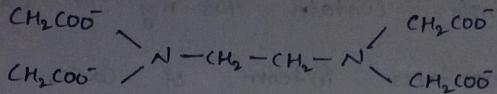


5/8
EDTA :

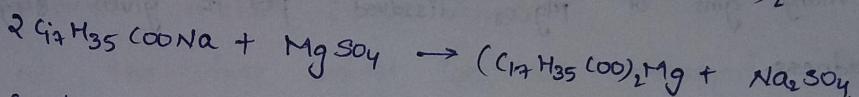
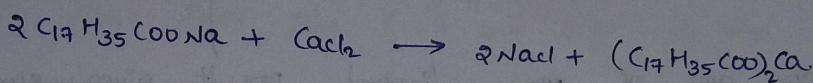


(1)

Hardness of water:

It is defined as the soap consuming capacity of a water sample. This is due to the presence in water of certain salts like Ca, Mg and other heavy metal ions.

e.g:



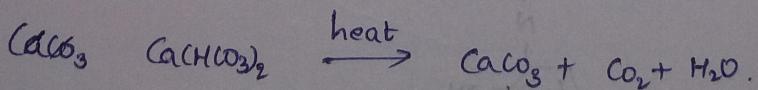
Types of hardness:

1. Temporary hardness: This is caused by the presence of dissolved bicarbonates of calcium and magnesium and other heavy metals and the carbonates of iron.

Temporary hardness can be removed by boiling of water, when bicarbonates are decomposed, yielding insoluble bicarbonates or hydroxides which are deposited as a crust at the bottom of the vessel. The salt responsible for the temporary hardness are $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$.

Temporary hardness is also known as carbonate and alkaline hardness.

e.g: Calcium bicarbonate



Permanent hardness:

This is due to the presence of dissolved chlorides and sulphates of Ca and Mg, iron (Fe) and other heavy metals.

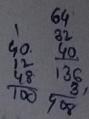
118

Q. A water sample contain 408 mg of Calcium sulphate per lt.
Calculate the hardness in term. of CaCO_3 .

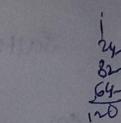
Solt

$$\text{CaSO}_4 = 136 \text{ gm.}$$

(2)



$$\begin{aligned} \text{Hardness} &= \frac{\text{Mass of } \text{CaSO}_4 \text{ in mg per lt}}{\text{che. eq. of } \text{CaSO}_4} \times \frac{\text{che. eq. of } \text{CaCO}_3}{\text{che. eq. of } \text{CaSO}_4} \\ &= \frac{408 \times 100}{136} = 300 \text{ ppm.} \end{aligned}$$

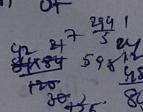


3 How many gms of MgCO_3 dissolved per lt given 84 ppm of the hardness.

Solt

$$84 \text{ ppm} = \frac{84}{100}$$

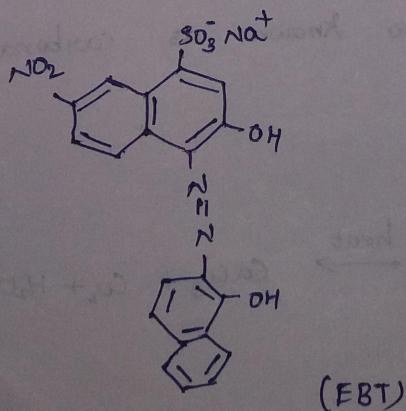
$$\text{Hardness} = \frac{\text{Mass of } \text{MgCO}_3}{\text{che. eq. of } \text{MgCO}_3}$$



→ Ca is more stable than Mg. and CaCO_3 is standard.

Eriochrome - Black-T :

It is the typical metal Iron Indicator, chemically it is Sodium - 1- (1-hydroxy-2-naphtho) - 6-nitro-2-naphthol - 4-sulphonate



The ha
NH₄OH
solution
metal is
combined
and
After
drops
from

Mechan

Ore

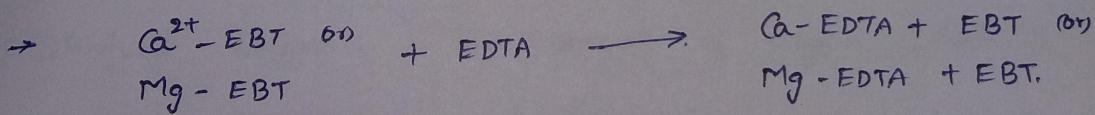
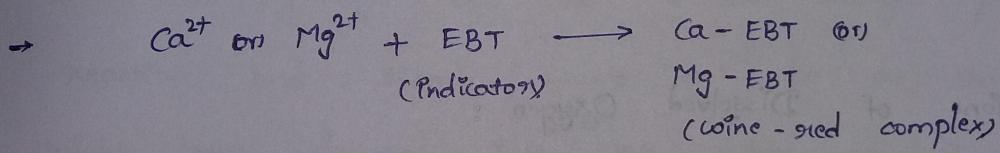
(3)

per lit.

