DIRECTORATE OF DISTANCE & CONTINUING EDUCATIONS

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI – 627012

OPEN AND DISTANCE LEARING(ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRMMES FROM THE ACADEMIC YEAR 2023 – 2024)

M.Sc. CHEMSITY
COURSE MATERIALS
INORGANIC CHEMISTRY PRACTICAL - II
SCHP31

By
S. NAGARAJAN
Assistant Professor
Department of Chemistry
Manonmaniam Sundaranar University
Tirunelveli 627012

Inorganic Chemistry Practical-II

I Preparation and analysis of metal complexes by titrimetric analysis

1. Preparation of tris(thiourea)copper(I)sulphate dihydrate
2. Preparation of potassium tris(oxalato)chromate(III) trihydrate
3. Preparation of tetramminecopper(II) sulphate
4. Preparation of hexa(thiourea)copper(I) chloride dihydrate
5. Preparation of potassium tris(oxalato)ferrate(III) trihydrate

II Quantitative estimation of a mixture containing two metal ions (Volumetric (V) and Gravimetric(G) Estimations)

1. Estimation of mixture of Cu^{2+}(V) and Ni^{2+}(G)ions.
2. Estimation of mixture of Fe^{2+}(V) and Cu^{2+}(G)ions.
3. Estimation of mixture of Fe^{2+}(V) and Ni^{2+}(G)ions.
4. Estimation of Cu^{2+}(V) and Ba^{2+}(G) ions.
5. Estimation of Cu^{2+}(V) and Zn^{2+}(G) ions

Text Book

1. Mounir A. Malati, Experimental Inorganic/Physical Chemistry - An Investigative, Integrated Approach to Practical Project Work, Woodhead Publishing Limited, Reprint, 2010.
2. G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, Revised 5 th edition, ELBS, 1989.
3. Douglas A. Skoog, Donald M. West, F. James Holler and Stanley R. Crouch, Fundamentals of Analytical Chemistry, 8 th Edition, Brooks/ColeThomson Learning, USA, 2004.

INORGANIC CHEMISTRY PRACTICAL-II

Introduction

In the field of analytical chemistry, the accurate identification and quantification of metal ions in complex mixtures are of utmost importance. These analyses are crucial for a wide array of applications, ranging from environmental monitoring and industrial processing to pharmaceutical development and biological studies. The separation and estimation of metal ions can be effectively achieved using classical techniques such as volumetric and gravimetric methods. These methods are both reliable and highly precise, allowing chemists to quantify metal ions even in the presence of multiple components that may interfere with analysis.

This section covers the principles, procedures, and applications of volumetric and gravimetric techniques in the estimation of metal ions, particularly focusing on mixtures containing several different metal ions. The purpose is to provide an understanding of how these classical methods are applied to separate and determine metal ions in various combinations. Through this, students will learn to utilize these techniques to achieve accurate results in practical applications, regardless of the complexity of the mixture.

Objective

After reading this unit you will be able to:

- ✓ Maintain a laboratory notebook.
- ✓ Have knowledge of commonly used apparatus in the laboratory.
- ✓ Know the method of using a pipette, burette, volumetric flask and analytical balance.
- ✓ Explain different terms like precipitation, digestion, filtration and ignition, drying, cooling etc.
- ✓ Describe the process of titration.

- ✓ Classify the titration.
- ✓ Classify the indicator.
- ✓ Determine the strength of given sodium hydroxide (NaOH) solution.
- ✓ Have knowledge of lab reagents.
- ✓ Know the safety measures taken in the laboratory.

Volumetric Methods of Metal Ion Estimation

Volumetric analysis, also known as titration, is one of the most widely used quantitative methods for the estimation of metal ions. In this technique, a solution of a known concentration (titrant) is gradually added to a solution containing the metal ion of interest (analyte) until the reaction reaches its endpoint. The volume of titrant used is then correlated to the amount of analyte through stoichiometric calculations, allowing for the precise estimation of the ion's concentration.

Volumetric methods offer several advantages, including speed, simplicity, and cost-effectiveness. However, they require careful selection of titrants and conditions that are specific to each metal ion. Some commonly used methods for metal ion estimation include:

- ➢ Complexometric Titrations: A widely applied method for the estimation of metal ions like calcium (Ca^{2+}), magnesium (Mg^{2+}), copper (Cu^{2+}), and zinc (Zn^{2+}). In complexometric titrations, a chelating agent such as EDTA (ethylenediaminetetraacetic acid) forms stable complexes with metal ions, allowing their concentration to be determined based on the volume of the titrant used.

- ➢ Precipitation Titrations: This method is particularly useful for ions like chloride (Cl^{-}), sulfate (SO_4^{2-}), and carbonate (CO_3^{2-}). A precipitating reagent is added to the solution to form an insoluble precipitate, which can then be quantified by titration.

- ➢ Redox Titrations: Involving the transfer of electrons, redox titrations are used for the determination of metal ions that undergo oxidation-reduction reactions, such as iron (Fe^{2+}/Fe^{3+}), copper (Cu^{+}/Cu^{2+}), and manganese (Mn^{2+}/Mn^{3+}).

One of the challenges in volumetric analysis, especially when dealing with mixtures of multiple metal ions, is the selective separation of ions to prevent interference. For this reason, it is essential to utilize masking agents, pH adjustments, and other techniques that can isolate one ion from another during the titration process. For example, EDTA can selectively form complexes with specific metal ions, while other ions in the mixture may remain unreactive under controlled conditions.

Gravimetric Methods of Metal Ion Estimation

Gravimetric analysis is another classical technique used to estimate the concentration of metal ions, based on the measurement of the mass of a solid product that forms during the reaction. This method involves precipitating the metal ion from the solution in the form of an insoluble compound, which is then isolated by filtration, washed, dried, and weighed. The mass of the precipitate is directly related to the amount of metal ion present in the sample.

Gravimetric methods are known for their high precision and accuracy, often achieving results with minimal uncertainty. However, these methods are typically more time-consuming than volumetric methods, as they require steps like filtration and drying to ensure accurate mass measurements. The typical steps involved in gravimetric analysis include:

- Precipitation: The metal ion of interest is reacted with a reagent that forms an insoluble precipitate. For example, calcium (Ca^{2+}) can be precipitated as calcium oxalate (CaC_2O_4), and copper (Cu^{2+}) can form copper(II) hydroxide ($Cu(OH)_2$).

