

## Module 9 : Experiments in Chemistry

### Lecture 40 : Kinetics and Photochemistry : Iodine Clock Reaction and Photochemical Reduction

#### Objectives

After studying the present lecture, you will be able to

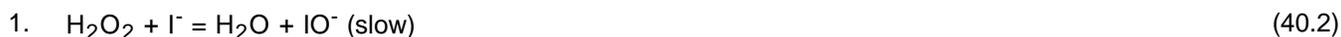
- Outline the kinetics and mechanism of the iodine clock reaction.
- Relate this reaction to the other chemical oscillation reactions studied earlier.
- Outline the experiment involving blue printing.

#### 40.1 Introduction to the iodine clock experiment

In this lecture, the kinetics of the reaction between  $\text{H}_2\text{O}_2$  and HI will be investigated. The reaction



is kinetically of the second order. The overall reaction seems to involve two steps as follows:



The first step is the rate determining step.

In the presence of a constant excess of HI (i.e., excess of  $\text{I}^-$ ), the reaction becomes pseudo-first order with respect to  $\text{H}_2\text{O}_2$ . This condition is achieved by continuously adding small amounts of  $\text{Na}_2\text{S}_2\text{O}_3$  to convert  $\text{I}_2$  to iodide ions. Volume change of the reaction mixture due to addition of a small amount of concentrated  $\text{Na}_2\text{SO}_3$  may be treated as negligible.

The progress of the reaction can readily be followed by noting the time of appearance of iodine, indicated by the appearance blue colour after the addition of small known volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Amount of  $\text{H}_2\text{O}_2$  reacted during the time lapse for the appearance of blue colour corresponds to the  $\text{Na}_2\text{S}_2\text{O}_3$  added.

Since the reaction rate depends on the concentration of  $\text{H}_2\text{O}_2$  present in the reaction mixture, time for the reappearance of blue colour will increase with the progress of the reaction.

#### 40.2 Procedure

1. Take 20 mL  $\text{H}_2\text{SO}_4$  (1 volume of concentrated acid to 2 volume of water) in a conical flask and dilute it to 100 mL. Add to it about 2 g of solid KI and 10mL of  $\text{H}_2\text{O}_2$  (2 Vol) solution. Mix well and warm to  $30^\circ\text{C}$ . Titrate the liberated iodine with 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution using starch solution as indicator.
2. In a 500 mL conical flask, place 250 mL of KI (4g/l) solution; and add to it 15 mL of dil  $\text{H}_2\text{SO}_4$  and 10 mL of starch solution. Suspend the flask in a thermostatic bath at  $25^\circ\text{C}$ . Add 10 mL of  $\text{H}_2\text{O}_2$  (2 Vol) from a stock solution previously thermostated at  $25^\circ\text{C}$ . Start the stop watch when the pipette is half discharged into the flask containing KI, etc. Shake vigorously and add to it 1 mL of 0.1M  $\text{Na}_2\text{S}_2\text{O}_3$  solution from a burette. Record the time at which blue colour appears. Then, again add immediately 1 mL of  $\text{Na}_2\text{S}_2\text{O}_3$  and note the time of appearance of blue colour after each addition until the time of a appearance of blue colour becomes 5-6 times the initial time. Shake the reaction mixture throughout the addition of  $\text{Na}_2\text{S}_2\text{O}_3$  solution. For rapid mixing, an electric motor with glass stirrer may also be arranged in the flask.

In order to determine the order with respect to HI, the experiment may be repeated by changing only the KI concentration and keeping other parameters constant. In all such experiments pseudo 1 st order condition must be maintained keeping KI in excess.

Activation energy of the reaction may also be determined by repeating the reaction at different temperatures e.g.

10°, 15°, 30° and 35°C keeping the other reaction parameters constant.

#### 40.3 Calculations

Volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution added will correspond to the amount of H<sub>2</sub>O<sub>2</sub> reacted with I<sup>-</sup> during the time of appearance of blue colour of starch. Since one mole of I<sub>2</sub> is liberated for every mole of H<sub>2</sub>O<sub>2</sub>, the amount of H<sub>2</sub>O<sub>2</sub> remaining and the amount of H<sub>2</sub>O<sub>2</sub> decomposed ( x ) at any time can be calculated.

The titre value, V of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution with 10 mL H<sub>2</sub>O<sub>2</sub> as determined in step 1 is proportional to the initial concentration a, of H<sub>2</sub>O<sub>2</sub>. If V<sub>t</sub> is the volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> at any time t corresponding to the appearance of blue colour, then x is proportional to V<sub>t</sub> and (a - x ) at any time t will be (V - V<sub>t</sub>). Applying first order rate equation, we have

$$k_{obs} = \frac{2.303}{t} \log \frac{V}{V - V_t} \quad (40.4)$$

A plot of log (V - V<sub>t</sub>) versus t is a straight line showing first order reaction. Slope of the curve will be equal to k<sub>obs</sub>/2.303 from which k<sub>obs</sub> can be determined.

