Semester-III

18CHU312 COORDINATION CHEMISTRY - PRACTICAL 4H 2C

Instruction Hours/week: L: 0 T:0 P:4 Marks: Internal:40 External: 60 Total:100

Programme Objectives

To enable the students to understand
1. The principles of gravimetric analysis and apply the same for coordination complexes.
2. To train how to prepare coordination complexes.
3. To characterise the coordination compounds.

Programme Outcome

This laboratory course enables the students to
1. Understand the principle of gravimetric analysis and able to estimate Ni, Cu, Fe and Al.
2. Know how to prepare coordination complexes
3. Know to measure 10 Dq by spectroscopic method.

Experiments

Gravimetric Analysis:

- i. Estimation of nickel (II) using Dimethylglyoxime (DMG).
- ii. Estimation of copper as CuSCN
- iii. Estimation of iron as Fe_2O_3 by precipitating iron as $Fe(OH)_3$.
- iv. Estimation of Al(III) by precipitating with oxine and weighing as $Al(oxine)_3$(aluminium oxinate).

Inorganic Preparations:

- i. Tetraamminecopper (II) sulphate, $[Cu(NH_3)_4]SO_4.H_2O$
- ii. Acetylacetonate complexes of Cu^{2+}/Fe^{3+}
- iii. Tetraamminecarbonatocobalt (III) nitrate
- iv. Potassium tri(oxalato)ferrate(III)

Properties of Complexes

- i. Measurement of 10 Dq by spectrophotometric method
- ii. Synthesis of ammine complexes of Ni(II) and its ligand exchange reactions (e.g.bidentate ligands like acetylacetone, DMG, glycine) by substitution method.

Suggested Readings

TextBook

1. Vogel, A.I. (2002).*A text book of Quantitative Analysis*.ELBS.

Reference Book

1. Marr, G. & Rockett, B.W.(1972).*Practical Inorganic Chemistry*. Van Nostrand Reinhold.

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DEPARTMENT OF CHEMISTRY

Title of the course: Coordination Chemistry- Practical **Course code: 18CHU312**
Class : II-B.Sc., Chemistry **Semester - III**

S. No.	Duration Hours	Name of the Experiment
1.	4	Writing experimental procedure and Demonstration
2.	4	Estimation of nickel (II) using Dimethylglyoxime (DMG).
3.	4	Estimation of copper as CuSCN
4.	4	Estimation of iron as Fe_2O_3 by precipitating iron as Fe $(OH)_3$.
5.	4	Estimation of Al (III) by precipitating with oxine
6.	4	Preparation of Tetraamminecopper (II) sulphate, $[Cu(NH_3)_4]SO_4.H_2O$
7.	4	Preparation of Acetylacetonate complexes of Cu^{2+}/Fe^{3+}
8.	4	Preparation of Tetraamminecarbonatocobalt (III) nitrate
9.	4	Preparation of Potassium tri(oxalato)ferrate(III)
10.	4	Repetition class
11.	4	Viva-voice questions
12.	4	Model practical examination

Coordination
Chemistry
Practical-Manual
(18CHU312)

Coordination Chemistry Practical (18CHU312)

Ex.No	Title	Page No
Inorganic Preparations		
1.	Preparation of Tetraamine Cu(II) sulphate	
2.	Preparation of Hexaammine Co(III)chloride	
3.	Preparation of Potassium tri(oxalato)ferrate (III)	
Gravimetric Analysis		
4.	Estimation of Cu as Cuprousthiocyanate (CuCNS)	
5.	Estimation of Ni using Dimethylglyoxime (DMG)	
6.	Estimation of Iron as Ferric oxide (Fe_2O_3)	
7.	Estimation of Al as Aluminium oxide (Al_2O_3)	

INORGANIC PREPARATIONS

Exp. No: 1 Preparation of Tetraaminecopper (II) sulphate

Aim:

To prepare the pure sample of Tetraaminecopper (II) sulphate

Principle:

When solution of cuso4 to mixed with an excess of ammonium solution initially while precipitate of cuprous hydroxide formed, dissolved again to give a deep blue solution of cuprammonium sulphate complexes. The complex is precipitated form the solution by the addition of alcohol in which it is insoluble.