- Filtration and Washing: The precipitate is filtered from the solution and washed to remove any impurities or soluble ions that might affect the purity of the precipitate.

- Drying and Weighing: After filtration, the precipitate is dried to remove any residual moisture, and its mass is carefully measured. The mass of the precipitate can be used to calculate the concentration of the metal ion in the original sample.

The gravimetric method can be employed for a variety of metal ions, including transition metals like copper (Cu^{2+}), iron (Fe^{2+}/Fe^{3+}), and lead (Pb^{2+}), as well as alkaline earth metals like calcium (Ca^{2+}) and magnesium (Mg^{2+}). Similar to volumetric methods, the separation of ions in mixtures is crucial in gravimetric analysis. Selective precipitation techniques, pH control, and the use of specific reagents are often employed to isolate the metal ion of interest from other components in the mixture.

Separation Techniques for Metal Ion Mixtures

The separation of metal ions from complex mixtures is a critical aspect of both volumetric and gravimetric methods. In many real-world applications, metal ions are not found in isolation but are present in mixtures with other ions. Therefore, the ability to selectively isolate a metal ion is essential to avoid interference during the estimation process. Various separation techniques can be employed to achieve this:

- Precipitation: Precipitating agents can be used to selectively precipitate one metal ion from a mixture while leaving others in solution. This method is particularly effective when the metal ions differ significantly in their solubility products.
- Solvent Extraction: This technique involves using an organic solvent to selectively extract a metal ion from an aqueous solution. The metal ion is transferred into the organic phase, where it can be further analyzed.
- Ion-Exchange Chromatography: Ion-exchange resins are used to separate metal ions in mixtures based on their charge and size. This method is particularly useful for separating metal ions in aqueous solutions.
- Electrochemical Methods: Electrochemical separation methods, such as electrolysis, can also be employed to selectively reduce or oxidize specific metal ions, thereby isolating them from others.

The use of masking agents is also an important strategy for separating metal ions in mixtures. Masking agents bind to interfering ions, preventing them from reacting during the titration or precipitation process. For example, in a mixture containing iron and copper, the presence of a masking agent for iron allows copper to be selectively estimated.

Applications and Importance of Metal Ion Estimation

The separation and estimation of metal ions are vital in many fields, including:

- Environmental Chemistry: Metal ion analysis is crucial for detecting pollutants in water, soil, and air, as well as monitoring the effectiveness of water treatment processes.
- Pharmaceutical Industry: Many drugs contain metal ions or are influenced by metal ion concentrations. Estimation methods are used for quality control and formulation.
- Material Science: The analysis of metal alloys and composites often requires the estimation of specific metal ions, which is essential for understanding their properties and behavior.
- Biological and Clinical Studies: Metal ions play a vital role in biological processes, and their accurate estimation is necessary for research in areas like biochemistry, toxicology, and nutrition.
- Food and Agriculture: Metal ion analysis is used in the assessment of food quality, soil analysis, and the development of fertilizers and pesticides.

Through the study and application of both volumetric and gravimetric methods, students will gain a solid foundation in analytical chemistry, enhancing their ability to work with complex mixtures and accurately estimate the concentration of metal ions in various samples.

I Preparation and analysis of metal complexes by titrimetric analysis

1. Preparation of tris(thiourea)copper(I)sulphate

Aim

To prepare tris(thiourea) copper (I) sulphate from thiourea and copper(II) sulphate.

Principle

When a solution of copper sulphate and thiourea are shaken together they readily yield the complex. In the first step, thiourea reduces Cu^{2+} to Cu^{+} and then forms the complex as follows

$$\begin{array}{l}
2CuSO_4 + H_2N-CS-NH_2 \rightarrow Cu_2SO_4 + H_2N-CS-NH-HSO_4 \\
Cu_2SO_4 + 6H_2N-CS-NH_2 \rightarrow [Cu(H_2N-CS-NH_2)_3]_2SO_4 \\
\hline
2CuSO_4 + 7H_2N-CS-NH_2 \rightarrow [Cu(H_2N \bullet CS \bullet NH_2)_3]_2SO_4 + \\
\qquad\qquad\qquad\qquad\qquad\qquad H_2N-CS-NH-HSO_4
\end{array}$$

Chemicals Required

Thiourea – 4g; Copper sulphate – 4g;

Procedure

Dissolved 2g of thiourea in 12.5ml of hot water and then cooled the solution to room temperature. Shaken the solution well while adding to it in portions a cold solution of 4g of copper sulphate in 20ml of water. Finally cooled thoroughly in running water while the separated yellowish oil adheres to the walls of the flask. Decanted and rejected the mother liquor. Shaken the oil vigorously with the solution of 2g of thiourea in 12.5ml of water, untill crystallization is complete. Filtered and washed the crystals with small amount of water. Recrystallised with 5% aqueous thiourea containing 2ml of 1N sulphuric acid. The recrystallisation temperature should not be allowed to rise above 80°C. Noted the yield.

Result

Yield of tris(thiourea) copper(I) sulphate is ______g.

2. Preparation of potassium tris(oxalato) chromate(III) trihydrate

Aim

To prepare the complex potassium trioxalatochromate(III).

Principle

When potassium dichromate is treated with oxalic acid and potassium oxalate, green complex of potassium trioxalatochromate (III) is formed.

$$2K_2C_2O_4 + 7H_2C_2O_4 + K_2Cr_2O_7 \rightarrow 2K_3[Cr(C_2O_4)_3] + 6CO_2 + 7H_2O$$

Chemicals Required

Oxalic acid – 3g; Potassium dichromate – 1g; Ethyl alcohol – 2ml; Potassium oxalate – 1.2g.

Procedure

To the solution of 3g of oxalic acid in 8ml of warm water, added in portions 1g of potassium dichromate. When the vigorous reaction has subsided, the resulting solution was heated to boiling and in it 1.2g of potassium oxalate was dissolved. The whole solution was cooled to room temperature. Added 1.2ml of ethanol and cooled. The green crystals separated out from an almost black solution. Collected the precipitate from Buchner funnel, washed with 1% ethanol and finally with pure ethanol. The yield was noted.