$$\begin{array}{r} 64 \\ 32 \\ 40 \\ 48 \\ \hline 100 \\ 90 \end{array}$$

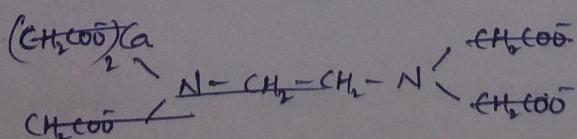
The hardwater is buffered through a pH value of 10 using NH_4OH and NH_4Cl buffer and a few drops of EBT indicator solution are added to stop. EBT form a big complex with metal iron, which has a wine blood colour. During the titration of water sample, it gives EDTA, EDTA first combines with free ions (Ca and Mg) to give very stable and colourless metal EDTA complex.

After all the free metal ion are consumed, the next drops of added EDTA solution displace the indicator (EBT) from metal EBT complex.

Mechanism:Order of stability

- 1, Ca-EBT ,
- 2, Mg-EBT
- 3, Ca-EDTA
- 4, Mg-EDTA

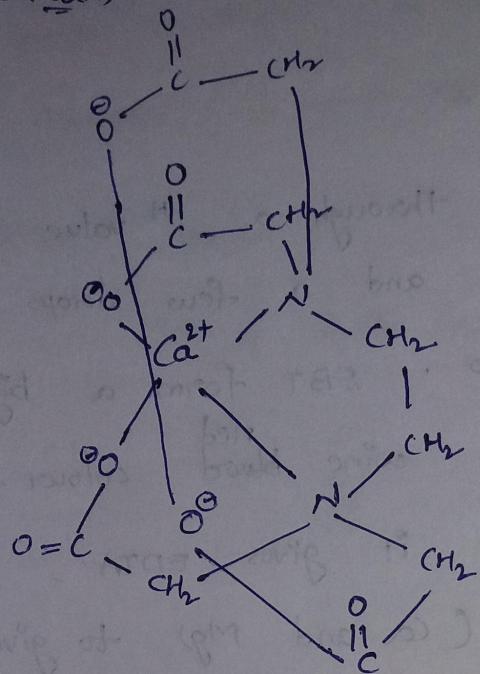
3>4>1>2



EDTA with calcium

(4)

Denticity of EDTA = 6
ie, hexadentate ligand.



18/8

Which type of titrations is used for the determination of water

Ans Complexometric Titration.

exp: 4

Determinations of Dissolved Oxygen :

(4)

= 6
Ligand

Iodimetric Titration: When an analyte that is a reducing agent is titrated directly with a standard iodine solution, then the method is called Iodimetric Titration.

Iodometric: When an analyte is an oxidizing agent is added to excess iodide to produce iodine and the iodine produced is determined by titration with sodium thiosulphate (Hypo) then it is called Iodometric Titration.

→ Starch : Amylose and Amylopectine

↓

responsible for blue colour (Iodine)

Q Why do you need freshly prepared starch solution for the iodometry titration.

A! Because, starch undergo a photochemical reaction. So, with the passage of time it can undergo photochemical reaction and starch would not be as starch but it might have changed into any other product.

Q Dissolved Oxygen: The amount of oxygen which is present in water and is used by microorganisms.

Q Winkler's Method:

Winkler's method is used for estimation of dissolved oxygen.

Dissolved oxygen is usually determined by Winkler's method.

It is based on the fact that DO oxidize KI to I₂.

The liberated Iodine is titrated against standard sodium thiosulphate (Hypo). solution using starch as an indicator.

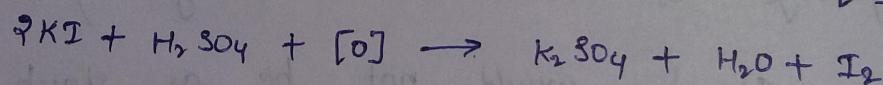
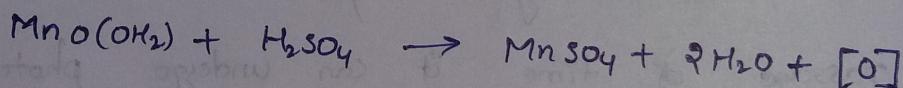
This D_2O in water is in the molecular stage, it has as such can't oxidise KI solution. Hence Manganese hydroxide (6) is used as an oxygen carrier to bring about the reaction between KI and oxygen.