For energy of activation, E, plot of log k against 1/T will give a straight line and slope is equal to - E/2.303R. From the slope, E can be determined.

Order of reaction with respect (HI) can be calculated applying principles of isolation method i.e., repeating the experiment with different concentration maintaining pseudo first order condition and keeping all other reaction parameters constant. Hence determining various k obs as follows:

$$K_{obs} = k [HI]^n \quad (n = \text{order of reaction respect to } [HI]) \quad (40.5)$$

$$\text{or } \log k_{obs} = \log k + n \log [HI] \quad (40.6)$$

$$\text{and hence, } n = \frac{\log (k_{obs})_2 - \log (k_{obs})_1}{\log [HI]_2 - \log [HI]_1} \quad (40.7)$$

#### 40.4 Experiment on Blue Printing (Photochemical reduction)

The printing and developing of blue print involves, in addition to the usual electrochemical aspects, a photochemical reaction.

Ferric ions are reduced by oxalic acid to the ferrous state and the rate of reduction is enhanced by exposing the reactants to sunlight. When ferrous ions react with ferricyanide ions, blue colour (Turnbull's blue) is developed. The quantity of ferric salt reduced to ferrous salt under the influence of light is made apparent by the depth of blue colour.

The following solutions are required for performing this experiment:

(a) 0.5 M oxalic acid, (b) 0.67 M ferric chloride, (c) 0.1 M potassium ferricyanide, (d) 3.5 M diammonium phosphate, (e) 0.03 M potassium dichromate and (f) 0.1 M hydrochloric acid.

In a 250 mL beaker mix 50 mL of oxalic acid solution with 10 mL of diammonium phosphate solution. Place the beaker in diffuse light (inside locker or cupboard ). Add 50 mL of ferric chloride solution to the solution of oxalic acid and diammonium phosphate under stirring in diffuse light. A small precipitate initially formed dissolves on further stirring. Close your locker and open it only when needed.

Take four pieces of type writer paper (or just regular plain paper) (8cm x 5cm). Open the locker and immerse the papers in the solution of ferric oxalate, rotate the beaker so that the papers are thoroughly wet and no dry spots are left (diffuse light). Now place these wet papers between the sheets of filter papers and keep them in a locker for 15 – 20 minutes. After the papers have dried, take them out and place a piece of negative (film sheet) on the top of the sensitized paper. Compress these between two sheets of glass and expose to direct bright sunlight for a measured amount of time (say 4 – 5 minutes).

After exposure, immerse the paper entirely in the 0.1 M potassium ferricyanide solution, kept in a trough. Remove the paper and dip it in potassium dichromate solution and then in 0.1 M HCl solution (also kept in a trough). And finally wash in tap water.

Repeat with the other papers, varying the time of exposure in order to obtain the most satisfactory result.

Mount the blue prints that you have made in your record book and indicate exposure time for each.

In your report, (i) write equations for the chemical reactions involved, and (ii) explain why potassium dichromate solution makes the print sharper.

#### 40.5 Exercise

1. What is the role of light in the blue printing experiment?
2. Why do you add di-ammonium phosphate to oxalic acid solution before adding ferric chloride solution?
3. Why does potassium dichromate solution make the print sharp?
4. Write equations for the chemical reactions involved in this experiment.
5. Can we get a photo-quality prints using this method?
6. Write an overall mechanism for the iodine clock reaction
7. Compare the iodine clock reaction with the chemical oscillations studied in an earlier chapter and classify it suitably.

#### Recap

**In this lecture you have learnt the following**

#### 40.6 : Summary

In this lecture, the procedure for kinetics of the reaction between  $\text{H}_2\text{O}_2$  and HI is investigated. This reaction is an example of chemical oscillations and the chemical oscillations continue until all the  $\text{H}_2\text{O}_2$  has reacted. Many reactions in our body too need chemical oscillations, the best example is the heart beat.

The second reaction studied in this lecture is the blueprinting reaction. The printing and developing of blue print involves, in addition to the usual electrochemical aspects, a photochemical reaction. Ferric ions are reduced by oxalic acid to the ferrous state and the rate of reduction is enhanced by exposing the reactants to sunlight. When ferrous ions react with ferricyanide ions, blue colour (Turnbull's blue) is developed. The quantity of ferric salt reduced to ferrous salt under the influence of light is made apparent by the depth of blue colour.