

**Experiment 8****AIM**

To standardize  $KMnO_4$  using sodium oxalate.

**REQUIREMENTS**

(a) *Chemicals :*

- (i) Sodium oxalate solution (0.1 N),
- (ii) Potassium permanganate solution (approx. 0.1 N),
- (iii) Sulfuric acid (dilute).

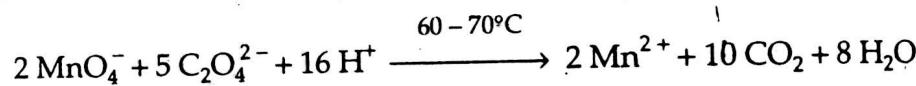
(b) *Apparatus :*

Burette, Pipette, Two beakers, Conical flask, Stand and clamp, Hot plate.

**THEORY**

Potassium permanganate is a secondary standard since it contains traces of manganese dioxide as impurity, therefore a solution of approximate normality is obtained when a definite weight of it is dissolved in definite volume of water.

Potassium permanganate is an oxidising agent and can be titrated against sodium oxalate at 60 – 70°C. Sodium oxalate solution of definite strength is taken in the conical flask and  $KMnO_4$  solution in the burette. From the volumes of sodium oxalate solution taken and  $KMnO_4$  used, normality of  $KMnO_4$  can be calculated.



In this equation,  $MnO_4^-$  (having  $Mn^{+7}$ ) is reduced to  $Mn^{2+}$  and oxalate ions are oxidised to  $CO_2$ .

*Indicator.*  $KMnO_4$  acts as self-indicator.

*End point.* Colourless to light pink.

*Detection of end point.* In dilute solution,  $KMnO_4$  has pink colour. During titration, potassium permanganate is reduced by sodium oxalate solution to nearly colourless manganous ions. When the whole of the reducing agent is consumed, the addition of even one extra drop of  $KMnO_4$  imparts pink colour to the solution. Thus,  $KMnO_4$  acts as self-indicator and no extra indicator is required.

**PROCEDURE**

- (i) Rinse the burette with  $KMnO_4$  solution and fill it with  $KMnO_4$  solution. Clamp this filled burette in stand and remove the air bubble, if any, from the burette tip by releasing some solution. Note the initial reading of burette by carefully observing the upper meniscus.
- (ii) Rinse the pipette with sodium oxalate solution and then take 10 mL of it in the pipette. Transfer this to the titration flask.
- (iii) Add approximately 10 mL of dilute  $H_2SO_4$  to the titration flask (which already has sodium oxalate solution) and heat to 60 – 70°C, so that the flask is just unbearable to touch on the back side of the hand.

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determines  
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sample of

determines  
water for  
EDTA n

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oxalate solution. If the result was correct. Otherwise repeat.

(vi) Repeat the steps (ii) to (v), till three concordant readings are obtained.

## OBSERVATIONS

Normality of sodium oxalate solution = 0.1 N.

Observation Table

Sr. No.	Volume of sodium oxalate solution taken (mL)	Burette readings		Volume of $KMnO_4$ solution used (mL)
		Initial	Final	
1.	10			
2.	10			
3.	10			
4.	10			

Concordant volume =  $x$  mL (let)

## CALCULATIONS

From the law of chemical equivalence,

$$N_1 V_1 \text{ of } KMnO_4 = N_2 V_2 \text{ of sodium oxalate}$$

$$\Rightarrow N_1 x = 0.1 \times 10 \quad \Rightarrow \quad N_1 = \frac{0.1 \times 10}{x} = \frac{1}{x} \text{ N}$$

$$\therefore \text{Normality of } KMnO_4 \text{ solution} = \frac{1}{x} \text{ N}$$

and strength of  $KMnO_4$  solution = Normality of  $KMnO_4 \times$  Eq. wt. of  $KMnO_4$

$$= \frac{1}{x} \times 31.6 = \frac{31.6}{x} \text{ gm/L.}$$

## RESULTS

The Normality of  $KMnO_4$  solution = .... N

and the strength of  $KMnO_4$  solution = .... gm/L.

## PRECAUTIONS

- Always take  $KMnO_4$  solution in the burette and use only glass stoppered burette because  $KMnO_4$  reacts with rubber.
- Carry out titration fast so that acidified, sodium oxalate solution does not become cold.
- Do not overheat the acidified sodium oxalate solution.
- Avoid using freshly prepared  $KMnO_4$  solution.

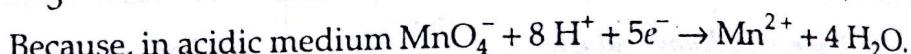
### GUIDELINES FOR THE PREPARATION OF SOLUTIONS

(i) Preparation of mixture of oxalic acid and sulphuric acid. Add 6.3 gm of oxalic acid and 3.0 mL of conc. sulphuric acid in distilled water and make up the volume to 1000 mL.

(ii) Preparation of 0.1 N NaOH solution. First make approx. NaOH solution ( $> 0.1$  N), standardize it with 0.1 N oxalic acid dihydrate solution and then dilute it with requisite amount of water. Also refer to page 40 for more details.

(iii) Preparation of 0.1 N  $\text{KMnO}_4$  solution.

- Molecular weight of  $\text{KMnO}_4$  is 158.03 and its equivalent weight is  $\frac{158.03}{5} = 31.606$ .



- Dissolve about 3.2 gm of  $\text{KMnO}_4$  crystals in 1 L of solution and standardize it with 0.1 N oxalic acid dihydrate solution. Then prepare 0.1 N  $\text{KMnO}_4$  by diluting with water.

(iv) Preparation of phenolphthalein indicator solution. Dissolve 1 gm of phenolphthalein in 100 mL of 95% alcohol.

### SAFETY FIRST

(i) Sodium oxalate. It is poison so avoid inhalation and ingestion. Avoid contact with skin and eye because it can be caustic. Avoid moisture areas.

(ii) Sulfuric acid. It can cause chemical burns that can seriously damage skin and eyes. Wear, gloves and avoid contact. Inhalation of the mist will cause severe irritation of the lungs and throat. Repeated exposure may lead to increased risk of developing cancer of the larynx.

(iii) Potassium permanganate  $\text{KMnO}_4$ . It can react violently with oxidizable materials. Keep it away from other chemicals and combustibles.

- Dry crystals and concentrated solutions are caustic, causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer.
- eye contact with crystals and concentrated solutions can cause severe damage, possibly permanent.
- If swallowed, may cause severe burns to mucous membranes, throat, esophagus and stomach and may be fatal.

Wear gloves, lab coat, boot to prevent skin contact.

Use chemical safety goggles and/or full face shield where dusting or splashing of solution is possible.

### CHEMICAL KNOWLEDGE

**Sodium oxalate.** Sodium oxalate has versatile applications viz.

- It is used in electroplating bath,
- It is used in metal cleaning preparations,
- It is used for metal extraction and separation,

- It is used in blue print coatings,
- It is used in manufacture of special cements,
- It is used in plant nutrition and disease control.
- It is used in leather and tanning industries.

### VIVA-VOCE

**Q. 1. What types of titrations are permanganate titrations ?**

Ans. Redox titration.

**Q. 2. Why do we heat the solution to  $60^{\circ} - 70^{\circ}$  C in case of oxalic acid vs  $\text{KMnO}_4$  titration ?**

Ans. The reaction between oxalic acid and  $\text{KMnO}_4$  is very slow. Thus, to increase the rate of reaction, heating is done.

**Q. 3. Can we heat the solution up to  $100^{\circ}$  C ?**

Ans. No, because oxalic acid may decompose to form  $\text{CO}_2$  and  $\text{CO}$ .

**Q. 4. Why is dil.  $\text{H}_2\text{SO}_4$  suitable for  $\text{KMnO}_4$  titration ?**

Ans.  $\text{KMnO}_4$  acts as a good oxidizing agent in acidic medium. If  $\text{H}_2\text{SO}_4$  is not used  $\text{KMnO}_4$  may be oxidized to  $\text{MnO}_2$  giving brown ppt.

**Q. 5. Can we use  $\text{HCl}$  or dil.  $\text{HNO}_3$  in  $\text{KMnO}_4$  titration ? Give reason.**

Ans. No.

(a) dil.  $\text{HNO}_3$  itself is a oxidizing agent.