Chemicals required:

Copper sulphate	-	2.5 g
Con. NH_3 (1:1) solution	-	5ml
Alcohol	-	10ml

Procedure:

In a 100 ml beaker 2.5 g $CuSO_4$ in dissolved in about 10ml if water. A few drops of con.H_2SO_4 is added to it. To this solution (1:1) Con. NH_3 solution is slowly added until a clear blue liquid is obtained. If there appear as the white precipitate or turbidity a little more Con. NH_3 solution is added. Now 10 ml of alcohol is added in drop wise with constant stirring. When a purple precipitate of cuprous ammonium sulphate is obtained. The beaker is heated on the water bath about 50°c for 10-15 minutes to dissolve the precipitate. The solution is allowed to cool collect the blue crystals are filtrate at the pump washed with alcohol dried and the percentage of yield is noted.

Result:

The weight of the Tetraaminecopper (II) sulphate complex salt is obtained =____________g

Exp. No: 2 Preparation of Hexaamminecobalt (III) chloride

Aim:

To prepare the sample of Hexaamminecobalt (III) chloride

Principle:

Preparation of Hexaamminecobalt(III)chloride involves the mixing of NH_4Cl and $CoCl_2$ followed by the addition of con. NH_4 and H_2O_2

$2\ CoCl_2 + 2\ NH_4Cl + 10\ NH_3 + H_2O_2$——>$2\ [Co(NH_3)_6\ Cl_3] + 2\ H_2O$

Chemicals required:

NH_4Cl	-	12g
$CoCl_2$	-	18g
H_2O_2	-	35 ml

Procedure:

18 g of $CoCl_2$ is dissolved in a boiling solution of 12g of NH_4Cl in 20ml of water. Add 1 ml if animal charcoal and cool the condense in the running water. Washed out the vessel in which the solution was first made with 40 ml of con. NH_3 and then add the ammoniacal liquid to the flask. Cool the whole condense of preparation in the ice bath to 10°c. 35 ml of 20 volume H_2O_2 is added slowly in portions while briskly shaking the flask and its condense all the oxidizing agents having been added, heat the mixture gradually to 60°c with mixing by shaking until the pinkish tint in liquid is removed. Crystals being to separate at the close of heating and deposit in quantity on cooling in an ice bath. Filter off crude solid and without Washing it, transfer it to a beaker Containing a boiling mixture of 150 ml of water and 5 ml of con. HCl. When all solid expert the charcoal is dissolved, filter the liquid while hot. Add 20 ml of con. HCl to the filtrate and then cool this in an ice bath. Golden brown crystals are separated out.

Result:

The amount of Hexaamminecobalt (III) chloride =_____________g

Exp. No: 3

Preparation of Potassium tri(oxalato)ferrate (III)

Aim:

To prepare Potassium tri(oxalato)ferrate (III) from ferrous ammonium sulphate and oxalic acid.

Principle:

Ferrous oxalate is obtained by mixing ferrous ammonium sulphate and oxalic acid, to which Potassium oxalate and H_2O_2 are added to get the complex of Potassium tri(oxalato)ferrate (III)

Chemicals required:

Ferrous ammonium sulphate - 5g
Oxalic acid - 3g
Potassium oxalate - 3.5g
H_2O_2 (6%) - 9 ml
C_2H_5OH - 15ml

Procedure:

5 ml of ferrous ammonium sulphate are dissolved in 50 ml of water containing 1 ml of 3M H_2SO_4. It is mixed with a solution containing 3.5 g of oxalic acid dissolved in 25 ml of water. The mixture which now contains a yellow precipitate of ferrous oxalate is carefully heated to boiling point, allowed to settled and cooled to room temperature. The supernatant liquid is decanted and the solid is washed again by decantation with 20 ml of hot water. The hydrated ferrous oxalate is then suspended in a solution of 3.5 g of Pota.oxalate mono hydrate in 100 ml of H_2O and the mixture is warmed to 40°c. About 9 ml of 6% H_2O_2 is then added drop wise from a burette with continues agitation. The greenish liquid with red brown precipitate of ferric hydroxide is heated to boiling, while a solution 0.8 g of oxalic acid is added slowly with stirring. The hot liquid is filtered, it necessary, andcooled in ice while 30 ml of 95% ethanol are added. The product is filtered and dried.

