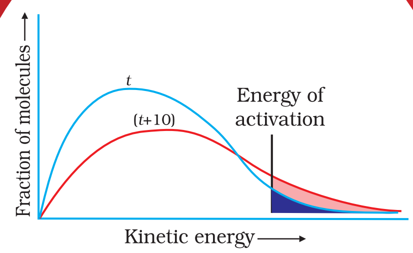
UNIT-2

CHEMICAL KINETICS



RATE of reaction can be measured either in terms of decrease in concentration of any one of the reactants or increase in concentration of any one of the products with time. For a hypothetical reaction,

$$A \longrightarrow B$$

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta T} = \frac{\Delta[B]}{\Delta T}$$

Factors such as concentration, temperature and catalyst affect the rate of a reaction. In this unit you will learn the technique of determining the rate of a reaction and technique of studying the effect of concentration and temperature on the reaction rate.

EXPERIMENT 2.1

Aim

To study the effect of concentration and temperature variation respectively on the rate of reaction between sodium thiosulphate and hydrochloric acid.

Theory

Sodium thiosulphate reacts with hydrochloric acid and produces a colloidal solution of sulphur, which makes the solution translucent. The reaction occurs as follows:

$$Na_2S_2O_3\ (aq) + 2HCl\ (aq) \longrightarrow 2NaCl\ (aq) + H_2O(l) + SO_2\ (g) + S(s)$$

Ionic form of the above reaction is written as:

$$S_2O_3^{2-}\ (aq) + 2H^+\ (aq) \longrightarrow H_2O\ (l) + SO_2\ (g) + S(s)$$

The property of the colloidal solution of sulphur to make the system translucent is used to study the rate of precipitation of sulphur. The rate of precipitation of sulphur increases with an increase in the concentration of the reacting species or with an increase in the temperature of the system. With an increase in the concentration, the number of molecular collisions per unit time between the reacting species increase and consequently chances of product formation increase. This results in an increase in the rate of precipitation of sulphur. Similarly, on increasing the temperature, the kinetic energy of the reacting species increases, so the number of collisions that result in the formation of products increase leading to a faster rate of reaction.

Material Required

- Beaker (100 mL) : One
- Burette (50 mL) : One
- Pipette (25 mL) : One
- Pipette(5 mL) : One
- Burette stand : One
- Stop watch : One
- Thermometer (110°C) : One

- 0.1M Sodium thiosulphate : As per need
- 1.0 M Hydrochloric acid : As per need

Procedure

A. The effect of concentration on the rate of reaction

(i) Take a trough and fill half of it with water. This will serve as constant temperature bath, maintained at room temperature.

(ii) Rinse and fill the burette with 1.0 M HCl solution.

(iii) Take a 100 mL beaker and make a mark 'X' in the centre of the outer surface of the bottom with the help of a glass marker pencil. Fill 50 mL of 0.1M sodium thiosulphate solution in it. Place the beaker in the trough. The mark 'X' will be visible to the naked eye on account of the transparent nature of the system. Allow the beaker to stand in the trough for a few minutes so that it attains the temperature of the bath.

Hydrochloric acid 

(iv) Add 1.0 mL of 1.0 M HCl solution with the help of a burette. Start the stopwatch when half the HCl solution i.e. (0.5 mL) has been transferred. Swirl the beaker while adding HCl.

(v) Record the time required for the mark 'X' on the bottom of the beaker to become invisible (This is considered as a stage of completion of the reaction).

(vi) Repeat the experiment by adding 2 mL, 4 mL, 8 mL and 16 mL of 1.0 M hydrochloric acid solution to fresh sodium thiosulphate solution every time and record the time required for the disappearance of the mark 'X' in each case separately.

B. The effect of temperature on the rate of reaction

(i) Take 50 mL of 0.1M sodium thiosulphate solution in a 100 mL beaker, on the outer surface of the bottom of which a mark 'X' has been made. Keep the beaker in a thermostat maintained at 30°C. Add 5 mL of 1.0 M hydrochloric acid solution with swirling. Start the stopwatch immediately when half the amount (i.e. 2.5 mL) of hydrochloric acid has been transferred.

(ii) Record the time at which the mark 'X' becomes invisible.

(iii) Repeat the experiment at temperatures 40°C, 50°C, 60°C and 70°C using fresh sodium thiosulphate solution each time and record the time required for the disappearance of the mark 'X'.

(iv) Record your observations in Tables 2.1 and 2.2.

(v) Plot two graphs, one for the volume of HCl added (which determines concentration of HCl) and the time taken for the mark to become invisible and the other between temperature and the time taken for the mark to become invisible. For plotting the graph, the variation in time is plotted on *x*-axis and the variation in volume or temperature is plotted on *y*-axis.