Result

Yield of potassium trioxalatochromate (III) is ______g.

3. Preparation of tetramminecopper(II) sulphate

Aim

To prepare tetramminecopper(II) sulphate from copper sulphate.

Principle

When a solution of copper sulphate is mixed with an excess of ammonia solution, initially a white precipitate of cuprous hydroxide formed, dissolved again to give a deep blue solution of cuprammonium sulphate complex. The complex is reprecipitated from the solution by the addition of alcohol in which it is insoluble.

$$\underset{}{CuSO_4 + 4NH_4OH} \rightarrow \underset{\text{Tetramminecopper(II) sulphate tetrahydrate}}{[Cu(NH_3)_4]SO_4 \,.\, 4H_2O}$$

Chemicals Required

Copper sulphate – 2g; Ammonia – 3ml; Alcohol – 3ml.

Procedure

2.5g of copper sulphate was dissolved in 10ml of distilled water shaken well. To the clear solution 8ml of liquor ammonia (1:1) was added and shaken well. 8ml of ethanol was added to the resulting blue solution. Blue crystalline ppt obtained was heated on a water bath, filtered of not clear. Kept aside for 45 minutes Blue crystals were formed.

Result

Yield of tetramminecopper(II) sulphate is ______g.

4. Preparation of hexa(thiourea)copper(I) chloride dihydrate

Aim:

To synthesize hexa(thiourea)copper(I) chloride dihydrate by reacting copper(II) chloride dihydrate with thiourea under controlled conditions.

Chemicals Required:

Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), Thiourea (CH_4N_2S), Ethanol, Distilled water

Principle:

The synthesis of hexa(thiourea)copper(I) chloride dihydrate involves the reduction of copper(II) ions to copper(I) ions by thiourea, followed by complexation with thiourea ligands. Ethanol aids in crystallization, and the product is obtained as pale yellow crystals upon cooling.

Procedure:

Preparation of Copper(I) Solution:

Weigh approximately 1.0 g of copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) and dissolve it in 50 mL of distilled water in a 250 mL beaker with stirring. Prepare a reducing agent solution by dissolving 0.5 g of thiourea in 10 mL of distilled water in a separate beaker. Add the reducing agent solution dropwise to the copper(II) chloride solution while stirring continuously to produce a pale yellow or colorless copper(I) chloride solution. Weigh 3.5 g of thiourea and add it gradually to the copper(I) chloride solution while stirring. Stir the mixture for 15-20 minutes at room temperature to allow complete complexation, forming hexa(thiourea)copper(I) chloride. Add 20 mL of ethanol to the reaction mixture to promote crystallization. Place the beaker in an ice bath to cool the solution gradually, resulting in the precipitation of the hexa(thiourea)copper(I) chloride dihydrate crystals. Filter the solution using a funnel lined with filter paper to collect the crystals. Wash the crystals with a small amount of cold ethanol to remove impurities. Air-dry the crystals on the filter paper or transfer them to a clean watch glass.

Result

Yield of hexa(thiourea)copper(I) chloride dihydrate is -------------g

5. Preparation of potassium tris(oxalato)ferrate(III) trihydrate

Aim

To prepare the complex potassium trioxalatoferrate(III).

Principle

Ferrous oxalate is obtained by mixing ferrous sulphate and oxalic acid to which potassium hydroxide and hydrogen peroxide are added to get the complex potassium trioxalatoferrate(III).

Chemicals Required

Ferrous oxalate – 3.3g; Hydrogen peroxide – 12.5ml; Oxalic acid – 5g and potassium hydroxide – 5g; Ethanol – 50 ml.

Procedure

Suspended about 3.3g of ferrous oxalate in a warm solution of 5g of KOH in 15ml of water. Added 12.5ml of 20 volume of H_2O_2 from a burette stirring the liquid continuously during the addition and keeping its temperature to 40°C. Heated the mixture containing some ferrous hydroxide to boiling and dissolved the precipitate by adding first in one portion a 10ml solution of oxalic acid containing 5g of crystals per 50ml. Then a further small amount of about 2.5ml carefully drop by drop from a burette. During the addition of oxalic acid the solution should be nearly boiling. Excess of acid is to be added. Filtered the hot solution, added to the filtrate 50ml of ethanol, redissolved any precipitated crystals by gentle heating and then set aside the solution in cupboard for crystallization. Washed the precipitate at the pump using an equimolar mixture of ethanol, water and finally with acetone. The yield was noted.

Result

Yield of potassium trioxalatoferrate(III) is ______g.

II Quantitative estimation of a mixture containing two metal ions (Volumetric (V) and Gravimetric(G) Estimations)

1. Separation and estimation of Cu^{2+} - Ni^{2+} mixtures by volumetric method and the other by gravimetric method

Objectives

After studying and performing this experiment you should be ableto separate and estimate the Cu^{2+} - Ni^{2+} mixtures by volumetric method and the other by gravimetric method.

Volumetric Estimation of Copper

Principle: Cu(II) reacts with KI giving a brown precipitate of Cu_2I_2 and liberating iodine. When an excess of KI is added to the solution containing Cu^{2+} in neutral or slightly acidic medium, quantitative liberation of iodine takes place.

$$2CuSO_4.5\,H_2O + 4KI \rightarrow 2CuI_2 + 2K_2SO_4 + 5H_2O$$

$$2CuI_2 \rightarrow Cu_2I_2 + I_2$$

The liberating I_2 is titrated against thiosulphate which ispreviously standardized against std. $CuSO_4$ solution, equivalent Weight of Cu= 63.54

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

From the above equation it is evident that

$$2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-} \equiv 2e$$

The Equivalent weight of Cu^{2+} will be one half of twice themolecular involves two electrons per two moles of Cu^{2+}. Equivalentweight of Cu^{2+} = (2 x 63.5)/2 = 63.5.