Result:

The amount of Potassium tri(oxalato)ferrate (III) = ______________

GRAVIMETRIC ANALYSIS

Exp. No: 4 Estimation of Cu as Cuprousthiocyanate (CuCNS)

Aim:

To estimate the mass of Cu in the whole of the given $CuSO_4$ solution.

Principle:

The given Cu salt solution is made up to a definite volume. Cu present in a definite volume of this solution is precipitated as Ni Dimethyl glyoxime by the addition of ammonium sulphocyanide in presence of sulphurous acid. The reaction takes place according to the following equation,

$$\mathbf{2CuSO4 + 2\,NH_4CNS + 2H_2O + SO_2 \rightarrow 2\,CuCNS + (NH_4)_2SO_4 + H_2SO_4}$$

The Cuprous thiocyanate is separated and weighed as such. From the mass of cuprous thiocyanate, the mass of Cu in the whole of the given solution can be calculated knowing that 121.54 g of cuprous thiocyanate contains 63.54 g of Cu.

Procedure:

The given $CuSO_4$ solution is made up to 100 ml in a standard flask. 20 ml of the made-up solution is pipetted out into a 250 ml beaker. About 5 ml dil.H_2SO_4 added followed by 25-30 ml of freshly prepared saturated sulphurous acid solution. The solution is diluted to 150 ml and heated to boiling. About 10 ml of 10% freshly prepared ammonium thiocyanate is added slowly and with constant stirring (ammonium thiocyanate must be in slight excess), when white cuprous thiocyanate gets precipitated. The solution should be colourless and must smell strongly of SO_2 if the precipitation has been correctly done. The precipitate is allowed to stand several hours preferably overnight. The solution is filtered through a previously weighed sintered glass crucible (IG-4). The precipitate is washed 10-15 times with small quantities of a cold solution prepared by adding to every 100 ml of water, 1 ml of 10% ammonium sulphocyanide and 5 drops of saturated sulphurous acid solution. The precipitate is finally washed several times with 20% alcohol to remove ammonium thiocyanate. The precipitate is then dried at 110°c – 120°c for one hour, cooled and weighed as CuCNS. Heating, cooling and weighing are repeated till the mass becomes constant. A duplicate experiment is conducted. From the mass of copper thiocyanate obtained, the mass of copper in the whole of the given solution is calculated knowing that 121.54 g of copper thiocyanate contains 63.54 g of Cu.

Calculation:

Mass of crucible (a) =__________g

Mass of crucible + CuCNS (b) =__________g

Mass of CuCNS (b-a) =__________g

121.54 g of CuCNS contains 63.54 of Cu

Mass of Cu in (b-a)g of CuCNS = 63.54 × (b-a) / 121.54g

Mass of Cu in the whole of the given solution

= 63.54 × (b-a) ×5 / 121.54g

=

Result:

Mass of Cu in the whole of the given solution =_______g

Exp. No: 5 Estimation of Ni using Dimethylglyoxime (DMG)

Aim:

To estimate the mass of Ni in the whole of the given Nickel ammonium sulphate solution.

Principle:

The given Ni salt solution is made up to a definite volume. Ni present in a definite volume of this solution is precipitated as Nickel dimethylglyoxime by adding alcoholic solution of dimethyl glyoxime in presence of slight excess of aqueous ammonia

$$\mathbf{NiSO_4 + 2C_4H_8O_2N_2 \rightarrow Ni(C_4H_7O_2N_2)_2 + H_2SO_4}$$

The precipitate is filtered through a sintered glass crucible, washed, dried andweighed. From the mass of Ni dimethyl glyoxime obtained, the mass of Ni in the whole of the solution is calculated, knowing that 288.69 g of Ni dimethyl glyoxime contains 58.69g of Ni.