Note : *If thermostat (i.e. constant temperature bath) is not available for studying the rate of the reaction. Ordinary water bath may also be used for maintaining constant temperature but in this case heating of the bath from outside might be required for the adjustment of temperature. Water in the bath should also be stirred continuously.*

Table 2.1 : Effect of concentration of HCl on the rate of reaction between sodium thiosulphate and hydrochloric acid

Amount of $Na_2S_2O_3$ solution used each time = 50 mL
Concentration of $Na_2S_2O_3$ solution = 0.1M, Room temperature = C
Concentration of the HCl solution used in the reaction mixture = 1.0 M

Sl. No.	Volume of HCl added in mL	Time 't' in seconds for the mark 'X' to become invisible
1.	1.0	
2.	2.0	
3.	4.0	
4.	8.0	
5.	16.0	

Table 2.2 : The effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid

Volume of sodium thiosulphate solution used each time = 50 mL
Volume of HCl used each time = 5 mL

Sl. No.	Temperature of the reaction mixture/ C	Time 't' in seconds for the mark 'X' to become invisible
1.	30	
2.	40	
3.	50	
4.	60	
5.	70	

Result

Write your conclusions on the basis of data in Tables 2.1 and 2.2.

Precautions

(a) Start the stopwatch when half of the hydrochloric acid solution has been transferred to the reaction flask and stop the watch when the mark 'X' becomes invisible.

(b) If a constant temperature bath is not available to maintain the constant temperature, heat the water of the bath in which the beaker is kept from time to time with constant stirring, and remove the burner when the required temperature is attained.

(c) Select suitable scale for plotting the graph.

Discussion Questions

(i) The reaction under examination is as follows:

$$S_2O_3^{2-}\,(aq) + 2H^+\,(aq) \longrightarrow H_2O\,(l) + SO_2\,(g) + S(s)$$

Write the conditions under which the rate law expression for this reaction can be written in the following manner.

Rate of precipitation of sulphur = $k\,[S_2O_3^{2-}][H^+]^2$

(ii) Suppose the above rate law expression for the precipitation of sulphur holds good, then on doubling the concentration of $S_2O_3^{2-}$ ion and H^+ ion, by how many times will the rate of the reaction increase?

(iii) Comment on the statement that for a given reaction, rate of the reaction varies but the rate constant remains constant at a particular temperature.

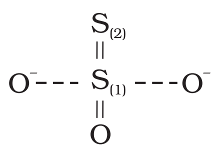
(iv) How does the rate constant of a reaction vary with temperature?

(v) Devise an experiment to study the dependence of rate of precipitation of sulphur upon the nature of monobasic acid for the reaction given below :

$$S_2O_3^{2-}\,(aq) + 2H^+(aq) \longrightarrow H_2O\,(l) + SO_2\,(g) + S(s)$$

(vi) Why is the stop watch/stop clock started when half of the reactant is delivered into the beaker?

(vii) The structure of $S_2O_3^{2-}$ ion is described as follows:



The two sulphur atoms are marked here as (1) and (2). Which of the sulphur atoms, according to you, is precipitated as colloidal sulphur? How can you verify your answer experimentally?

(viii) What is the difference between the order and the molecularity of a reaction?

(ix) The molecularity of a reaction can't be zero but the order can be zero? Explain.

(x) Can the order of a reaction be a fractional quantity?

(xi) Suppose the above reaction follows third order kinetics, then in what units, will the rate of the reaction and the rate constant be expressed?

EXPERIMENT 2.2

Aim

To study the effect of variation in concentration of iodide ions on the rate of reaction of iodide ions with hydrogen peroxide at room temperature.

Theory

The reaction between iodide ions and hydrogen peroxide occurs in the acidic medium and can be represented in the following manner:

$$2I^-(aq) + H_2O_2\,(l) + 2H^+(aq) \longrightarrow I_2(g) + 2H_2O\,(l)$$

In this reaction, hydrogen peroxide oxidises iodide ions (I^-) to molecular iodine. If calculated amount of sodium thiosulphate is added in the presence of starch solution as an indicator to the above reaction mixture, the liberated iodine reacts with thiosulphate ions as fast as it is formed and is reduced back to iodide ions till all the thiosulphate ions are oxidised to tetrathionate ions.

$$I_2(g) + 2S_2O_3^{2-}\,(aq) \longrightarrow S_4O_6^{2-}\,(aq) + 2I^-(aq)$$

After the complete consumption of thiosulphate ions, the concentration of iodine liberated in the reaction of hydrogen peroxide with iodide ions increases rapidly to a point where iodine forms intense blue complex with starch. The time required to consume a fixed amount of the thiosulphate ions is reproducible. Since the time for the appearance of colour is noted, the reaction is some times called a **clock reaction**.