(b)  $\text{HCl}$  gets oxidized to  $\text{Cl}_2$  by  $\text{KMnO}_4$  solution



**Q. 6. Why is  $\text{KMnO}_4$  solution not filtered through filter paper ?**

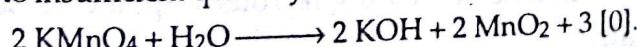
Ans.  $\text{KMnO}_4$ , being oxidizing agent, will oxidize organic matter of filter paper.

**Q. 7. Bottle containing  $\text{KMnO}_4$  solution develops a brown layer on glass. Why ?**

Ans. It is due to the formation of  $\text{MnO}_2$ .

**Q. 8. Sometimes a brown ppt. is observed in  $\text{KMnO}_4$  titrations. Why ?**

Ans. It is due to insufficient quantity of dil.  $\text{H}_2\text{SO}_4$ , brown ppt. of  $\text{MnO}_2$  is formed.



**Q. 9. Why does  $\text{KMnO}_4$  act as a self indicator ?**

Ans. When all the reducing agents have been oxidized, excess of  $\text{KMnO}_4$  imparts its pink colour to the solution.

**Q. 10. What is auto-catalyst in  $\text{KMnO}_4$  vs oxalic acid or sodium oxalate titration ?**

Ans.  $\text{Mn}^{2+}$  produced in the reaction catalyses the reaction, it is called auto catalyst.

**Q. 11. A burette used for  $\text{KMnO}_4$  becomes light brown in colour. How do we clean it.**

Ans. It is cleaned by washing well with dil.  $\text{FeSO}_4$  solution and then with water.

**Q. 12.  $\text{KMnO}_4$  can oxidize water also. Why do we take aqueous solution ?**

Ans. Oxidation rate of  $\text{H}_2\text{O}$  by  $\text{KMnO}_4$  is very slow. Hence, if solution is freshly prepared we can use aqueous solution.

**Q. 13. Can we prepare standard solution of  $\text{KMnO}_4$  directly ? If not, why ?**

Ans. No, we can't, because  $\text{KMnO}_4$  is moderately soluble in water. Moreover it cannot be obtained in perfectly pure state as it always contains traces of  $\text{MnO}_2$ . Its solution slowly decomposes when exposed to bright sun light, reducing gases etc. (However, decomposition can be prevented by storing in dark coloured bottles).

## **AIM**

*To determine ferrous iron in Mohr's salt by KMnO<sub>4</sub>.*

## **REQUIREMENTS**

(a) *Chemicals :*

- (i) KMnO<sub>4</sub> (0.1 N),
- (ii) Mohr's salt solution,
- (iii) H<sub>2</sub>SO<sub>4</sub> (dil.).

(b) *Glass-ware :*

Burette, Pipette, Two beakers, Conical flask.

(c) *Others :*

Stand and clamp, White tile or filter paper, Antiparallex card.

## **THEORY**

Mohr's salt is ferrous ammonium sulphate, FeSO<sub>4</sub> · (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6 H<sub>2</sub>O. It is a double salt. In it, iron is in + 2 oxidation state. When it is titrated with potassium permanganate, Ferrous ions are converted into ferric ions according to the following equation :



By knowing the normality of KMnO<sub>4</sub>, the normality and strength of ferrous iron in Mohr's salt can be estimated. This redox titration between Mohr's salt and KMnO<sub>4</sub> is done in cold because on heating ferrous sulphate present in the Mohr's salt gets oxidised by air.

## **PROCEDURE**

- (i) Rinse and fill the glass stoppered burette with 0.1 N KMnO<sub>4</sub> solution. Read the upper meniscus of solution and record it as initial reading.
- (ii) Pipette out 10 mL of Mohr's salt solution in a clean titration flask, and add about 10 mL of dil. H<sub>2</sub>SO<sub>4</sub>.
- (iii) Add the solution of KMnO<sub>4</sub> from burette, very slowly with constant swirling until a light pink tinge just appears. This is the end point. Check its accuracy by doing back titration. For this, add a drop of Mohr's salt solution, if the pink colour disappears, the end point is correct. Read the upper meniscus of the solution in burette and record it as final reading.
- (iv) Repeat steps (ii) and (iii), till three concordant readings are obtained.

Sr. No.	Volume of Mohr's salt solution taken (mL)	Burette readings		Volume of $KMnO_4$ solution used (mL)
		Initial	Final	
1.	10			
2.	10			
3.	10			
4.	10			

Concordant volume of 0.1 N  $KMnO_4$  solution used =  $y$  mL (let).

## CALCULATIONS

From the law of chemical equivalence,

$$N_1 V_1 \text{ of Mohr's salt solution} = N_2 V_2 \text{ of potassium permanganate}$$

$$\Rightarrow N_1 \times 10 = 0.1 \times y \Rightarrow N_1 = \frac{0.1 y}{10} = 0.01 y \text{ N}$$

$$\therefore \text{strength of ferrous iron in Mohr's salt} = 0.01 y \times 56 \text{ gm/L}$$

## RESULT

The strength of ferrous iron in Mohr's salt = ..... gm/L.

## PRECAUTIONS

- (i) Do not heat the acidified, Mohr's salt solution for its redox titration with  $KMnO_4$ .
- (ii) Add dil.  $H_2SO_4$  in sufficient quantity, otherwise a brown precipitate of hydrated manganese dioxide is formed so end point is not properly detected.

## SAFETY FIRST

(i)  $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$  (Mohr's Salt). May cause eye and/or skin irritation; if ingested, may cause gastrointestinal irritation with nausea, vomiting and diarrhea, inhalation may cause respiratory tract irritation, prolonged or repeated skin contact may cause dermatitis.

(ii)  $KMnO_4$ . Dry crystals and concentrated solutions are caustic, causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer.

- eye contact with crystals and concentrated solutions can cause severe damage, possibly permanent.
- If swallowed, may cause severe burns to mucous membranes, throat, esophagus and stomach and may be fatal.

Wear gloves, lab coat, boot to prevent skin contact.  
or full face shield where dusting or splash-

**Experiment 1****AIM**

To determine the amounts of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  in the given mixture of these two, provided 0.1 N  $\text{HCl}$

**REQUIREMENTS****(a) Apparatus**

Burette, Pipette, Two beakers, Titration flask, Stand with clamp.

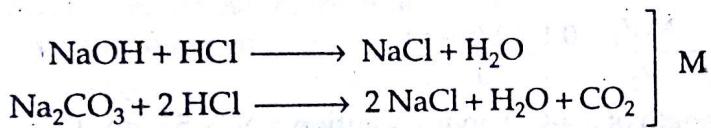
**(b) Chemicals**

- (i) A mixture of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  (Unknown strength).
- (ii)  $\text{HCl}$  (0.1 N).
- (iii) Phenolphthalein and methyl orange indicators.

**THEORY**

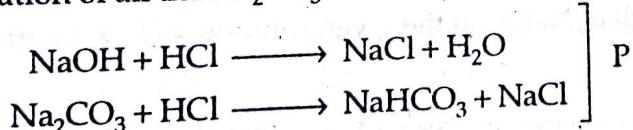
The determination of the strength of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  present in a solution is based on the selective use of indicators.

When unknown solution is titrated with standard  $\text{HCl}$ , using methyl orange indicator, the end-point corresponds to the complete neutralization of  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ .



Let the volume of 0.1 N  $\text{HCl}$  used using methyl orange indicator is  $x$  mL.

When unknown solution is titrated with standard  $\text{HCl}$ , using phenolphthalein indicator, the end-point corresponds to the neutralization of all the  $\text{NaOH}$  and partial neutralization of all the  $\text{Na}_2\text{CO}_3$  to the  $\text{NaHCO}_3$  stage :



Let the volume of 0.1 N  $\text{HCl}$  used, using phenolphthalein indicator is  $y$  mL.

Therefore, the volume of 0.1 N  $\text{HCl}$  used for complete neutralization of  $\text{Na}_2\text{CO}_3$  will be  $[2(x - y)]$  mL. And volume of 0.1 N  $\text{HCl}$  used for the neutralization of all the  $\text{NaOH}$  will be  $[x - 2(x - y)] = (2y - x)$  mL.

**PROCEDURE**

It involves the following steps :

1. *Using methyl orange as indicator.* Rinse and fill the burette with 0.1 N  $\text{HCl}$ . Pipette out 20 ml of alkali mixture solution into a conical flask. To it add 2 – 3 ml of methyl orange. Run  $\text{HCl}$  into the flask till the yellow colour of the solution changes to pink. Suppose the volume of the acid used is  $x$  ml.