The titration fails when any mineral acid is present in the solution and therefore before commencing the titration the acid should be neutralized. This is done by dropwise addition of NH_4OH until a slight blue precipitate just appears. The precipitate can be removed by additionof CH_3COOH in the solution.

$$Cu(OH)_2 + 2CH_3COOH \rightarrow Cu^{2+} + 2CH_3COO^- + 2H_2O$$

Moreover the precipitate of Cu_2I_2 absorbs I_2 from the solution andreleases it slowly making the detection of sharp end point difficult. So, a small amount of NH_4SCN is added near the end point to displace the absorbed iodine from Cu_2I_2 precipitate

$$2NH_4OH + Cu^{2+} \rightarrow 2NH_4^+ + \underset{\text{Blue precipitate}}{Cu(OH)_2}$$

Calculation

Weight of $CuSO_4$ = 1.25 g

Strength of $CuSO_4$ = 1000 x 1.25/ 100 x 249.68 = 0.05 N

Titration-I:

Standard $CuSO_4$Vs Sodium thiosulphate

Indicator: starch

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings (mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		
3	20	0		

Volume of $CuSO_4$ V_1 = 20 mL

Normality of $CuSO_4$ N_1 = 0.050 N

Volume of Sodium thiosulphate V_2 =

Normality of Sodium thiosulphate N_2 = ?

$V_1N_1 = V_2N_2$

Strength of sodium thiosulphate N_2 $= V_1 \times N_1 / V_2$

$= 20 \times 0.05 / V_2$

Procedure

The thiosulphate is standardized by titrating against standard $CuSO_4$ for this 1.25g of $CuSO_4$ is weighed accurately and made up to a 100 mL SMF with few drops of con.H_2SO_4. The given solution is made up into 250 mL SMF. Pipetted out 20 mL of solution in a 250 mL conical flask and neutralized the solution by drop wise addition of ammonium solution (1:1) until a blue precipitate appears. Redissolve the precipitate with minimum amount of acetic acid (CH_3COOH) and adding about 0.5 ml in excess. Dilute the solution to about 80 ml and add 10 ml of potassium iodide solution (10%). Keep the flask covered with watch glass in a dark and cool place for about 3–5 minutes and titrate the liberated iodine with standard sodium thiosulphatesolution from burette. When the colour of the solution fades to a light yellow, add 2 drops of starch followed by 2 ml of ammonium thiocyanate(NH_4SCN) solution (10%). Titrate the solution till the blue colour discharges and a white or flesh white residue is left in the flask. Repeat the titration to get concordant value.

Titration-II

Standard Sodium thiosulphate Vs given Copper Solution

Indicator: starch

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings(mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		
3	20	0		

Volume of thiosulphate V_1 = _____ mL

Normality of thiosulphate N_1 =

Volume of $CuSO_4$ V_2 = 20 mL

Normality of $CuSO_4$ $N_2 = x$

Strength of $CuSO_4$ $N_2 = \frac{V1 \text{ X } N1}{V2}$

The amount of copper ions presents in the whole of the given solution

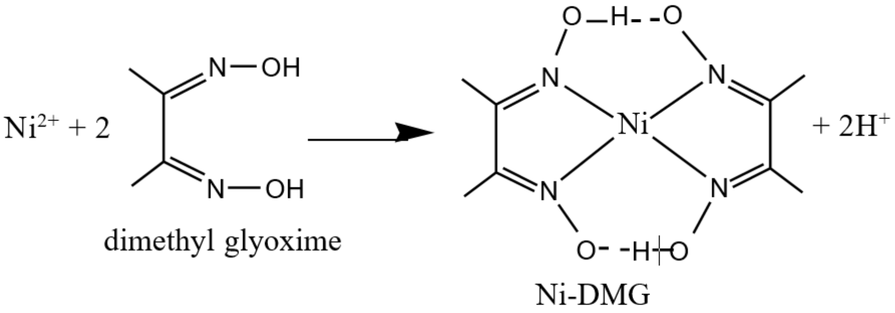
=Normality of $CuSO_4$(N_2) X Equivalent weight of copper x 250/1000

=N_2 X 63.54 x 250/1000

From this we can calculate the amount of copper ions present in the given solution.

Precipitate Gravimetric Estimation of Nickel

40 mL of the made-up solution is pipetted out into a beaker. A few drops of dilute HCl (1:1) is added and heated. H_2S gas is passed for about 15 minutes till the precipitation is filtered through Whatman 42 filter paper. The precipitate is washed with warm water and throughout. The solution is heated to expel the dissolved H_2S gas and the solution is concentrated to about 50 mL in hot condition a slight excess (20mL) of dimethyl glyoxime (1%) is added. Ammonia solution (1:1) is added drop wise with constant stirring until the precipitation is completed and slight excess of ammonia is added. It is digested and kept aside; completion of the precipitation is tested with drop of DMG in sintered crucible. The precipitation is tested with cold water until the filtrate is free from chloride. A duplicate experiment is also performed.



Precipitative Gravimetric Estimation of Nickel

1	Empty Crucible weight (a)	
2	Weight of Precipitate+ Crucible (b)	
3	Weight of Precipitate (b-a)	

Calculation

288.69g of Ni-DMG complex contains 58.69 of nickel

288.69g of Ni-DMG complex contains 58.69 of nickel

-------- g of Ni-DMG complex contains $= \frac{58.69 \text{ X } (b-a)}{288.69} = A =$ ______

40mL of solution containing (A)__________g of nickel

250mL of whole of the solution $= \frac{\text{A X 250}}{40} =$

Result:

The amount of copper ions presents in the whole of the givensolution =

The amount of nickel ions presents in the whole of the givensolution =

2 Separation and estimation of Fe^{2+}– Cu^{2+} mixtures by volumetric method and the other by gravimetric method

Aim

To estimate the amount of iron by volumetrically and copper by gravimetrically in the whole of the given iron - copper solution.

Volumetric Estimation of iron

Principle

The given ferric solution is reduced to the ferrous state using tin and hydrochloric acid. Tin (II) chloride formed on heating reduces iron (III) to iron (II).

$$2Fe^{3+} + Sn^{2+} \leftrightarrow 2Fe^{2+} + Sn^{4+}$$

Slight excess of $SnCl_2$ present is removed by the addition of $HgCl_2$ and a silky white Hg_2Cl_2 is obtained

$$2HgCl_2 + Sn_2+ \rightarrow Hg_2Cl_2 + Sn_{4+} + 2Cl^-$$

The iron (II) solution thus obtained is reacted with acidified $K_2Cr_2O_7$ solution using diphenylamine as the internal indicator. The reaction is as follows.

$$Cr_2O\ ^{2-} + 6Fe^{2+} + 14H^+ \leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Calculation

Weight of iron (FAS) = 3.92 g

Strength of FAS = 1000 x 3.92/ 100 x 392 = 0.1 N

Titration-I:

Standardization of $K_2Cr_2O_7$ Vs FAS.

