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**.

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 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			

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?

In a true solution, solute particles mix homogeneously with the molecules of the solvent and thus form a single phase. However, a colloidal solution is a heterogeneous system in which very fine particles of one substance disperse **dispersed phase)** in another substance called **dispersion medium**. Particles of the dispersed phase do not form a single phase with the particles of the dispersion medium because of the fact that they are either very large molecules or essentially aggregates of small molecules. Colloidal particles are larger in size than simple molecules but small enough to remain suspended in the dispersion medium (10^{-9}–10^{-6} m). Some examples of very large molecules which form collidal dispersion are starch, gum and proteins, whereas colloidal sulphur is an example of aggregates of small molecules. Further, a heterogeneous system of a solid as dispersed phase and a liquid as dispersion medium is called a sol. Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, **lyophilic** (solvent attracting) and **lyophobic** (solvent repelling). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic. Egg albumin, starch and gum are lyophilic sols. Freshly prepared ferric hydroxide, aluminium hydroxide and arsenic sulphide sols are examples of lyophobic sols. A few methods of preparation of colloids are – chemical methods, electrical disintegration and peptization. In this unit you will learn to prepare both the types of sols. Also, you will learn a method of purification of sols.

EXPERIMENT 1.1

Aim

To prepare (a) lyophilic sol; and (b) lyophobic sol.

Theory

Since particles of dispersed phase in lyophilic sols have an affinity for the particles of dispersion medium, these sols are more stable as compared to lyophobic sols. Two factors responsible for the stability of sols are – charge and the solvation of the colloidal particles by the solvent. Stability of lyophilic sols is primarily due to the solvation of colloidal particles by the solvent whereas lyophobic sols are stabilised by the charge on the colloidal particles. Due to their charges, colloidal particles remain suspended in solution and coagulation does not take place. These charges may be positive or negative. Some examples of negatively charged sols are starch and arsenious sulphide. Positively charged sol of hydrated ferric oxide is formed when $FeCl_3$ is added to excess of hot water and a negatively charged sol of hydrated ferric oxide is formed when ferric chloride is added to NaOH solution. The lyophilic sols are directly formed by mixing and shaking the substance with a suitable liquid. Lyophobic sols cannot be prepared by direct mixing and shaking. Special methods are employed to prepare these.

A. Preparation of Lyophilic Sol

I. *Egg Albumin Sol*

(i) Prepare 100 mL of 5% (w/*v*) solution of NaCl in water in a 250 mL beaker.

(ii) Break one egg in a porcelain dish and pipette out the albumin and pour it in sodium chloride solution. Stir well to ensure that the sol is well prepared.

II. *Starch/gum Sol*

(i) Measure 100 mL of distilled water with the help of a measuring cylinder and transfer it to a 250 mL beaker and boil it.

(ii) Make a paste of 500 mg starch or gum in hot water and transfer this paste to 100 mL of boiling water with constant stirring. Keep water boiling and stirring for 10 minutes after addition of paste. To judge the efficacy of the prepared sol, you may compare it with the original paste prepared.

B. Preparation of Lyophobic Sol

I. *Ferric hydroxide/Aluminium hydroxide*

(i) Take 100 mL of distilled water in a 250 mL beaker and boil it.

(ii) Add 2g of ferric chloride/aluminium chloride powder to boiling water and stir it well.

(iii) Take 100 mL of distilled water in another 250 mL beaker and boil it.

(iv) Pour 10 mL of ferric chloride/aluminium chloride solution prepared in step (ii) drop by drop into the boiling water with constant stirring. Keep the water boiling till brown/white sol is obtained.

II. Arsenious Sulphide Sol

(i) Transfer 100 mL of distilled water to a beaker of 250 mL capacity.

(ii) Add 0.2 g of arsenious oxide to it and boil the content of the beaker.

(iii) Cool and filter the solution.

(iv) Pass hydrogen sulphide (H_2S) gas through the filtered solution till it smells of H_2S. (Use Kipp's apparatus to pass hydrogen sulphide gas).

(v) Expel H_2S gas from the sol by slow heating and filter it.

(vi) Label the filtrate as arsenious sulphide sol.

Precautions

(a) While preparing colloidal solutions of starch, gum, ferric chloride, aluminium chloride etc., pour the paste or solution gradually into the boiling water with constant stirring. Addition of these substances in excess may cause precipitation.

(b) Arsenious oxide is poisonous in nature; so wash your hands immediately every time after handling this chemical.

Discussion Questions

(i) How will you differentiate between a true solution and a colloidal dispersion?

(ii) Identify some sols (colloids) that you use in your daily life and mention their importance.

(iii) How do colloids acquire a charge? Why is ferric hydroxide/aluminium hydroxide sol prepared in the experiment, positively charged while arsenious sulphide sol is negatively charged?

(iv) What is coagulation? How is coagulation different from peptization?

(v) How can you convert a colloidal dispersion of sulphur into a true solution?

(vi) Out of lyophilic and lyophobic sols, which one can be easily converted into a gel and why?

(vii) Differentiate between a gel and a sol.