2. *Using phenolphthalein as indicator.* Pipette out 20 ml of alkali mixture solution into a conical flask. To it add 2 – 3 drops of phenolphthalein. Run 0.1 N  $\text{HCl}$  from the burette into the flask till the pink colour of the solution changes to colourless. Suppose the volume of the acid used is  $y$  ml.

**OBSERVATIONS**

**Observation Table - I : (Using methyl orange as indicator) :**

S.No.	Volume of sample solution taken (ml)	Burette Reading		Volume of standard HCl solution used (ml)
		Initial	Final	

**Observation Table - II : (Using phenolphthalein as indicator) :**

S.No.	Volume of sample solution taken (ml)	Burette Reading		Volume of standard HCl solution used (ml)
		Initial	Final	

**CALCULATIONS**

(i) Let  $N_1$  be normality of HCl (given 0.1 N) and  $N_2$  be normality of  $\text{Na}_2\text{CO}_3$ .  
From the law of chemical equivalence,

$$N_1 V_1 \text{ of HCl} = N_2 V_2 \text{ of } \text{Na}_2\text{CO}_3$$

$$\Rightarrow N_2 = \frac{N_1 V_1}{V_2} = \frac{0.1 \times 2(x-y)}{20}$$

Hence, strength of  $\text{Na}_2\text{CO}_3$  in the solution =  $N_2 \times 53 \text{ gm/L}$ .

(ii)  $N_1' V_1'$  of HCl =  $N_2' V_2'$  of NaOH

$$\Rightarrow N_2' = \frac{N_1' V_1'}{V_2'} = \frac{0.1(2y-x)}{20}$$

Hence, strength of NaOH in the given solution =  $N_2' \times 40 \text{ gm/L}$ .

**RESULT**

The given mixture contains  $\text{Na}_2\text{CO}_3$  = ..... gm/L and NaOH = ..... gm/L.

**GUIDELINES FOR THE PREPARATION OF SOLUTIONS**

(i) Preparation of solution of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ . Dissolve about 5.3 gm of  $\text{Na}_2\text{CO}_3$  and about 8.4 gm of  $\text{NaHCO}_3$  in 1 L of distilled water.

(b) Preparation of 0.1 N HCl solution. (a) Measure 10 mL of conc. HCl (12 N) into a 1 L measuring flask. Pour 30 mL of distilled water and shake. Add more distilled water to make the solution upto the mark. Stopper the flask and shake vigorously.

(b) Rinse and fill the burette with the HCl prepared. Pipette out 10 mL of 0.1 N  $\text{Na}_2\text{CO}_3$  into a conical flask. To it add 2 drops of methyl orange as indicator. Run HCl from the burette into the flask till the colour of the solution changes from yellow to pink. Repeat the titration until at least three titrations give the same result.

## EXPERIMENTS

E.11

$$\text{As } N_1 V_1 \text{ of } \text{Na}_2\text{CO}_3 = N_2 V_2 \text{ of HCl}$$

$$\therefore 0.1 \times 10 = N_2 \times V_1 \Rightarrow N_2 (\text{HCl}) = \frac{0.1 \times 10}{V_1} = \frac{1}{V_1} \text{ N}$$

suppose, you want to make 1 L (or 1000 mL) of 0.1 N HCl, then for dilution of the conc. acid,

$$1000 \text{ mL of } 0.1 \text{ N HCl} \equiv V_2 \text{ mL of } \left( \frac{1}{V_1} \text{ N} \right) \text{ HCl}$$

$$\Rightarrow 1000 \times 0.1 = V_2 \times \frac{1}{V_1} \Rightarrow 100 V_1 = V_2$$

(c) Thus, take  $100 V_1$  of the HCl (prepared in step (a)) in 1 L measuring flask and make the volume upto 1 L by adding distilled water. This gives you 0.1 N HCl (1 L).

(iii) Preparation of indicator solutions. (a) Phenolphthalein. Dissolve 1 gm of phenolphthalein in 100 mL of 95% alcohol.

(b) Methyl orange. Dissolve 20 mg of methyl orange in 100 mL of hot water. Allow to cool and filter if necessary.

## SAFETY FIRST

1.  $\text{Na}_2\text{CO}_3$ . Causes severe eye irritation on exposure, repeated skin contact may cause dermatitis in individuals with sensitive skin. If ingested, causes irritation of the mucous membranes of the mouth, throat, stomach, and digestive tract. Hence, avoid eye and skin contact.

2.  $\text{NaHCO}_3$ . Inhalation of high conc. of dust may cause sneezing and coughing, if ingested in large doses, may cause gastrointestinal disturbance, contact with eye may cause mild irritation, redness and pain.

## VIVA-VOCE

Q. 1. (a) What do you mean by alkalinity of water? (b) How alkalinity is estimated?

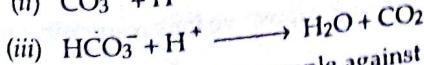
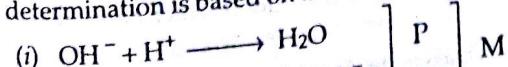
Ans. (a) By alkalinity of water we mean the total content of those substances in it which causes an increased concentration of hydroxide ion's upon dissociation or due to hydrolysis.

The alkalinity of water is attributed to the presence of the : (i) caustic alkalinity (due to

$\text{OH}^-$  to  $\text{CO}_3^{2-}$  ions), and (ii) temporary hardness (due to  $\text{HCO}_3^-$  ions).

(b) These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicators.

The determination is based on the following reactions:



The titration of the water sample against a standard acid upto phenolphthalein end-point (P) marks the completion of reactions (i) and (ii) only. This amount of acid used thus corresponds to hydroxide plus one-half of the normal carbonate present.

On the other hand, titration of the water sample against a standard acid to methyl orange end-point (M) marks the completion of reactions (i), (ii) and (iii). Hence the total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonate and carbonate ions).

ity of  $\text{Na}_2\text{CO}_3$ .

L.

..... gm/L

about 5.3 gm of

HCl (12 N) into

and more distilled

take vigorously.

at 10 mL of 0.1 N

indicator. Run

on changes from

readings are

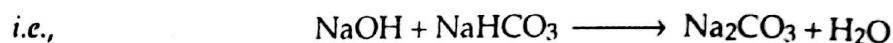
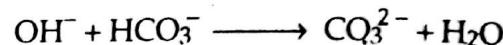
 $\text{Na}_2\text{CO}_3$  solution

Q. 2. Why  $\text{OH}^-$  and  $\text{HCO}_3^-$  ions cannot exist together in water?

Or

Why  $\text{OH}^-$  and  $\text{HCO}_3^-$  ions cannot exist together in water?

**Ans.** The possibility of  $\text{OH}^-$  and  $\text{HCO}_3^-$  together is ruled out, because of the fact that they combine instantaneously to form  $\text{CO}_3^{2-}$  ions.



Thus,  $\text{OH}^-$  and  $\text{HCO}_3^-$  ions cannot exist together in water.

On the basis of same reasoning, all the three ( $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ) cannot exist together.

Q. 3. What are the drawbacks of using highly alkaline water?

**Ans.** Drawbacks of using highly alkaline water are

(a) It may lead to caustic embrittlement,

(b) It may lead to deposition of precipitates and sludges in boiler tubes and pipes.

Q. 4. What is caustic embrittlement and what are its drawbacks?

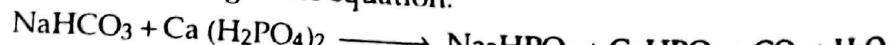
**Ans.** It is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. It is caused by the use of alkaline water in high pressure boilers. Stressed parts like bends, joints, rivets etc. are more prone to embrittlement so caustic embrittlement may even cause failure of the boiler.

Q. 5. What are the Disadvantages of Scale formation?

**Ans.** Wastage of fuel, lowering of boiler safety, decrease in efficiency and danger of explosion.

## CHEMICAL KNOWLEDGE

1. **Sodium Bicarbonate ( $\text{NaHCO}_3$ ).** Sodium bicarbonate is also known as *baking soda*. In place of baking soda alone, baking powders are generally used as leavening agents. This is due to the thermal decomposition of  $\text{NaHCO}_3$ , some sodium carbonate is formed which has an unpleasant taste. That's why, anhydrous monocalcium phosphate is added to baking powder to completely decompose the sodium bicarbonate. When the powder is moistened,  $\text{CO}_2$  gas is liberated according to the equation.