Indicator: Diphenylamine

S. No.	Volume of FAS (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		
2	20	0		
3	20	0		

Volume of FAS V_1 = 20 mL

Strength of FAS N_1 = 0.1 N

Volume of $K_2Cr_2O_7$ V_2 =

Normality of $K_2Cr_2O_7$ N_2 = ?

$V_1N_1 = V_2N_2$

Strength of $K_2Cr_2O_7$ $N_2 = \frac{V1 \text{ X } N1}{V2} = \frac{20 \text{ X } 0.1}{V2} =$

Procedure

The given solution is made up into a 250mL standard flask. 20mLof this solution is pipetted out into a beaker. It is heated and to the hot solution 2 drops of Con. HCl is added followed by concentrated tin (II) chloride in drops with stirring until the yellow colour disappears. Then dil. HCl is added till the solution becomes green. The solution is then rapidly cooled under the tap. A slight excess of stannous chloride present is removed by adding 10mL of a saturated solution of mercuric chloride rapidly in one portion with through mixing. A silky white precipitate of mercurous chloride is obtained, if a grey or black precipitate is obtainedit has to be thrown out. To the resulting solution about 5mL of syrupy phosphoric acid and 2 drops of diphenylamine indicator are added and titrated against the standard dichromate solution. The solution first becomes straw yellow, greenish and dark green. The end point is the permanent appearance of blue – violet colour. The titration is repeatedfor concordant values.

Standard $K_2Cr_2O_7$ solution is prepared by weighing accurately about 1.25g of analar $K_2Cr_2O_7$ and making up in 250mL standard flask. Equivalent weight of $K_2Cr_2O_7$ = 49.

Titration-II

Standard $K_2Cr_2O_7$ Vs given unknown iron solution.

Indicator: DiphenylAmine

S. No.	Volume of unknown ironsolution (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		

2	20	0		
3	20	0		

Volume of $K_2Cr_2O_7$ V_1 =_____mL

Normality of $K_2Cr_2O_7$ N_1 =

Volume of given unknown iron solution V_2 = 20 mL

Normality of given unknown iron solution N_2 = x

Strength of given unknown iron solution $N_2 = \frac{V1\ X\ N1}{V2}$

$$= \frac{\text{volume of } K_2Cr2O7 X \text{ Normality of } K2Cr2O7}{V2}$$

The amount of iron ions presents in the whole of the given solution

= Strength of given unknown iron solution(N2) X Equivalent weight of iron / 1000

= N_2 X 55.84 x 250/ 1000

= ?

The amount of iron ions presents in the whole of the given solution=

Precipitative Gravimetric Estimation of Copper

The gravimetric estimation of copper ions (Cu^{2+}) is based on the formation of a sparingly soluble complex between copper and oxine (8-hydroxyquinoline). Oxine reacts with Cu^{2+} ions in an ammonium acetate buffer to form copper oxinate, which is a bright yellow precipitate. This reaction occurs in a slightly acidic medium, maintained by a mixture of acetic acid and ammonium acetate, ensuring the selective and quantitative precipitation of Cu^{2+} ions.

The chemical reaction can be written as:

$$Cu^{2+}+2(C_9H_6ON)\longrightarrow Cu(C_9H_6ON)_2$$

The ammonium acetate buffer stabilizes the pH around 5–6, which is essential for the complete precipitation of copper oxinate. The precipitate is insoluble in water, making it ideal for gravimetric analysis. It is stable at higher temperatures, allowing it to be dried and weighed without decomposition. The precipitate is filtered using a sintered crucible or Whatman filter paper, washed to remove impurities, dried in an oven at 130–140°C, and weighed. The mass of the precipitate corresponds to the amount of copper in the solution.

Procedure

The gravimetric estimation of copper begins by transferring 40 mL of the prepared copper solution into a clean 250 mL beaker. To acidify the solution, 5 mL of dilute hydrochloric acid (HCl) is added, ensuring the copper ions remain in solution and ready for reaction. The solution is then heated to boiling to guarantee complete dissolution of the copper ions and to remove any dissolved gases that might interfere with the precipitation process. Once boiling, 5 g of ammonium acetate and 4 mL of glacial acetic acid are added to the solution to create a buffered medium, maintaining the pH necessary for the selective precipitation of copper as its oxinate complex. With the solution maintained at 60°C, a 2% solution of oxine (8-hydroxyquinoline) is added dropwise with constant stirring. The oxine reacts with copper ions, forming a yellow precipitate of copper oxinate. The addition of oxine is continued until the supernatant liquid becomes clear, indicating complete precipitation. The precipitate is allowed to digest in the hot solution for about 10 minutes to ensure thorough crystallization and removal of colloidal impurities. The precipitate is then filtered using a previously weighed sintered glass crucible or Whatman filter paper. Multiple washes with hot distilled water are performed to remove soluble impurities, leaving only pure copper oxinate. The crucible containing the precipitate is dried in an oven at 130–140°C for about one hour to remove moisture. It is then cooled in a desiccator to prevent atmospheric moisture absorption before being weighed accurately. To ensure reliability, the experiment is performed in duplicate, and the average result is used to determine the copper content in the sample.

Precipitative Gravimetric Estimation of Copper

1	Empty Crucible weight (a)	
2	Weight of Precipitate+ Crucible (b)	
3	Weight of Precipitate (b-a)	

Calculation

249.68 g of copper sulphate ($CuSO_4 \cdot 5H_2O$) contains 63.55 g of Cu^{2+}

________ g of copper sulphate contains =

$$63.55 \times (b-a) / 249.68 = A$$

A = ________ g Copper

40 mL of solution containing (A) ________ g of copper

250 mL of the whole solution =

$$A \times 250 / 40$$

The amount of copper ions presents in the whole of the given solution =

Results

1. The amount of iron ions presents in the whole of the given solution=
2. The amount of copper ions presents in the whole of the given solution=

3. Separation and estimation of Fe^{2+}– Ni^{2+} mixtures by volumetric method and the other by gravimetric method

Aim

To estimate the amount of iron by volumetrically and nickel by gravimetrically in the whole of the given iron - nickel solution.