Material Required

- Conical flasks (250 mL) : Five
- Conical flask (500 mL) : One
- Stop watch : One
- Measuring cylinder (100 mL) : One
- Trough : One

- Starch solution : As per need
- 2.5 M Sulphuric acid solution : As per need
- 0.1 M Potassium iodide solution : As per need
- 0.04M Sodium thiosulphate solution : As per need
- 3% Hydrogen peroxide solution : As per need

Procedure

(i) Take 25 mL of 3% hydrogen peroxide, 25 mL of 2.5 M H_2SO_4 solution, 5 mL of freshly prepared starch solution and 195 mL distilled water into a 500 mL conical flask marked as A. Stir this solution well and place it in a water bath maintained at room temperature.

(ii) Take four 250 mL conical flasks and mark them as B, C, D and E.

(iii) Take the sodium thiosulphate solution, potassium iodide solution, and distilled water in the flasks B, C and D in a proportion given in the following steps and keep the flask E for carrying out the reaction.

(iv) Take 10 mL of 0.04 M sodium thiosulphate solution, 10 mL of 0.1 M potassium iodide solution and 80 mL of distilled water in the conical flask marked B. Shake the contents of the flask well and keep it in a water bath.

(v) Take 10 mL of 0.04 M sodium thiosulphate solution, 20 mL of 0.1M potassium iodide solution and 70 mL of distilled water in the conical flask marked C. Shake the resulting solution well and place it in the same water bath in which reaction mixture of step (iv) is kept.

(vi) Take 10 mL of 0.04 M sodium thiosulphate solution, 30 mL of 0.1 M potassium iodide solution and 60 mL of distilled water in the conical flask marked D. Shake the solution well and keep this flask also in the above water bath.

(vii) Take conical flask E. Pour 25 mL solution from flask A into it after measuring it with the help of a measuring cylinder. Now add 25 mL of solution from flask B into this flask with constant stirring. Start the stop watch when half of the solution from flask B has been transferred. Keep the flask E in a water bath to maintain the constant temperature and record the time required for the appearance of blue colour.

(viii) In exactly the same manner, repeat the experiment with the solutions of flasks C and D separately by using once again 25 mL of the solution of these flasks and 25 mL of solution

Sulphuric acid 

Hydrogen peroxide 

Hazard Warning

- *Cotact of hydrogen-peroxide with combustible material may cause fire.*

from flask A. Note the time required for the appearance of blue colour in each case.

(ix) Repeat the experiment with solutions of flasks B, C and D twice and calculate the average time for the appearance of blue colour.

(x) Record your observations as given in Table 2.3.

(xi) Compare the time required for the appearance of blue colour for all the three systems and make a generalisation about the variation in the rate of the reaction with concentration of iodide ions.

Table 2.3 : Study of reaction rate between iodide ions and hydrogen peroxide in acidic medium

Sl. No.	Composition of the system	Time taken for appearance of the blue colour		Average Time
		First reading	Second reading	
1.	25 mL solution from flask A + 25 mL solution from flask B			
2.	25 mL solution from flask A + 25 mL solution from flask C			
3.	25 mL solution from flask A + 25 mL solution from flask D			

Result

Write your conclusions on the basis of the data recorded in Table 2.3.

Precautions

(a) Always keep the concentration of sodium thiosulphate solution less than that of potassium iodide solution.

(b) Always use freshly prepared starch solution.

(c) Use fresh samples of hydrogen peroxide and potassium iodide.

(d) Always use the same measuring cylinders for measuring solutions in two different sets of observations. If after measuring one solution, the cylinder is used for measuring another solution, clean it before using.

(e) Record the time immediately after the appearance of blue colour.

Discussion Questions

(i) Distinguish between the role of iodine and iodide ions in this experiment.

(ii) Calculate the oxidation number of sulphur in tetrathionate ion ($S_4O_6^{2-}$). Can the oxidation number be a fractional number?

(iii) Why does iodine impart blue colour to starch?

(iv) Explore the possibility of using an oxidant other than H_2O_2 in this experiment.

(v) Why is the reaction given the name clock reaction?

(vi) Why should the concentration of sodium thiosulphate solution taken be always less than that of potassium iodide solution?

EXPERIMENT 2.3

Aim

To study the rate of reaction between potassium iodate (KIO_3) and sodium sulphite (Na_2SO_3).

Theory

The reaction between KIO_3 and Na_2SO_3 indirectly involves the formation of iodide ions, which are oxidised in acidic medium by IO_3^- ions to iodine. The overall reaction proceeds in the following two steps.

$$IO_3^- + 3SO_3^{2-} \longrightarrow I^- + 3SO_4^{2-} \quad (1)$$

$$5I^- + 6H^+ + IO_3^- \longrightarrow 3H_2O + 3I_2 \quad (2)$$

The evolved iodine produces blue colour with the starch solution in a manner described in the previous experiment. This reaction like the earlier reaction is also known as 'clock reaction'.