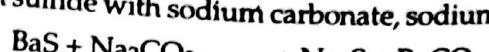
Baking powder contains about 28% baking soda ( $\text{NaHCO}_3$ ), enough acid such as anhydrous monocalcium phosphate, and 20 – 40% corn starch or flour filler. The filler is added to improve distribution in the dough and to prevent advance reaction between the acid and the  $\text{NaHCO}_3$ . About 20%  $\text{NaAl}(\text{SO}_4)_2$  is also added which slows down the reaction for the liberation of  $\text{CO}_2$ .

2. **Sodium Carbonate.** Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is also known as '*Washing soda*'.

(i) It is used to precipitate most of the di-and tripositive ions responsible for hardness of water.

For example, calcium ions ( $\text{Ca}^{2+}$ ) form insoluble carbonates, and Ferric ions ( $\text{Fe}^{3+}$ ) precipitate out as ferric hydroxide ppt. using  $\text{OH}^-$  produced by the reaction of carbonate with water :  $\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$ .

(ii) By treating barium sulfide with sodium carbonate, sodium sulfide ( $\text{Na}_2\text{S}$ ) is produced.



Sodium sulfide is used in the leather industry for the removal of hair from hides (*i.e.*, as a depilatory).

Synthetic rubber, thiokol, is made from sodium polysulfide, a derivative of sodium sulfide.

(iii) Sodium carbonate is also used in glass industry for making glass bottles, sheets and fibre.

(iv) It is also used for making paper, soap and detergents.

(v) The increased awareness of the effect of 'acid rain' on buildings & plants has led to a new use for  $\text{Na}_2\text{CO}_3$  in treating the flue gases from coal and oil-fired power stations.

## Experiment 2

~~KMnO<sub>4</sub>~~ pain, severe burns, broach stains in the contact area with possible discolouring or ulcer skin layer.

- Eye contact with crystals and concentrated solutions can cause severe damage, possibly permanent.
- If swallowed, may cause severe burns to mucous membranes, throat, esophagus and stomach and may be fatal.

∴ wear gloves, lab coat, both to prevent skin contact.  
use chemical safety goggles and / or full face shield where dusting or splashing of solution is possible.

## Experiment 13

### AIM

To determine dissolved oxygen in the given sample of water.

### REQUIREMENTS

#### (a) Apparatus

Stoppered bottle (250 mL), Burette, Conical flask, Pipette, Dropper.

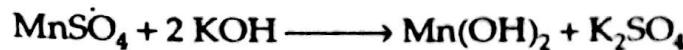
#### (b) Chemicals

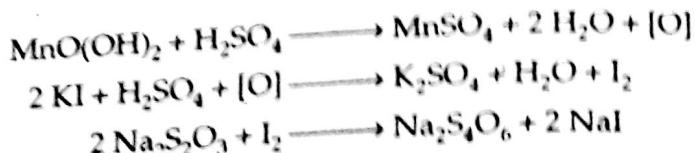
- |                                |                                 |
|--------------------------------|---------------------------------|
| (i) Manganese sulphate,        | (ii) Alkaline KI solution,      |
| (iii) Conc. HCl,               | (iv) Hypo solution (N/100), and |
| (v) Starch indicator solution. |                                 |

### THEORY

5 to 7 ppm of dissolved oxygen is present in unpolluted water and is a must for supporting aquatic lives. In presence of a good amount of dissolved oxygen (> 8 ppm), aerobic bacteria lead to oxidation of organic compounds present in water. This kind of oxidation is called 'aerobic oxidation'. But if the dissolved oxygen is (< 5 ppm), anaerobic oxidation of organic compounds present in water takes place by anaerobic bacteria. If the water is polluted with large amount of organic matter, a large amount of dissolved oxygen is rapidly consumed in the biological aerobic oxidation. The decrease in the dissolved oxygen in turn decreases the population of aquatic life.

Dissolved oxygen is usually determined by Winkler's method. It is based on the fact that dissolved oxygen oxidises potassium iodide (KI) to iodine. The liberated iodine is titrated against standard sodium thiosulphate (also known as hypo) solution using starch as indicator. Since dissolved oxygen in water is in the molecular state, it as such cannot oxidise KI. Hence, manganese hydroxide is used as an oxygen carrier to bring about the reaction between KI and oxygen. Manganese hydroxide, in turn, is obtained by the action of KOH on manganese sulphate ( $MnSO_4$ ).



**PROCEDURE**

1. Take 250 mL of sample water in a bottle avoiding as far as possible contact with air.
2. Immediately add 2 mL of manganous sulphate solution and 2 mL of alkaline KI solution.
3. Stopper the bottle and shake the contents thoroughly. Allow the brown precipitate of  $\text{MnO(OH)}_2$  to settle down.
4. Add 2 mL of concentrated HCl when the precipitate is settled. Shake the bottle until the precipitate has completely dissolved.
5. Allow the solution to stand for 5 minutes.
6. Take 100 mL of this solution and titrate against N/100 hypo solution. Until the solution becomes pale yellow. Add 2 mL of starch indicator, the solution will turn blue. Continue titration till you get the end point.

*End Point.* Disappearance of blue colour.

**SAFETY FIRST**

(i) **Hydrochloric acid.** It is poisonous and corrosive. Contact or inhalation can cause severe damage to the eyes, skin, and respiratory tract. Wear gloves and dispense under a hood ; avoid contact and do not breathe the vapours.

(ii)  **$\text{Na}_2\text{S}_2\text{O}_3$ .** A mild eye irritant  $\Rightarrow$  Preferably wear safety glasses.

- Harmful by inhalation of  $\text{Na}_2\text{S}_2\text{O}_3$  dust,
- If swallowed, may cause gastric irritation.
- Decomposes on heating emitting noxious fumes of  $\text{SO}_2$  (a highly toxic gas) high concentration of which causes respiratory paralysis.
- On contact with acids,  $\text{Na}_2\text{S}_2\text{O}_3$  liberates  $\text{SO}_2$  which is a highly toxic gas.

**OBSERVATIONS**

Normality of hypo solution ( $N_2$ ) = 1/100 N

Volume of sample water taken for titration ( $V_1$ ) = 100 mL

*Observation Table*

S.No.	Volume of sample solution taken (ml)	Burette Reading		Volume of standard hypo solution used (ml)
		Initial	Final	

Let  $V_2$  mL of hypo solution is used for titration.

RINK CHEMISTRY

EXPERIMENTS

CALCULATIONS

1.87

$$\text{Normality of sample water } (N_1) = \frac{N_2 V_2}{V_1} \Rightarrow N_1 = \frac{\frac{1}{100} \times V_2}{100} = \frac{V_2}{10,000} \text{ Normal}$$

Since, equivalent weight of  $O_2 = 8$

Hence, strength of oxygen =  $N_1 \times 8 \text{ gm/L}$

$$= \frac{V_2}{10,000} \times 8 \text{ gm/L} = \frac{V_2}{10,000} \times 8 \times 1000 \text{ (mg/L or ppm)}$$

$\Rightarrow$  Amount of dissolved oxygen =  $0.8 V_2 \text{ ppm}$ .

### RESULT

The amount of dissolved oxygen was found to be ....ppm.

### PRECAUTIONS

- No bubble should be there in the stoppered bottle. Because, if present, the oxygen of air present inside the bubble will also take part in the reaction and this will lead to high value of dissolved oxygen.
- Avoid air contact while introducing the reagents in the bottle.
- As far as possible, the sample should not be allowed to come in contact with air.

### GUIDELINES FOR THE PREPARATION OF SOLUTIONS

(i) Preparation of  $MnSO_4$  solution. Dissolve 50 gm of it in distilled water and make up the volume to 1 L.

(ii) Preparation of  $N/100 Na_2S_2O_3 \cdot 5 H_2O$  solution. Dissolve 2.482 gm of hydrated sodium thiosulphate in distilled water and make up the volume to 1 L.

(iii) Preparation of alkaline potassium iodide reagent solution. Dissolve 20 gm KI, 40 gm NaOH in distilled water and make up the volume to 100 mL.

(iv) Preparation of starch indicator solution.

(a) Prepare a paste of 1 gm of starch (sodium starch glycollate) with water.

(b) Add it gradually to 100 mL of boiling water with constant stirring.