Volumetric Estimation of Iron

Principle:

The given ferric solution is reduced to the ferrous state using tin and hydrochloric acid. Tin (II) chloride formed on heating reduces iron (III) to iron (II).

$$2Fe^{3+} + Sn^{2+} \leftrightarrow 2Fe^{2+} + Sn^{4+}$$

Slight excess of $SnCl_2$ present is removed by the addition of $HgCl_2$ and a silky white Hg_2Cl_2 is obtained

$$2HgCl_2 + Sn_2+ \rightarrow Hg_2Cl_2 + Sn_{4+} + 2Cl^-$$

The iron (II) solution thus obtained is reacted with acidified $K_2Cr_2O_7$ solution using diphenylamine as the internal indicator. The reaction is as follows.

$$Cr_2O\ ^{2-} + 6Fe^{2+} + 14H^+ \leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Calculation

Weight of iron (FAS) = 3.92 g

Strength of FAS = 1000 x 3.92/ 100 x 392 = 0.1 N

Titration-I:

Standardization of $K_2Cr_2O_7$ Vs FAS. .

Indicator: Diphenylamine

S. No.	Volume of FAS (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	
1	20	0		
2	20	0		
3	20	0		

Volume of FAS V_1 = 20 mL

Strength of FAS N_1 = 0.1 N

Volume of $K_2Cr_2O_7$ V_2 =

Normality of $K_2Cr_2O_7$ N_2 = ?

$V_1N_1 = V_2N_2$

Strength of $K_2Cr_2O_7$ $N_2 = \frac{V1 \times N1}{V2} = \frac{20 \times 0.1}{V2} =$

Procedure:

The given solution is made up into a 250mL standard flask. 20mLof this solution is pipetted out into a beaker. It is heated and to the hot solution 2 drops of Con. HCl is added followed by concentrated tin (II) chloride in drops with stirring until the yellow colour disappears. Then dil. HCl is added till the solution becomes green. The solution is then rapidly cooled under the tap. A slight excess of stannous chloride present is removed by adding 10mL of a saturated solution of mercuric chloride rapidly in one portion with through mixing. A silky white precipitate of mercurous chloride is obtained, if a grey or black precipitate is obtainedit has to be thrown out. To the resulting solution about 5mL of syrupy phosphoric acid and 2 drops of diphenylamine indicator are added and titrated against the standard dichromate solution. The solution first becomes straw yellow, greenish and dark green. The end point is the permanent appearance of blue – violet colour. The titration is repeatedfor concordant values. Standard $K_2Cr_2O_7$ solution is prepared by weighing accurately about 1.25g of analar $K_2Cr_2O_7$ and making up in 250mL standard flask. Equivalent weight of $K_2Cr_2O_7$ = 49.

Titration-II

Standard $K_2Cr_2O_7$ Vs given unknown iron solution.

Indicator: DiphenylAmine

S. No.	Volume of unknown iron solution (mL)	Burette Readings (mL)		Volume of $K_2Cr_2O_7$ (mL)
		Initial	Final	

1	20	0		
2	20	0		
3	20	0		

Volume of $K_2Cr_2O_7$ V_1 =_____mL

Normality of $K_2Cr_2O_7$ N_1 =

Volume of given unknown iron solution $V_2 = 20$ mL

Normality of given unknown iron solution $N_2 = x$

Strength of given unknown iron solution $N_2 = \frac{V1 \text{ X } N1}{V2}$

$$= \frac{\text{volume of } K_2Cr2O7 \text{X Normality of } K2Cr2O7}{V2}$$

The amount of iron ions presents in the whole of the given solution

= Strength of given unknown iron solution(N2) X Equivalent weight of iron / 1000

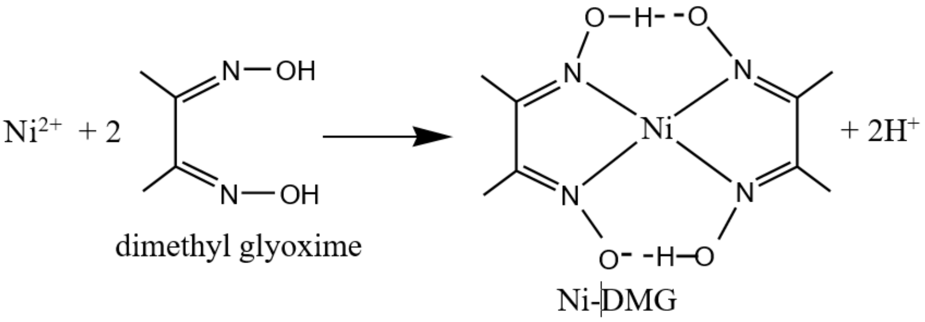
= N_2 X 55.84 x 250/ 1000

= ?

The amount of iron ions presents in the whole of the given solution=

Precipitative Gravimetric Estimation of Nickel

40 mL of the made-up solution is pipetted out into a beaker. A few drops of dilute HCl (1:1) is added and heated. H_2S gas is passed for about 15 minutes till the precipitation is filtered through Whatman 42 filter paper. The precipitate is washed with warm water and throughout. The solution is heated to expel the dissolved H_2S gas and the solution is concentrated to about 50 mL in hot condition a slight excess(20mL) of dimethyl glyoxime (1%) is added. Ammonia solution (1:1) is added drop wise with constant stirring until the precipitation is completed and slight excess of ammonia is added. It is digested and kept aside; completion of the precipitation is tested with drop of DMG in sintered crucible. The precipitate is washed with cold water until the filtrate is free from chloride. It is then dried in hot air oven at 130 – 140^{o}C and weighed. A duplicate experiment is also performed.