Manganese hydroxide is obtained by the actions of KOH and Manganese sulphate. The oxidizing agent present in water such as nitrate and the ferric ion. oxidize I^- to I_2 and gives the tve result.

Mechanism:



(Basic manganese hydroxide) \rightarrow oxygen carrier



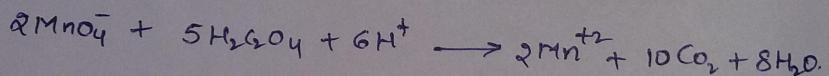
Alstenberg's Modification (mechanism is same as that of comkler's method)

Experiment - 6

(7)

The first few drops of permanganate added to acidify oxalic acid solution ^{will} not decolourise immediately. Mn^{2+} ion produced in this reaction acts as a catalyst. Then the reaction with permanganate to form intermediate oxidation states of manganese. This in turn react do rapidly with oxalate to give the product. So, $KMnO_4$ acts as an auto catalyst in this reaction. This is the advantage of $KMnO_4$ is that, it serves as own indicator. Therefore no indicator is used in this reaction.

When a solution of permanganate ion is added to one of the manganese ion in which acid and the oxalic ion is also present, a cherry red solution of complex ion is formed, from manganese ion and oxalate ion.



In the $KMnO_4$ solution, there remain some impurity mainly MnO_2 . Some Mn^{2+} are produced from MnO_2 which reacts with $KMnO_4$ and form more MnO_2 . This is known as Auto decomposition.



Reason (Acid)

The solution must be strongly acid in order to avoid other side reactions. Here sulphuric acid is normally used, HNO_3 is unsplittable, that is why we are not using HNO_3 .

(7)

HNO_3 is unsuitable because NO_3^- ion is strong oxidizing agent which may interfere with KMnO_4 .

(8)

If HCl is used, it may be oxidized to chlorine by permanganate. If Cl^- ion is present, high error results are obtained because some permanganate is used up in the oxidizing the HCl to eliminate the interference of Cl^- ion.

The main reasons for using acid in this titration is that it transforms oxalate to oxalic acid, and this acid solution reduce the KMnO_4 .

Side Reactions when HCl is used:

Test for Cl^-
If AgNO_3 is added ppt is formed.



→ Why KMnO_4 acts as a self - indicator?

Why are we using H_2SO_4 in this titration?

Reaction Mechanism.

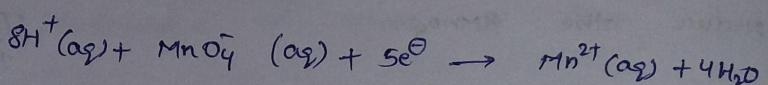
* H_2SO_4 : 1M , acid medium, the formal standard potential (E°) for the dichromate - chromic ion couple is +1V.

Explaining note that under the later conditions ΔE is only +0.3V. To enhance ΔE , a mixture of phosphoric acid and the sulphuric acid is added to the sample.

Experiment - 7 (Fe^{2+})

Determine amount of Iron (II) present in the solution using standard KMnO_4 .

In The purpose of this experiment is to find out the percentage of Iron in an unknown sample, which can be determined through the titration with the standard solution of KMnO_4 .



In acid solutions the permanganate ion undergoes reduction to Manganese (oxi. state +2) ion. Since, the permanganate ion is violet and Mn²⁺ ion is colourless. So, the end point in the titration using Potassium Permanganate as a titrant can be taken as the first permanent pink colour that appears in the solution.

This titrations involve the oxidations of Fe^{2+} ion to Fe^{3+} ion by permanganate ion and it carried out in H_2SO_4 solution to prevent the air oxidations of the Fe^{2+} ion. The end point of the titration is

* Reasons of using acid mixture :

\rightarrow $\text{Fe}^{(II)} \text{Fe}^{(III)}$ $[\text{Fe}^{(III)}] \text{Cl}$ complex are yellow and they can make it difficult to spot the end point. so, acid mixture is added in the solution.

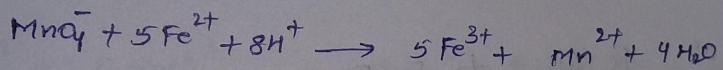
The phosphate complex has higher stability constant phosphoric acid formed complex with iron, lowering the concentrations of the sample (Iron) and decreasing the potential of the $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ solution.