(c) Boil it for a minute and then cool it before use.

Note. A fresh starch solution should always be used or about 2 mL of mercuric chloride should be added as preservative.

### VIVA-VOCE

Q. 1. Discuss the factors which affect the solubility of oxygen in water.

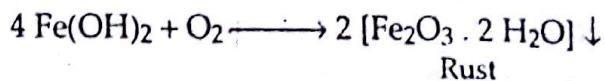
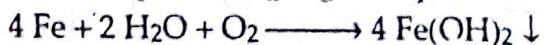
Ans. (a) Temperature. The solubility of oxygen in water decreases with increase in temperature. For example, the solubility of oxygen of air in fresh waters (with low salt concentration) decreases from 14.5 ppm at  $0^\circ\text{C}$  to about 7.5 ppm at  $30^\circ\text{C}$ .

(b) Concentration of impurities. The solubility of dissolved  $O_2$  in water decreases with increase in the concentration of impurities. For example,  $O_2$  is soluble in saline water to less extent.

Q. 2. With the help of an example, explain why the determination of dissolved  $O_2$  is important for industrial purposes.

Ans. Dissolved oxygen is the most usual corrosion causing factor in boilers. Oxygen is introduced in boilers through the raw water supply. Water usually contains about 8 ppm of

dissolved oxygen at room temperature. As the water is heated, the dissolved oxygen is set free and the boiler starts corroding. Dissolved oxygen reacts with the iron of boiler in presence of water and under prevailing high temperature to form ferric oxide rust.

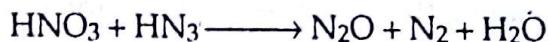


The disadvantages of boiler corrosion are :

Shortening of boiler life ; Leaks of the joints and rivets ; and increased cost of repairs and maintenance. So, to overcome these difficulties, removal of dissolved oxygen is necessary. And this removal of dissolved oxygen is done either by mechanical deaeration or by adding hydrazine ( $\text{N}_2\text{H}_4$ ) or sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) or sodium sulphide ( $\text{Na}_2\text{S}$ ).

**Q. 3. Discuss (a) Alsterberg's modification and (b) Rideat-Stewart modification of Winkler's method of dissolved oxygen determination.**

**Ans. (a) Alsterberg's modification.** If some oxidising agents like nitrite and ferric ions are present in water, they will oxidize  $\text{I}^-$  to  $\text{I}_2$  and give positive error. To overcome this difficulty, Alsterberg's modification is done in the Winkler's method. In this, sodium azide is used in alkaline iodide solution to decompose the nitrite or sulphite.



**(b) Rideat-stewart modification.** If some reducing agents like  $\text{Fe}^{2+}$ ,  $\text{SO}_3^{2-}$  or  $\text{S}^{2-}$  are present in water, they will reduce  $\text{I}_2$  to  $\text{I}^-$  and produce negative error. To overcome this problem,  $\text{KMnO}_4$  is used for pre-treatment in this Rideat-Stewart modification. Excess of  $\text{KMnO}_4$  is removed by reaction with potassium oxalate.

**Q. 4. How the dissolved oxygen test is helpful in determining the pollution extent of sewage or any other pollutant ?**

**Ans.** For aerobic biological activities in water, dissolved oxygen is necessary. In the absence of sufficient amount of dissolved oxygen in water, the anaerobic degradation of the pollutants make the water foul smelling. Thus, in determining the pollution extent, dissolved oxygen test is helpful.

### DO YOU KNOW !

Worldwide every 90 seconds, 1000 kg steel are converted into rust.

### Experiment 14

1. What improvements in the procedure are required to estimate the percentage of calcium in lime-stone or dolomite?
2. Why is it necessary to wash the precipitate of calcium carbonate with water? What is the role of  $\text{Cl}^-$  and  $\text{COO}^-$  ions?
3. Why do we heat the solution to  $70^\circ\text{C}$  in case of oxalic acid Vs.  $\text{KMnO}_4$  titrations?
4. What is the significance of estimation of calcium in lime-stone or dolomite?

## Experiment 4

### AIM

To determine the percentage of available chlorine in a given sample of bleaching powder.

### REQUIREMENTS

#### (a) Apparatus

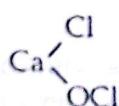
Burette, pipette, measuring flask, weighing bottle.

#### (b) Chemicals

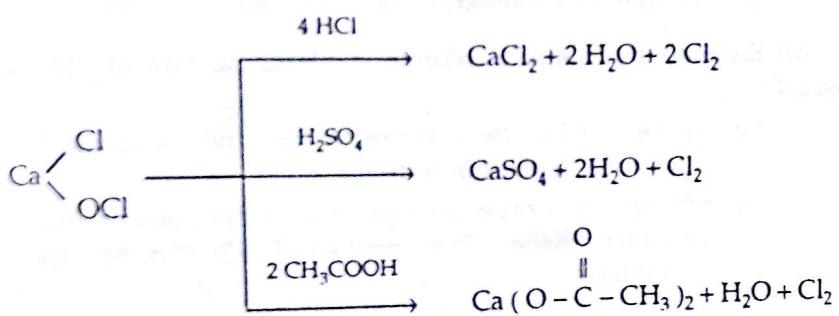
- |                            |  |
|----------------------------|--|
| (i) Bleaching powder,      | (ii) Potassium iodide,                 |
| (iii) Glacial acetic acid, | (iv) Sodium thiosulphate solution, and |
| (v) Starch solution.       |  |

## THEORY

Bleaching powder is famous for its bleaching action. It is also used as disinfectant. The main constituents of bleaching powder are calcium hypochlorite [ $\text{Ca(OCl)Cl} \cdot 4\text{H}_2\text{O}$ ], basic calcium chloride [ $\text{CaCl}_2\text{Ca}(\text{OH})_2\text{H}_2\text{O}$ ] and some free calcium hydroxide  $\text{Ca}(\text{OH})_2$ . Out of these constituents, the active constituent of bleaching powder is hypochlorite. Calcium hypochlorite,  $\text{Ca(OCl)Cl}$ , may be represented as

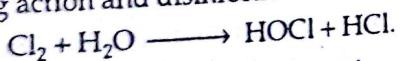


when dilute acid reacts with bleaching powder then free chlorine is liberated, according to one of the following reactions :

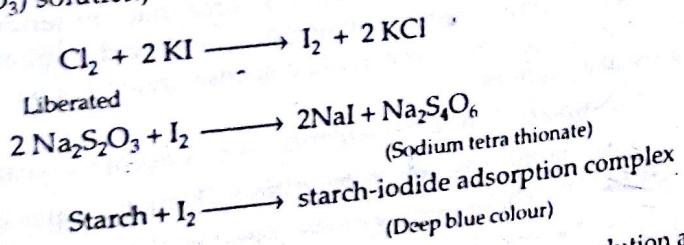


The amount of chlorine that can be obtained by the action of dilute acid on bleaching powder is known as **available chlorine**. It is expressed in percentage weight of bleaching powder.

The liberated chlorine in water forms hypochlorous acid ( $\text{HOCl}$ ) which is responsible for bleaching action and disinfection.



The available chlorine is estimated by iodometric method. In this method, a suspension of bleaching powder is treated with dilute acid in the presence of  $\text{KI}$  solution. The liberated chlorine from bleaching powder sets free an equivalent amount of iodine from  $\text{KI}$ , which is titrated against hypo solution (i.e., sodium thiosulphate,  $(\text{Na}_2\text{S}_2\text{O}_3)$  solution)



All such titrations in which liberated iodine is titrated with hypo solution are known as **iodometric titrations**. In such titrations, freshly prepared starch solution is used as indicator.

**PROCEDURE**

- (i) First prepare the bleaching powder solution by the following method :
- Weigh about 2 – 5 gms of bleaching powder in a clean and pre-weighed weighing bottle.
  - Transfer it into a mortar, crush with pestle and add little water.
  - Make a thin paste of the powdered bleaching powder sample with water.
  - Transfer the paste into 250 mL volumetric flask using small quantities of water.
  - Wash the mortar and pestle with distilled water. Now transfer the water (used for washing) to volumetric flask.
  - After transferring all the bleaching powder to volumetric flask, add more water to make the solution upto the mark.
  - Shake, until a homogeneous suspension is obtained.