Precipitative Gravimetric Estimation of Nickel

1	Empty crucible weight (a)	
2	Weight of precipitate+ crucible (b)	
3	Weight of precipitate (b-a)	

Calculation:

288.69g of Ni-DMG Complex contains 58.69 of Nickel

-------- g of Ni-DMG Complex Contains $=\frac{58.69 \text{ X } (b-a)}{288.69} = A =$

$=$_______ g

40mL of solution containing (A)_______g of nickel

250mL of whole of the solution $=\frac{A \text{ X } 250}{40} =$

The amount of nickel ions presents in the whole of the given solution =

Result:

The amount of Iron ions presents in the whole of the givensolution =

The amount of nickel ions presents in the whole of the givensolution =

4. Separation and estimation of Cu^{2+}– Ba^{2+} mixtures by volumetric method and the other by gravimetric method

Aim

To estimate the amount of copper by volumetrically and calcium by gravimetrically present in the whole of the given copper-calcium solution.

Volumetric Estimation of Copper

Principle

Cu (II) reacts with KI giving a brown precipitate of Cu_2I_2 and liberating iodine. When an excess of KI is added to the solution containing Cu^{2+} in neutral or slightly acidic medium, quantitative liberation of iodine takes place.

$$2CuSO_4.5\,H_2O + 4KI \rightarrow 2CuI2 + 2K2SO4 + 5H2O$$

$$2CuI_2 \rightarrow Cu_2I_2 + I_2$$

The liberating I_2 is treated against thiosulphate which is previously standardized against std. $CuSO_4$ solution, equivalent Weight of Cu= 63.54

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

From the above equation it is evident that

$$2Cu^{2+} = I_2 \equiv 2S_2O_3{}^{2-} = 2e$$

The Equivalent weight of Cu^{2+} will be one half of twice the molecular involves two electrons per two moles of Cu^{2+}. Equivalent weight of Cu^{2+} = (2 x 63.5)/2 = 63.5.

The titration fails when any mineral acid is present in the solution and therefore before commencing the titration the acid should be neutralized. This is done by dropwise addition of NH_4OH until a slight blue precipitate just appears.

The precipitate can be removed by addition of CH_3COOH in the solution

$$2NH_4OH + Cu^{2+} \rightarrow 2NH_4{}^{+} + \underset{\text{Blue precipitate}}{Cu(OH)_2}$$

$Cu(OH)2 + 2CH3COOH \rightarrow Cu^{2+} + 2CH_3COO^- + 2H_2O$

Moreover, the precipitate of Cu_2I_2 absorbs I_2 from the solution and releases it slowly making the detection of sharp end point difficult. So, a small amount of NH_4SCN is added near the end point to displace the absorbed iodine from Cu_2I_2 precipitate

Calculation

Weight of $CuSO_4$ = 1.25 g

Strength of $CuSO_4$ = 1000 x 1.25/ 100 X 249.68

= 0.05 N

Titration-I: Standard $CuSO_4$Vs Sodium thiosulphate.

Indicator: starch

S. No.	**Volume of $CuSO_4$ (mL)**	**Burette Readings (mL)**		**Volume of thio sulphate (mL)**
		Initial	**Final**	
1	**20**	**0**		
2	**20**	**0**		
3	**20**	**0**		

Volume of $CuSO_4$ V_1 = 20 mL

Normality of $CuSO_4$ N_1 = 0.050 N

Volume of Sodium thiosulphate V_2 =

Normality of Sodium thiosulphate N_2 = ?

V_1N_1=
V_2N_2

Strength of sodium thiosulphate $N_2 = \frac{V1 \text{ X } N1}{V2} = \frac{20 \text{ X } 0.05}{V2} =$

Procedure

The thiosulphate is standardized by titrating against standard $CuSO_4$ for this 1.25 g of $CuSO_4$ is weighed accurately and made up to a 100 mL SMF with few drops of con.H_2SO_4.

The given solution is made up into 250 mL SMF. Pipetted out 20 mL of solution in a 250 mL conical flask and neutralized the solution by drop wise addition of ammonium solution (1:1) until a blue precipitate appears. Redissolve the precipitate with minimum amount of acetic acid (CH_3COOH) adding about 0.5 mL in excess. Dilute the solution to about 80 ml and add 10 mL of potassium iodide solution (10%). Keep the flask covered with watch glass in a dark and cool place for about 3–5 minutes and titrate the liberated iodine with standard sodium thiosulphate solution from burette. When the colour of the solution fades to a light yellow, add 2 drops of starch followed by 2 mL of ammonium thiocyanate (NH_4SCN) solution (10%). Titrate the solution till the blue colour disappears and a white or flesh white residue is left in the flask. Repeat the titration to get concordant value.

Titration-II

Standard sodium thiosulphate Vs given copperion solution.

Indicator: Starch

S. No.	**Volume of $CuSO_4$ (mL)**	**Burette Readings(mL)**		**Volume of thio sulphate (mL)**
		Initial	**Final**	
1	**20**	**0**		
2	**20**	**0**		
3	**20**	**0**		

Volume of thiosulphate V_1 = -----mL

Normality of thiosulphate N_1 = ----- N

Volume of $CuSO_4$ V_2 = 20 mL N

Strength of $CuSO_4$ N_2 =?

$V_1N_1 = V_2N_2$

The amount of copper ions presents in the whole of the given solution =

$$= \frac{\text{Normality of CuSO4}(N_2)\text{ X Equivalent weight of copper x 250}}{1000}$$

$$= \frac{\text{N2X 63.54 x 250}}{1000} =$$

The amount of copper ions presents in the whole of the given solution =

Precipitative Gravimetric Estimation of Barium

1	Empty crucible weight (a)	
2	Weight of precipitate+ crucible (b)	
3	Weight of precipitate (b-a)	

Calculation

253.37g of barium chromate contains 137.36 of Ba^{2+}

-------- g of barium chromate Contains

= 137.36 X (b−a) / 253.36 = A =

=--------------g barium

40 mL of solution containing (A)-------------g of barium

250 mL of whole of the solution = A X 250 / 40

= The amount of barium ions presents in the whole of the given solution=

Result:

The amount of copper ions presents in the whole of the givensolution =

The amount of barium ions presents in the whole of the givensolution =

5. Separation and estimation of Cu^{2+}– Zn^{2+}mixtures by volumetric method and the other by gravimetric method

Aim

To estimate the amount of copper by volumetrically and zinc by gravimetrically present in the whole of the given copper-zinc solution.

