the change in volume except:

- $P_t$  replaces  $V_t$
- $\Delta P = \Delta h(\text{mm or cm Hg}) \times 2$  where  $\Delta h$  is the difference on one side.
- $\Delta P_t = \Delta P_\infty - \Delta P$

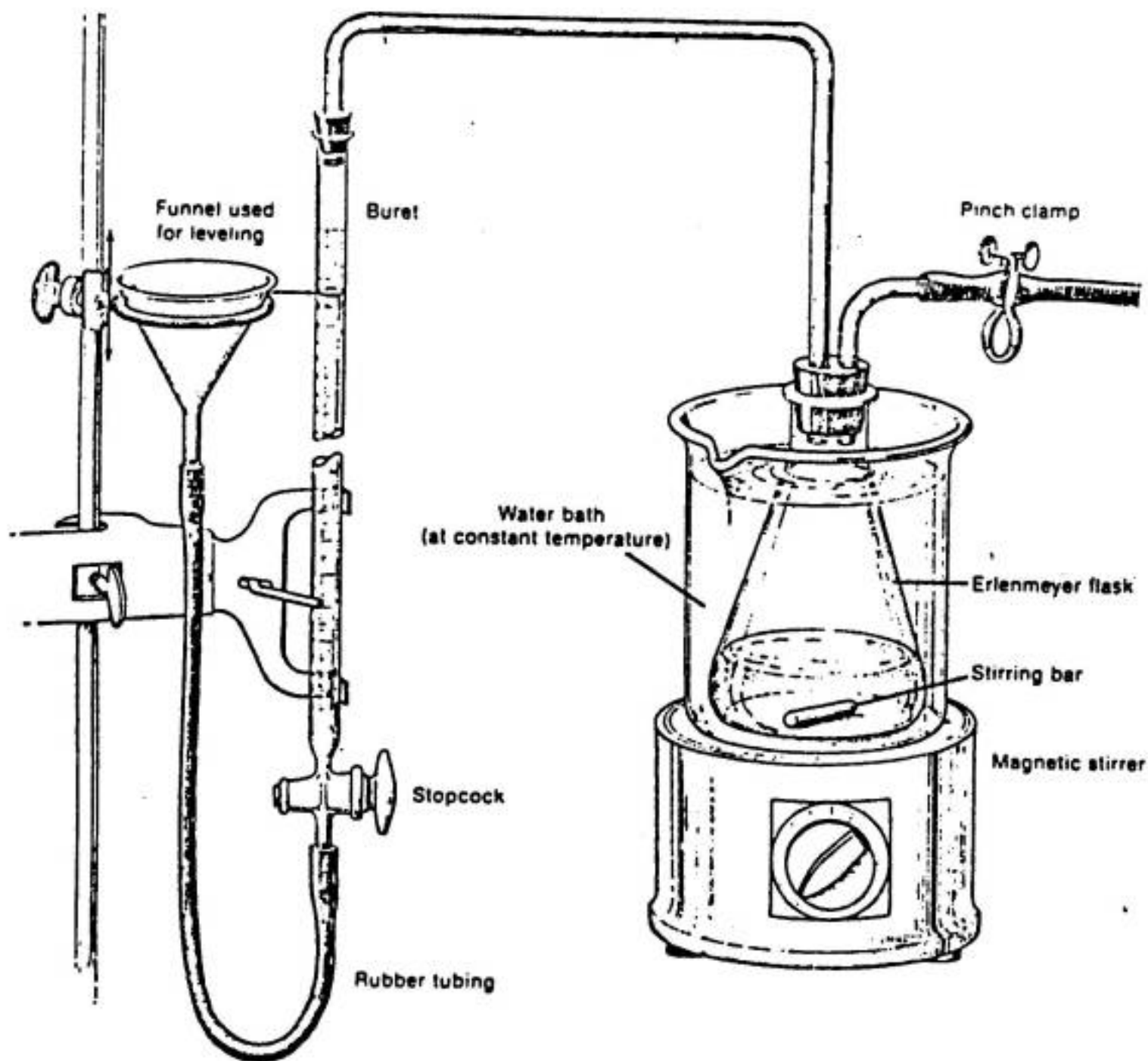


FIGURE 1. Apparatus for the measurement of the evolution of a gas.