(ii) Estimate the available chlorine in bleaching powder by the following method :

- Fill the clean burette, after rinsing, with hypo solution. Note down the initial reading of the burette.
- Similarly, first rinse the pipette with the homogeneous solution of bleaching powder. Then transfer 25 mL of it, by pipetting out, in conical flask.
- Add about 20 mg KI crystals or 10 mL of KI solution and about half test tube of glacial acetic acid. Solution turns brown.
- Titrate the liberated iodine against sodium thiosulphate (hypo) solution till a light yellow colour persists.
- Now add 5 – 10 drops of freshly prepared starch solution. Solution turns to blue or violet colour.
- Continue adding hypo solution till blue colour disappears. This is the end point. Note down the total volume of hypo solution added.
- Repeat the same procedure of titration to get concordant readings.

*End point : Disappearance of blue colour.*

**SAFETY FIRST**

- Acetic acid.** It causes chemical burns that can seriously damage skin and eyes. Its vapours are highly irritating to the eyes and respiratory tract. Wear nitrile gloves, safety glasses or face mask.

## EXPERIMENTS

**OBSERVATIONS**

(a) Weight of empty weighing bottle =  $w_1$  gm.

(a) Weight of weighing bottle with bleaching powder =  $w_2$  gm.

Weight of bleaching powder =  $(w_2 - w_1)$  gm.

(b) Titration of bleaching powder sample with standard sodium thiosulphate (hypo) solution.

S.No.	Volume of bleaching powder solution taken (ml)	Burette Reading		Volume of hypo solution consumed (ml)
		Initial	Final	
1.	25			
2.	25			
3.	25			
4.	25			

Let the volume of hypo solution consumed for 25 mL bleaching powder solution =  $V_H$  (mL)

## CALCULATIONS

(a) Calculation of Normality and strength of bleaching powder :

### From the Law of chemical equivalents,

$$\Rightarrow N_2 = \frac{N_1 V_1}{V_2} = \frac{N_1 V_H}{25} \text{ Normal}$$

$$(b) \text{As Na}_2\text{S}_2\text{O}_3 \equiv \text{Cl}_2 \equiv \text{CaOCl}_2$$

(b) As  $\text{Na}_2\text{S}_2\text{O}_3 = \text{S}_2\text{O}_3^{2-} + 2\text{Na}^+$   
Available chlorine (Amount of chlorine per litre of solution)

$$= N_2 \times 35.5 \text{ gm/Litre}$$

(c) Percentage of available chlorine

$$= (N_2 \times 35.5) \times \frac{250}{1000} \times \frac{1}{(w_2 - w_1)} \times 100$$

## RESULT

**RESULT** The percentage of available chlorine in a given sample of bleaching power  
= ..... %

## **PRECAUTIONS**

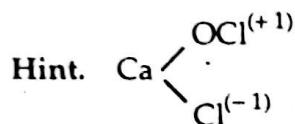
- (a) Use distilled water in the titration.  
(b) All the reagents should be freshly prepared.  
(c) The volume of starch indicator should be same in all the titrations.  
(d) Use neat and clean glass apparatus.

VIVA-VOCE

- VIVA-VOCE**

1. What do you mean by available chlorine in bleaching Powder?

2. Give the names of main constituents of bleaching powder.
  3. What is iodometric titration ?
  4. Describe, briefly, the method of estimation of available chlorine in bleaching powder.
  5. Which indicator is used in this experiment and what was the end point ?
  6. Write the chemical equations of the estimation of available chlorine in bleaching powder.
  7. Discuss the role of bleaching powder in disinfection of water.
  8. What is starch ?
- Ans.** Starch is a polysaccharide with general formula  $(C_6H_{10}O_5)_n$ .
9. Generally percentage of chlorine in a standard sample of bleaching powder is 36 – 39 %. (True or False).
- Ans.** True.
10. What is the oxidation state(s) of chlorine in bleaching powder ?



## CHEMICAL KNOWLEDGE

### IODINE

**Preparation.** Natural brine contains 50 – 100 ppm of  $I^-$ . It is treated with  $Cl_2$  to oxidize  $I^-$  ions to  $I_2$ . After oxidation with  $Cl_2$ , the solution is passed through an ion-exchange resin. The  $I_2$  is adsorbed on the column as the triiodide ion ( $I_3^-$ ), and finally it is removed from the resin by treatment with alkali.

**Applications.** (i) Small amounts of iodine are required in the human diet, so traces (10 ppm) of  $NaI$  are added to table salt. Deficiency of iodine causes the disease goitre.

(ii)  $KI$  is added to animal and poultry feeds.

(iii) Iodine is also used as antiseptic ; **tincture of iodine** is an aqueous solution of  $I_2$  in  $KI$ , and **French iodine** is a solution of  $I_2$  in alcohol.

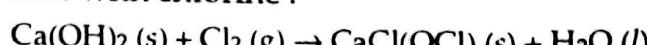
(iv) **Laboratory uses.** (a) In volumetric analysis, iodides and iodates are used ; and (b) Nessler's reagent  $K_2[HgI_4]$  is used to detect ammonia.

(v) **Compounds.** (a) Iodoform ( $CHI_3$ ), used as antiseptic ; (b) Silver iodide ( $AgI$ ) is used for photographic films, and for seeding clouds to produce rain.

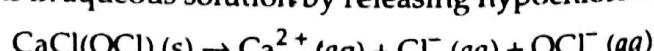
### DO YOU KNOW !

#### Bleaching powders

The Scottish Chemist Charles Tennant made bleaching powder in 1799 by saturating slaked lime with chlorine :



Bleaching powder acts in aqueous solution by releasing hypochlorite ion ( $OCl^-$ )



..... sodium salt of

(ii) Hydrochloric acid - It can cause severe damage to the eyes, skin, and respiratory tract. Wear gloves and dispense under a hood; avoid contact and do not breathe the vapours.

(iii) **Methanol.** It is flammable and harmful if ingested, inhaled, or absorbed through the skin. Avoid contact with the liquid and do not breathe its vapours.

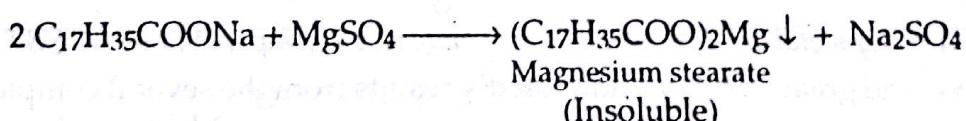
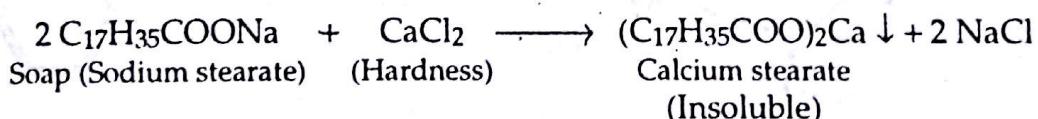
VIVA-VOCE

**O. 1. (a) What is hardness? (b) Why it is due to? (c) Why soaps are not effective in hard water?**

**Ans. (a)** Hardness in water is that characteristic, which "prevents the lathering of soap". Originally it was defined as the soap consuming capacity of water sample.

(b) This is due to presence in water of certain salts of Ca, Mg and other heavy metal ions like  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  dissolved in it.

(c) A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand, forms insoluble white scum or precipitate which do not possess any detergent action. This is due to the formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are shown below :

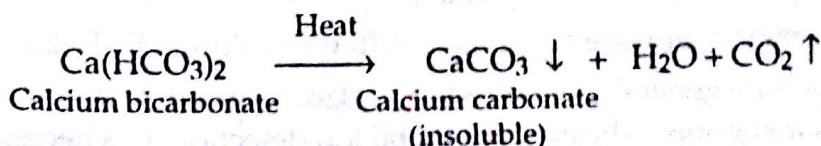


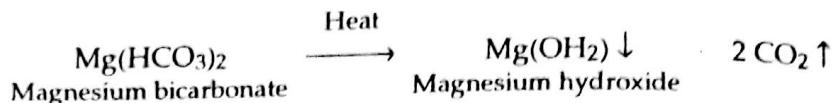
**Q. 2. Differentiate between temporary and permanent hardness.**

**Ans. Temporary Hardness.** (a) Temporary hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron.

Thus, the salts responsible for temporary hardness are  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ .

(b) Temporary hardness can be largely removed by mere boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.