Volumetric Estimation of Copper

Principle

Cu (II) reacts with KI giving a brown precipitate of Cu_2I_2 and liberating iodine. When an excess of KI is added to the solution containing Cu^{2+} in neutral or slightly acidic medium, quantitative liberation of iodine takes place.

$$2CuSO_4.5\,H_2O + 4KI \rightarrow 2CuI_2 + 2K_2SO_4 + 5H_2O$$

$$2CuI_2 \rightarrow Cu_2I_2 + I_2$$

The liberating I_2 is treated against thiosulphate which is previously standardized against std. $CuSO_4$ solution, equivalent Weight of Cu= 63.54

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

From the above equation it is evident that

$$2Cu^{2+} = I_2 \equiv 2S_2O_3^{2-} = 2e$$

The Equivalent weight of Cu^{2+} will be one half of twice themolecular involves two electrons per two moles of Cu^{2+}. Equivalentweight of Cu^{2+} = (2 x 63.5)/2 = 63.5.

The titration fails when any mineral acid is present in the solution and therefore before commencing the titration the acid should be neutralized. This is done by dropwise addition of NH_4OH until a slight blue precipitate just appears.

The precipitate can be removed by addition of CH_3COOH in the solution

$$2NH_4OH + Cu^{2+} \rightarrow 2NH_4^+ + Cu(OH)_2$$

Blue precipitate

$$Cu(OH)_2 + 2CH_3COOH \rightarrow Cu^{2+} + 2CH_3COO^- + 2H_2O$$

Moreover, the precipitate of Cu_2I_2 absorbs I_2 from the solution and releases it slowly making the detection of sharp end point difficult. So, a small amount of NH_4SCN is added near the end point to displace the absorbed iodine from Cu_2I_2 precipitate

Calculation

Weight of $CuSO_4$ = 1.25 g

Strength of $CuSO_4$ = 1000 x 1.25/ 100 X 249.68

= 0.05 N

Titration-I: Standard $CuSO_4$Vs Sodium thiosulphate.

Indicator: starch

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings (mL)		Volume of thiosulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		
3	20	0		

Volume of $CuSO_4$ V_1 = 20 mL

Normality of $CuSO_4$ N_1 = 0.050 N

Volume of Sodium thiosulphate V_2 =

Normality of Sodium thiosulphate N_2 = ?

$V_1N_1= V_2N_2$

Strength of sodium thiosulphate $N_2 = \frac{V1 \text{ X } N1}{V2} = \frac{20 \text{ X } 0.05}{V2} =$

Procedure

The thiosulphate is standardized by titrating against standard $CuSO_4$ for this 1.25 g of $CuSO_4$ is weighed accurately and made up to a 100 mL SMF with few drops of con.H_2SO_4.

The given solution is made up into 250 mL SMF. Pipetted out 20 mL of solution in a 250 mL conical flask and neutralized the solution by drop wise addition of ammonium solution (1:1) until a blue precipitate appears. Redissolve the precipitate with minimum amount of acetic acid (CH_3COOH) adding about 0.5 mL in excess. Dilute the solution to about 80 ml and add 10 mL of potassium iodide solution (10%). Keep the flask covered with watch glass in a dark and cool place for about 3–5 minutes and titrate the liberated iodine with standard sodium thiosulphate solution from burette. When the colour of the solution fades to a light yellow, add 2 drops of starch followed by 2 mL of ammonium thiocyanate (NH_4SCN) solution (10%). Titrate the solution till the blue colour disappears and a white or flesh white residue is left in the flask. Repeat the titration to get concordant value.

Titration-II

Standard sodium thiosulphate Vs given copper ion solution.

Indicator: Starch

S. No.	Volume of $CuSO_4$ (mL)	Burette Readings(mL)		Volume of thio sulphate (mL)
		Initial	Final	
1	20	0		
2	20	0		
3	20	0		

Volume of thiosulphate V_1 = -----mL

Normality of thiosulphate N_1 = ----- N

Volume of $CuSO_4$ V_2 = 20 mL N

Strength of $CuSO_4$ N_2 =?

$V_1N_1 = V_2N_2$

The amount of copper ions presents in the whole of the given solution =

$$= \frac{\text{Normality of CuSO4}(N_2)\text{ X Equivalent weight of copper x 250}}{1000}$$

$$= \frac{\text{N2X 63.54 x 250}}{1000} =$$

The amount of copper ions presents in the whole of the given solution =

Precipitative Gravimetric Estimation of Zinc

Oxine forms a sparingly soluble precipitate with zinc ion in aceticacid and ammonium acetate solution. It has the composition Zinc$(C_9H_6ON)_2$. Oxine is 8-hydroxy quinoline.

Procedure: 40ml of the made-up solution pipetted out into a beaker. The solution is made slightly acidic by the addition of 5mL of dil. HCl. It is heated to boiling. HCl is added and heated. H_2S gas is passed for about20 minutes. The precipitate is washed several times with water. The filtrate is then concentrated to about 50mL. The solution is made almost neutral by the addition of NH_3. About 5g of ammonium acetate and 4mL of acetic acid are added. The solution is warmed to 60°C. A slight excess of 2% solution of oxine (20mL) added by drop with stirring till the supernatant liquid is clear yellow in colour. It is then digested for about 2minutes and filtered through a previously weighed G_4 Sintered crucible. The precipitate is washed several times with hot water. It is then dried in hot air oven at 130-140ºC and weighed. A duplicate experiment is also performed.

Precipitative Gravimetric Estimation of Zinc

1	Empty Crucible weight (a)	
2	Weight of Precipitate+ Crucible (b)	
3	Weight of Precipitate (b-a)	

Calculation

353.69g of zinc Oxinate contains 63.37 of Zn^{2+}

-------- g of zinc Oxinate Contains $= \frac{63.37 \text{ X } ^{(b-a)}}{353.69} = A =$

A=___________g Zinc

40 ml of solution containing (A)______g of zinc

250 ml of whole of the solution $= \frac{A \text{ X } 250}{40} =$

The amount of zinc ions Present in the whole of the given solution=

Results

3. The amount of copper ions presents in the whole of the given solution=
4. The amount of zinc ions presents in the whole of the given solution=