(viii) What are the applications of colloids in the field of Medicine, Defense and in Rocket Technology?

Most of the reactions are carried out at atmospheric pressure, hence heat changes noted for these reactions are enthalpy changes. Enthalpy changes are directly related to the temperature changes by the relation:

$$\begin{aligned} \Delta H &= q_p \\ &= mC_p \Delta T \\ &= VdC_p \Delta T \qquad \dots (1) \end{aligned}$$

where V = Volume of the solution.
d = Density of the solution
C_p = Heat capacity
ΔT = Change in temperature

Measurement of heat changes are carried out in vessels called **calorimeters**. Reactions may also be carried out in beakers placed in thermos flask or in thermally insulated box or in styrofoam cup. Metallic calorimeters are not used for measuring thermochemical changes because metals may react with substances. Stainless steel or gold plated copper calorimeters may be used. During measurement of heat changes, calorimeter, thermometer and stirrer also absorb some heat; this amount of heat should also be known. It is called **calorimeter constant**. In the case of a glass vessel, (e.g. beaker) calorimeter constant for that part is found, which is actually in contact with the reaction mixture. This is so because when thermal conductivity of the material of calorimeter is low, only the area of the calorimeter in contact with the liquid absorbs maximum heat. Method of mixtures is used to determine the calorimeter constant. To determine calorimeter constant, known volume of hot water at a specified temperature is added to known volume of water contained in the calorimeter at room temperature. Since energy is conserved, the heat taken by calorimeter and cold water should be equal to heat given by hot water. Thus, we can write the following equation :

ΔH_1	+	ΔH_2	=	$-\Delta H_3$	... (2)
Enthalpy change of calorimeter, stirrer and thermometer		Enthalpy change of cold water		Enthalpy change of hot water	

Let t_c, t_h and t_m be temperatures of cold water, hot water and mixture respectively. Then, in view of the definition of enthalpy change given in equation

(1) we can rewrite equation (2) as

$$m_1 C_{p_1} (t_m - t_c) + m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h) = 0 \qquad \ldots (3)$$

where m_1, m_2 and m_3 are masses of calorimeter, cold water and hot water respectively and C_{p_1} and C_p are heat capacities of calorimeter and water respectively. Since, thermal conductivity of glass is low, only that part of the beaker gains maximum heat which comes in contact with water therefore, we can calculate only effective $m_1 C_{p_1}$ (i.e. calorimeter constant, W). On rewriting equation (3) we get

$$W (t_m - t_c) + m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h) = 0$$

$$W = \frac{m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h)}{(t_m - t_c)} \qquad \ldots (4)$$

but $mC_p = VdC_p$, where V, d and C_p are volume, density and heat capacity of water respectively. By definition, heat capacity of a substance is the amount of energy required to raise the temperature of 1 g of substance by 1 K (or 1°C). The amount of energy required to raise the temperature of 1 g of water by 1 K (or 1°C) is 4.184 Joules. This means that for 1 g water for rise of 1 Kelven temperature $VdC_p = 4.184\ JK^{-1}$. Therefore, product of density and heat capacity can be taken as $4.184\ J.mL^{-1}.K^{-1}$. Thus, equation (4) can be written as :

$$W = \frac{(4.184)\ [V_c (t_m - t_c) + V_h\ (t_m - t_h)}{(t_m - t_c)}\ J\ K^{-1} \qquad \ldots (5)$$

where V_c = volume of cold water

V_h = volume of hot water

Technique for measuring the enthalpy changes are given in the following experiments.

B. Determination of Enthalpy of Dissolution

(i) Take 100 mL of distilled water in the beaker of which calorimeter constant has been determined and place it on a wooden block kept in a larger beaker of capacity 500 mL (Fig. 3.1).

(ii) Pack the empty space between the larger and the smaller beaker with cotton wool and cover with a cardboard.

(iii) Record the temperature of water already taken in the small beaker. Let this be t'_1°C.

(iv) Add weighed amount, say W_1 g of well powdered copper sulphate in water and stir the solution with a stirrer till the entire amount of copper sulphate dissolves.

(v) Note down the temperature attained by the solution after the addition of copper sulphate. Let this be t'_2°C. Calculate the enthalpy of dissolution of copper sulphate as follows:

Total mass of the solution = Mass of Solvent + Mass of Solute

$$= (100 + W_1)\ \text{g}$$

(Assuming density of water to be equal to 1 gL^{-1} at the experimental temperature)

Change in temperature $= (t'_2 - t'_1)$ °C

Enthalpy change of the calorimeter (beaker) $= W\,(t'_2 - t'_1)$

where, W = Calorimeter constant

Enthalpy change of solution $= [(100 + W_1)\,(t'_2 - t'_1)]\ 4.184$ J for $(t'_2 - t'_1)$ °C rise in temperature

Total enthalpy change of the Calorimeter (beaker) and solution $= [W\,(t'_2 - t'_1) + (100 + W_1)\,(t'_2 - t'_1)] \times 4.184$ J

Heat liberated on dissolution of 1 g copper sulphate

$$= \frac{[W\,(t'_2 - t'_1) + (100 + W_1)\,(t'_2 - t'_1)] \times 4.184\ \text{J}}{W_1}$$

Since 1 mol of copper sulphate weighs 249.5 g. Therefore,

$$\Delta_{\text{Sol}}H \text{ of } CuSO_4.5H_2O = 249.5 \times \frac{[W(t'_2 - t'_1) + (100 + W_1)(t'_2 - t'_1)]\ 4.184}{W_1}\ \text{J mol}^{-1}$$

Result

Enthalpy change in the dissolution of copper sulphate/potassium nitrate is _______ Jmol^{-1}.