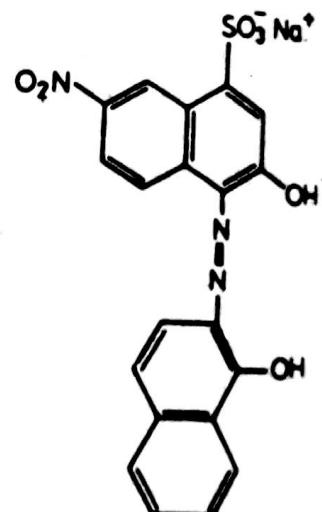
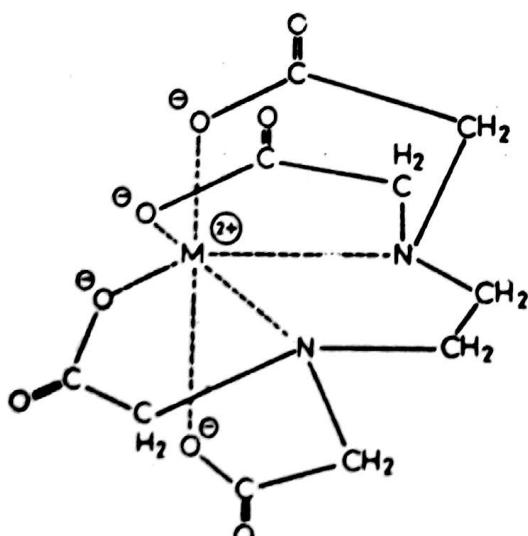
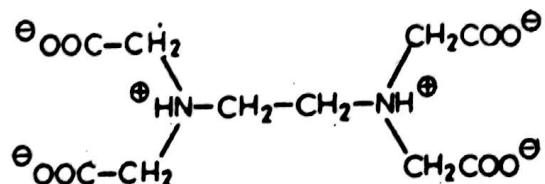


**Permanent Hardness.** (a) It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Hence, the salts responsible for permanent hardness are :  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$  etc.

(b) Unlike temporary hardness, permanent hardness is not destroyed on boiling.

**Q. 3.** Give the structures of : (a) EDTA (dianion form). (b)  $M^{2+}$  - EDTA chelate.  
 (c) Eriochrome black-T (EBT).

Ans.

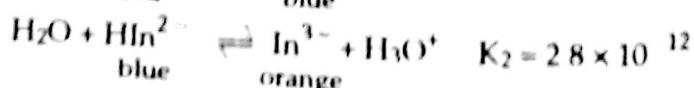
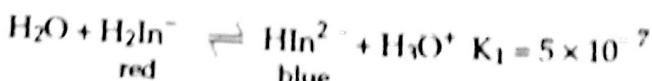


**Q. 4. Why metal-EDTA complexes are more stable compared to metal-FBT complexes?**

**Ans.** The great stability undoubtedly results from the several complexing sites within the molecule that give rise to a cage like structure in which the cation is effectively surrounded and isolated from solvent molecules.

**Q. 5. What is the role of a buffer solution in complexometric titrations?**

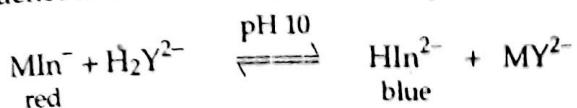
**Ans.** EBT contains a sulfonic acid group, which is completely ionized in water and two phenolic groups that only partially ionize. Its behaviour as a weak acid is described by the equations



The acids and their conjugate bases have different colours. EBT also forms complexes with metal ions which are generally wine-red, as is  $\text{H}_2\text{In}^+$ . Thus, EBT behaves as an acid/base indicator as well as metal-ion indicator. For metal ion detection, it is necessary to adjust the

## EXPERIMENTS

pH on the basic side so that the blue form of the species,  $\text{HIn}^{2-}$ , predominates in the absence of a metal ion. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is wine-red. With the first slight excess of EDTA, the solution turns blue as a consequence of the reaction (buffered at pH 10) :



**Q. 6. What is the principle of EDTA titrations ?**

**Ans. Principle of EDTA titrations.** The quick, complete and 1 : 1 interaction of metal ions with EDTA leading to the formation of stable complex is the basis of complexometric titrations.

**Q. 7. (a) What are the advantages of EDTA method for hardness determination ?**

**(b) What is the significance of hardness determination ?**

**Ans. (a) Advantages of EDTA method.** Advantages of EDTA method for hardness determination are its greater accuracy, convenience and more rapid procedure.

**(b) Significance of hardness determination.** The determination of hardness is a useful analytical test that provides a measure of the quality of water for household and industrial uses. The test is particularly important to industry because when hard water is heated, it precipitates calcium carbonate, which then clogs boilers and pipes.

**Q. 8. Why it is dangerous to pipette out a buffer solution with mouth ?**

**Solution.** Biochemical reactions, in particular, require maintenance of definite pH values. Normal human blood has a pH of about 7.4. Ordinarily variations are very small and an increase or decrease of as much as 0.4 pH unit is likely to be fatal and show pathological conditions such as diabetic, coma etc. Because of this risk, it is never recommended to pipette out a buffer solution with mouth.

**Q. 9. Why eriochrome black-T Indicator should be used in basic medium ( $\text{pH} = 7 - 11$ ) .**

**Ans.** Because in strongly acidic solutions ( $\text{pH} < 6.5$ ). It tends to polymerize to a red brown product.

**Q. 10: What are the colours of eriochrome, black-T in different pH ranges ?**

pH range	Ionic form of indicator	Colour of indicator
< 5.5	$\text{H}_2\text{In}^-$	Red
7 - 11	$\text{HIn}^{2-}$	Blue
> 11.5	$\text{In}^{3-}$	Yellowish orange

## DO YOU KNOW !

BIOLOGICAL ROLE OF  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ 

$\text{Mg}^{2+}$  ions are concentrated in animal cells, and  $\text{Ca}^{2+}$  ions are concentrated outside the cell, in the body fluids.

$\text{Mg}^{2+}$  ions form a complex with ATP, and are constituents of phosphotransferases and phosphohydrolases, which are enzymes for reactions involving ATP and energy release. They are also essential for the transmission of impulses along nerve fibers.  $\text{Mg}^{2+}$  is important in chlorophyll, in the green parts of plants.

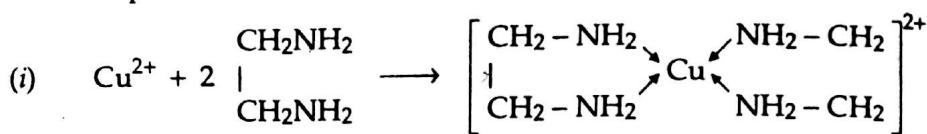
$\text{Ca}^{2+}$  is important in teeth and bones as  $\text{Ca}_3(\text{PO}_4)_2$ , and the enamel on teeth as fluoroapatite  $[3(\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2)]$ .  $\text{Ca}^{2+}$  ions are also important in blood clotting. Moreover,  $\text{Ca}^{2+}$  ions are required to trigger the contraction of muscles and to maintain the regular beating of the heart.

## CHELATION AND ITS APPLICATIONS

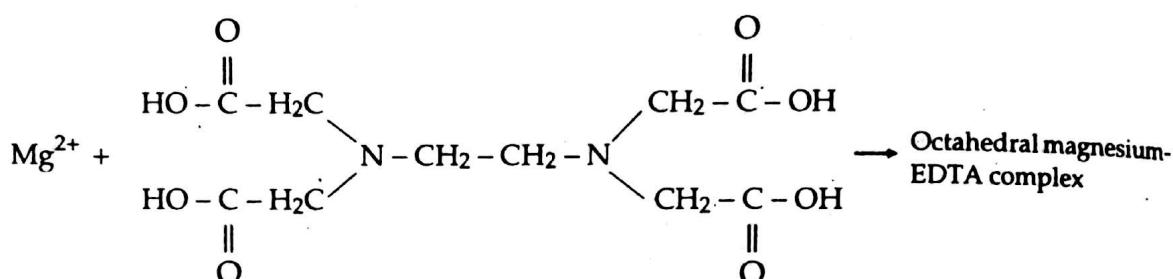
Complexes with polydentate ligands are referred to as chelates (after the Greek word for claw), since polydentate ligands surround the metal atom by attaching themselves at several points. In other words, more than one atom in the ligand is bonded to the central metal.

The phenomenon of the formation of chelates is termed as *chelation*.