Material Required

- Conical flasks (250 mL) : Six
- Measuring cylinder (100 mL) : One
- Stopwatch : One
- Trough : One

- 2 M Sulphuric acid : As per requirement
- 5% Starch solution : As per requirement
- 6% Potassium iodate solution : As per requirement
- 6% Sodium sulphite solution : As per requirement

Procedure

(i) Take a 250 mL conical flask and mark it as 'A'. Transfer 25 mL of 6% potassium iodate solution, 25 mL of 2.0 M H_2SO_4 and 50 mL of distilled water into it and shake the content of the flask well. Keep the flask in a trough half filled with water. This serves as constant temperature bath.

(ii) Take five 250 mL conical flasks and mark these as B, C, D, E and F respectively. Take 6% sodium sulphite solution, starch solution and distilled water in flasks B, C, D and E in the proportion given in the following steps and keep flask F for carrying out the reaction.

(iii) In the conical flask marked 'B' take 20 mL of sodium sulphite solution, 5 mL of starch solution and 75 mL of distilled water. Shake the contents of the flask well and keep it in the water bath.

Note :

- *Total amount of solution in each flask is 100 mL*
- *Same amount of indicator has been used.*

(iv) In the conical flask marked 'C', take 15 mL of sodium sulphite solution, 5 mL of starch solution and 80 mL of distilled water. Shake the resulting solution well and keep it in the water bath.

(v) In conical flask 'D', take 10 mL of sodium sulphite solution, 5 mL of starch solution and 85 mL of distilled water. Shake the solution well and place the flask in the water bath.

Sulphuric acid 

(vi) In conical flask 'E', take 5 mL of sodium sulphite solution, 5 mL of starch solution and 90 mL of distilled water. Shake the content of the flask well and keep it in the water bath.

(vii) Take conical flask 'F'. In this flask pour 25 mL of the solution from the conical flask marked 'A' and add 25 mL of the solution from the conical flask marked 'B'. Start the stop watch when half of the solution from flask B has been added. Mix these two solutions thoroughly by constant stirring and keep it in the water bath. Record the time required for the appearance of blue colour (you may use stop watch/wrist watch for noting the time).

(viii) In a similar manner, repeat the experiment with the solutions in flasks C, D and E respectively by using 25 mL of the solution as in the experiment with solution from flask B and record the time required for the appearance of blue colour in each case.

(Once again care should be taken to repeat the experiment for each case twice so as to take the average time required for the appearance of blue colour in each set).

(ix) Record your observations as given in Table 2.4.

(x) From the tabulated results, find out the relationship between the time of appearance of blue colour and the variation in concentration of sodium sulphite.

Table 2.4 : Study of the reaction rate between potassium iodate (KIO_3) and sodium sulphite (Na_2SO_3) in acidic medium

Sl. No.	Composition of the system	Time taken for appearance of the blue colour in seconds		Average Times/ sec.
		First reading	Second reading	
1.	25 mL solution from flask A + 25 mL solution from flask B			
2.	25 mL solution from flask A + 25 mL solution from flask C			
3.	25 mL solution from flask A + 25 mL solution from flask D			
4.	25 mL solution from flask A + 25 mL solution from flask E			

Result

Write your conclusions on the basis of data recorded in Table 2.4.

Precautions

(a) As sodium sulphite is likely to be easily oxidised in air, therefore, always use its fresh solution.

(b) Keep the concentration of potassium iodate solution higher than the concentration of sodium sulphite solution.

(c) Use a freshly prepared starch solution.

(d) Start the stop watch when half of the solution from conical flask B, C, D or E is added to the conical flask F containing 25 mL solution from flask A.

Discussion Questions

(i) How would the time for the appearance of blue colour vary if the temperature of the experiment in the above case is enhanced by 10°C ?

(ii) Mention the factors that affect the rate of reaction in the present study.

(iii) Which of the acids, hydrochloric or nitric, would be suitable to make the medium acidic in this experiment? Explain your answer with reasons.

(iv) Out of the reactions (1) and (2) given below:

$$IO_3^- + 3SO_3^{2-} \longrightarrow I^- + 3SO_4^{2-} \qquad (1)$$

$$5I^- + IO_3^- + 6H^+ \longrightarrow 3H_2O + 3I_2 \qquad (2)$$

which could be the rate determining reaction? What is the molecularity of the rate determining reaction?

(v) Can AsO_3^{3-} be used in place of SO_3^{2-} in the above reaction? Support your answer with proper reasoning.

(vi) Why is the concentration of potassium iodate solution kept higher than the concentration of sodium sulphite solution?