Precautions

(a) To record the temperature of water, use a thermometer with 0.1°C graduation.

(b) In the determination of calorimeter constant record the temperature of hot water just before mixing.

(c) Avoid using very large amounts of copper sulphate/potassium nitrate.

(d) Stir the solution well to dissolve the solid and record the temperature. Avoid too much stirring, it may produce heat due to friction.

(e) Weigh copper sulphate carefully as it is hygroscopic in nature.

(f) Use cotton wool to create insulation between the two beakers.

Discussion Questions

(i) What is meant by the term, calorimeter constant?

(ii) Why is $\Delta_{Sol}H$ for some substances negative while for others it is positive?

(iii) How does $\Delta_{Sol}H$ vary with temperature?

(iv) Will the enthalpy change for dissolution of same amount of anhydrous copper sulphate and hydrated copper sulphate in the same amount of water be the same or different? Explain.

(v) How will the solubility of copper sulphate and potassium nitrate be affected on increasing the temperature? Explain.

EXPERIMENT 3.2

Aim

To determine the enthalpy of neutralisation of a strong acid (HCl) with a strong base (NaOH).

Theory

A neutralisation reaction involves the combination of H^+(aq) ions furnished by an acid and OH^-(aq) ions furnished by a base, evidently leading to the formation of H_2O (l). Since the reaction envisages bond formation, therefore, this reaction is always exothermic. Enthalpy of neutralisation is defined as the amount of heat liberated when 1mol of H^+ ions furnished by acid combine with 1 mole of OH^- ions furnished by base to form water. Thus:

$$\underset{\text{(Acid)}}{H^+(aq)} + \underset{\text{(Base)}}{OH^-(aq)} \rightarrow H_2O\,(l), \quad \Delta_{neut}H \text{ is negative}$$

where $\Delta_{neut}H$ is known as enthalpy of neutralisation.

If both the acid and the base are strong then for the formation of 1 mol H_2O (l), always a fixed amount of heat, viz, 57 kJ mol^{-1} is liberated. If any one of the acid or the base is weak or if both of these are weak, then some of the heat liberated is used for the ionisation of the acid or base or both of them (as the case may be) and the amount of heat liberated is less than 57 kJ mol^{-1}.

B. Determination of Enthalpy of Neutralisation

(i) Take 100 mL of 1.0 M HCl solution in the calorimeter (beaker) and cover it with cardboard. In another beaker of 250 mL capacity take 100 mL of 1.0 M NaOH solution.

(ii) Note down the temperature of both the solutions, which is likely to be the same. Let it be t_1°C.

(iii) Pour 100 mL 1 M NaOH solution into the calorimeter containing 100 mL of 1.0 M HCl solution.

(v) Mix the solutions by stirring and note the final temperature of the mixture. Let it be t_2°C.

Calculate the enthalpy of neutralisation as follows:

(i) Note the rise in temperature of the mixture, which in this case is $(t_2 - t_1)$ °C.

(ii) Calculate the total amount of heat produced during the neutralisation process, using the following expression

Heat evolved = $(100 + 100 + W)\,(t_2 - t_1) \times 4.18$ J

(where W, is the calorimeter constant)

(iii) Finally calculate the heat evolved when 1000 mL of 1M HCl is allowed to neutralise 1000 mL of 1M NaOH. This quantity would be ten times the quantity obtained in step (ii).

(iv) Express the quantity of heat evolved in kJ mol^{-1}.

Result

Enthalpy change in the neutralisation of hydrochloric acid solution with sodium hydroxide solution ______ kJmol^{-1}.

Precautions

(a) Record the temperature carefully with the help of a thermometer graduated up to 0.1°C.

(b) Measure the volume of hydrochloric acid and sodium hydroxide solution to be taken for the experiment carefully.

(c) Proper insulation should be made between the two beakers.

(d) Avoid unnecessary and excessive stirring to prevent heating due to friction.

Discussion Questions

(i) Why do we calculate the heat evolved for the neutralisation of 1000 mL of a (1 M) acid by 1000 mL of a (1 M) monoacidic base?

(ii) In comparison to heat evolved in neutralisation reaction between a strong acid and a strong base. Why is lesser quantity of heat evolved when any one of the acid or the base is weak and still less when both are weak?

(iii) Why does the reaction: $H_2O\,(l) \qquad H^+(aq) + OH^-(aq)$ proceed in the forward direction with rise in temperature of the system?