For example :



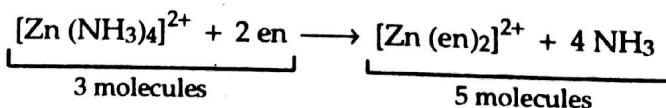
(ii)



Chelates are often much more stable than monodentate complexes due to following reasons :

- (i) Dissociation of chelate complex involves breaking more bonds rather than one,
- (ii) In some complexes like of acetylacetone and porphyrin, where ligands contain a system of alternate double and single bonds; electron density is delocalized and spread over the ring,
- (iii) Chelation always results in the increase in the number of molecules where the total system is less organized.

For example :



An increase in disorder or randomness, is accompanied by positive entropy change.

We know that  $\Delta G = \Delta H - T \Delta S$ ,

$\Delta H$  is positive so  $\Delta G$  will be negative when  $\Delta S$  is large positive number. This is found to be so.

### Applications of Chelation :

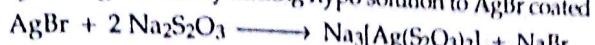
(i) *In medicines.* Metal poisoning by lead, copper, iron, chromium and nickel results in these materials forming unwanted complexes, thus preventing normal metabolism. That's why dermatitis from Cr or Ni salts is treated with EDTA cream.

Lead and copper poisoning are treated by drinking an aqueous solution of Ca-EDTA complex. EDTA complexes with the unwanted Pb or Cu ions.

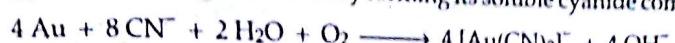
(ii) In synthesis. The process of photosynthesis, whereby  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are converted by plants to carbohydrates and  $\text{O}_2$  depends on a magnesium porphyrin chelate, chlorophyll which absorbs visible light and converts it to chemical energy.

(iii) In analytical chemistry: (a) To estimate the hardness of water. (b) To perform confirmatory tests for the detection of copper & nickel.

(iv) In photography. Fixing is done by adding hypo solution to  $\text{AgBr}$  coated on film:



(v) In metallurgy. Extraction of gold is done by forming its soluble cyanide complex, e.g.,

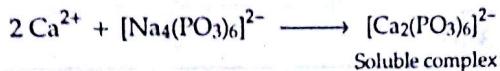


Soluble  
Dicyanoaurate (I) ion

This resultant solution is then treated with zinc to precipitate gold.



(vi) In water treatment. Sodium hexa meta phosphate (calgon) converts the scale forming impurity like  $\text{CaSO}_4$  into soluble complex compound.



This calgon conditioning is done inside boiler by adding calgon to boiler to prevent scale & sludge formation.

### WATER ANALYSIS

Although water is one of the basic elements for life, only 1% of all the water on the earth is suitable for drinking. Presently nearly 20% of the world's population (over one billion people) do not have suitable supply of drinking water. Around 35% of the deaths in the developing world are due to contaminated water. As living standards rise the demand for water will increase at twice the rate of the increase in the world's population. The situation is most critical for India as it is the 7th largest country in the world.

The various constituents of water, problems they create and preferred treatment methods are summarized below :

*Water Treatment (An overview)*

<i>Constituent</i>	<i>Difficulties caused</i>	<i>Treatment method(s)</i>
1. Suspended solids	Cause deposit in boilers, heat-exchangers, water lines etc.	Coagulation, settling and filtration.
2. Dissolved solids	Cause foaming in boilers, and process interference	Any softening method like lime-soda, zeolite or demineralization.
3. Turbidity	Imparts unsightly appearance to water, deposits in water lines, process equipment, etc.	Coagulation, settling and filtration.
4. Hardness	Forms curds with soap, interferes with dyeing, causes scale formation in boilers, heat-exchangers, pipelines etc.	Internal boiler water treatment, softening.

<i>Constituent</i>	<i>Difficulties caused</i>	<i>Treatment method(s)</i>
5. Alkalinity	Foaming and carry over of solids with steam, Embrittlement of boiler steel, carbonate and bicarbonate produce $\text{CO}_2$ in steam which causes corrosion in condensate lines.	Acid treatment ; softening.
6. Free mineral acids	Corrosion	Neutralization with alkalies.
7. Oxygen	Corrosion	Deaeration, sodium sulfite, corrosion inhibitors.
8. Carbon dioxide	Corrosion	Aeration, deaeration ; neutralization with alkalies.

### Experiment 3

(vii) Collect the product (i.e., fine crystals) by vacuum filtration on the Hirsch funnel. Using a very small quantity of ice water, complete the transfer of the product to the funnel.

(viii) Turn the product out onto a piece of filter paper and squeeze the crystals between sheets of paper to absorb excess water.

(ix) Allow the product to dry thoroughly in air.

(x) Determine the weight and calculate the yield.

Determine the melting point of aspirin and compare it with the tabulated aspirin (which is 128 – 137°C).

### CAUTIONS

(i) Wear gloves and avoid contact with acetic anhydride and sulfuric acid. This is because acetic anhydride can cause severe damage to skin and eyes, its vapours are very harmful if inhaled, and it reacts violently with water. Sulfuric acid causes chemical burns that can seriously damage skin and eyes.

(ii) Take acetic anhydride in excess.

### VIVA-VOCE

1. What are the roles of acetic anhydride in this experiment ?

Ans. Acetic anhydride serve as a solvent for the reaction. It also converts salicylic acid to aspirin.

2. One possible impurity in the aspirin is salicylic acid itself which might result from incomplete reaction of the starting materials or it might also result by hydrolysis of aspirin formed during the working of the product. How will you detect salicylic acid in aspirin ?

Ans. Aspirin is tested for the presence of salicylic acid by using ferric chloride. This is because, ferric chloride forms highly coloured complexes with phenolic compounds.

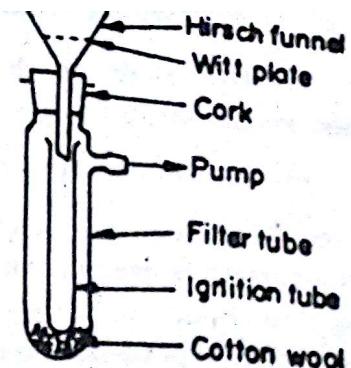


Fig: Hirsch filtration assembly.

**3. Why the melting point of aspirin is not a reliable indicator of its purity ?**

**Ans.** This is because, aspirin decomposes at high temperatures.

**4. How aspirin is purified ?**

**Ans.** In order to reduce the likelihood of hydrolysis, the following procedure is used to recrystallize the aspirin :

- (i) Dissolve the aspirin in the minimum volume of boiling 95% ethanol, and add another 6 – 8 drops of ethanol. Add twice the volume of warm (~ 60°C) water to the solution while it is still at the boiling point, and swirl to mix.
- (ii) If any precipitate forms, heat the solution gently until it is clear, but do not boil it.
- (iii) Let it cool slowly to room temperature, induce crystallization if necessary, and cool it in an ice/water bath until crystallization is complete.
- (iv) Collect the aspirin by vacuum filtration on a Hirsch funnel, washing it on the filter with ice-cold water.

**5. Name two reliable methods for the analysis of aspirin.**

**Ans.** (i) The infrared spectrum of aspirin.

(ii) The  $^1\text{H}$  NMR spectrum of aspirin.

**6. Starch is often used as a binder in commercial aspirin tablets. How you can find out whether starch is used or not ?**

**Ans.** Boil about 2 mg of ground-up aspirin tablets in 2 mL of water. Add a drop of solution of iodine in potassium iodide. Starch forms a blue-violet complex with iodine.

**7. Summarize the vacuum filtration operation.**

**Ans.** (i) Assemble apparatus for vacuum filtration,

(ii) Position and moisten filter paper, turn on vacuum,

(iii) Add filtration mixture to funnel,

(iv) Transfer any remaining solid to funnel,

(v) Wash solid on filter with cold solvent,

(vi) Air-dry solid on filter paper,

(vii) Transfer the dried solid to dry container for further analysis.

**8. Describe and explain the possible effect on your results of the following experimental errors or variations :**

- (a) The reagent bottle labelled "acetic anhydride" actually contained acetic acid.
- (b) The test tube used for analysis of the purified aspirin was rinsed with water and not completely dried, and you stored the aspirin sample for a week before testing it.
- (c) You boiled the recrystallization mixture after adding water.

**9. Which would you expect to be the stronger acid, aspirin or salicylic acid ? Explain your answer.**