(10)

→ (The titrations involve the oxidations of $\text{Fe}(\text{II})$ to $\text{Fe}(\text{III})$ by permanganate)

The reason being the Iron ion by itself has a yellow colour that can partly make the solution pink. But the addition of phosphoric acid, sulphuric acid form colourless complex with the Iron (II) ion.

* Overall Reactions:



Experiment No-8 (Fe^{3+})

11

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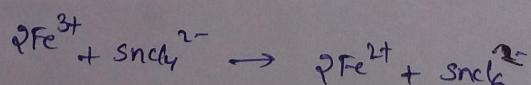
of

mixtu

Over

Reductions of $\underline{Fe(II)}$ to $\underline{Fe(II)}$: we are reducing $\underline{Fe(III)}$ to $\underline{Fe(II)}$ because the highest oxidation state of Fe is +3 and that shouldn't exceed +3

After the sample is dissolved the iron mainly exists as $Fe(II)$. Titration with standard oxidizing agent required and that all the iron exists as $Fe(II)$. A quantitative reductive of $Fe(III)$ to $Fe(II)$ is performed by adding SnCl₂ to the hydro hot HCl acid solution of the sample



Advantages of using SnCl₂:

- It reduces $Fe(III)$ to $Fe(II)$ quantitatively and rapidly.
- At the certain degree of selectivity of $Fe(II)$ because it is not so strong reducing agent that it reduces

Ind

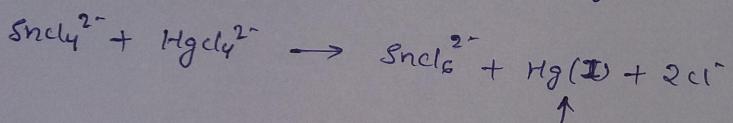
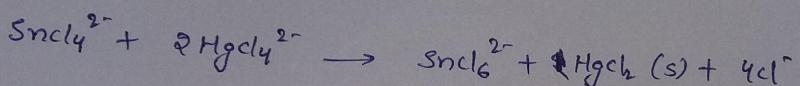
(11) other species in the solution

→ An excess amount of acid is easily destroyed with HgCl_2 so that it will not interfere with redox titration.

→ Due to the presence of chloride complex of $\text{Fe}(\text{III})$, the sample solution is yellow, whereas $\text{Fe}(\text{II})$ are colourless. So, tin solution is added drop wise until the yellow colour just disappears.

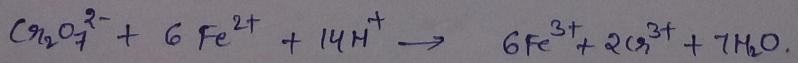
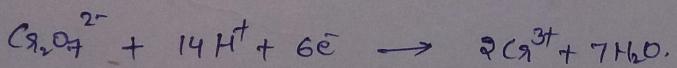
→ One drop acid should be added to ensure complete reduction of $\text{Fe}(\text{III})$.

Removal of excess reducing agent

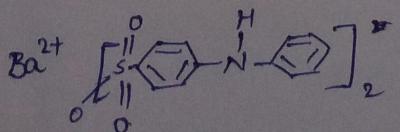


Excess SnCl_2 must be destroyed as it will interfere the titration. That's why for the removal of excess amount of reducing agent we have added HgCl_2 in the Mercuric Mercuric mixture.

Overall Reaction:

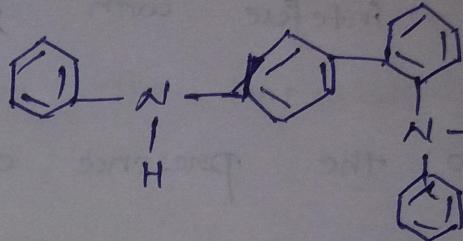
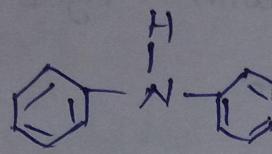


Indicator: Barium diphenyl diamine phenyl sulphonate.



Role of Indicator:

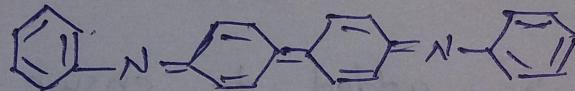
(13)



Colourless.

diphenyl amine.

Diphenyl benzidine (colourless)



Diphenyl benzidine (violet) (azo compound)