Procedure:

The given Ni salt solution is made up to 100 ml in a standard flask. 20 ml of the made up solution is pipetted out into a 250 ml beaker. About 5 ml of 1:1 HCl acid is added and the solution diluted to 150 ml. The solution is heated to 70°c to 80°c and 20 – 25 ml of 1% dimethyl glyoxime in rectified spirit is added, immediately followed by dill.NH_3 solution drop wise, directly to the solution and not along the sides of the beaker till the solution is slightly alkaline as indicated by the smell of NH_3 emanating from the solution. The solution containing the precipitate is heated on a steam bath for 30 minutes and the supernatant liquid tested for complete precipitation. The precipitate is allowed to stand for an hour. Cooling of the solution may be hastened by keeping the beaker in a basin of cold water.

The cold solution is then filtered through a previously weighed sintered glass crucible (IG-4). The precipitate is washed with cold water until free from chloride. The sintered glass crucible is then placed in dry 100 ml beaker and heated in an air oven at 110°c- 120°c for 1 hour. It is allowed to cool in a desiccator and weighed. Heating, cooling and weighing are repeated till the weight is constant. A duplicate experiment is conducted.

From the mass of dimethyl glyoxime complex, the mass of Ni is calculated knowing that 288.69 g of complex, contains 58.69 g of Ni.

Calculation:

Mass of crucible (a) =___________g

Mass of crucible + Ni complex (b) =___________g

Mass of Ni-DMG complex (b-a) =___________g

288.69 g Ni complex contains 58.69 g of Ni

Mass of Ni in (b-a) g of complex = 58.69 × (b-a) / 288.69g

Mass of Ni in the whole of the given solution

= 58.69 × (b-a) × 5 / 288.69g

=

Result:

Mass of Ni in the whole of the given solution =_______g

Exp. No: 6 Estimation of Iron as Ferric oxide (Fe_2O_3)

Aim:

To estimate the amount of iron in the whole of the given ferric alum solution

Principle:

The given ferric alum solution is made up to a definite volume. Iron in a measured volume of the solution is precipitated as ferric hydroxide by the addition of excess of ammonium hydroxide. The precipitate is ignited to ferric oxide and weighed.

$$Fe_2(SO_4)_3 + 6NH_4OH \rightarrow Fe(OH)_3 + 3(NH_4)_2SO_4$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

From the mass of the precipitate, the mass of iron in the whole of the solution is calculated knowing that one molecular mass of ferric oxide contains two atomic mass of iron.

Procedure:

The given ferric alum solution is made up to 100 ml. About 1 ml of concentrated HCl acid is added during the making up to prevent hydrolysis of the ferric salt. 20 ml of the made up solution is pipetted out into a 250 ml beaker provided with a cover glass and a glass rod. About 1 ml of concentrated HNO_3 is then added to oxidise any ferrous salt present to the ferric state. The solution is boiled to expel the oxides of nitrogen. The solution is then diluted to 120 ml with distilled water and then heated to boiling. Ammonium hydroxide solution is then added to the boiling solution with constant stirring till there is distinct smell of ammonia.

The mixture containing precipitated ferric hydroxide is boiled for 2-3 minutes. It is allowed to settle. To the clear supernatant liquid, a few drops of ammonium hydroxide is added to test whether precipitation is complete. The supernatant liquid is then decanted through a quantitative filter paper (Whatman No.41 and size 11 cm) keeping as much of the precipitate as possible in the beaker. The precipitate is washed with hot 1% ammonium nitrate solution till the washing is free from sulphate ions (chloride ions, if ferric chloride is used). Finally the precipitate is washed with hot water and transferred to the filter. Any particle sticking to the sides of the beaker are transferred to the filter by using a policeman. The precipitate is dried in an air oven for half an hour.

The filter paper is folded and placed in a previously weighed crucible. The crucible is then mounted on a clay pipe triangle. It is heated by a low flame until the paper chars without inflaming and the carbon burned off with free access of air in order to avoid reduction of the ferric oxide. Finally the precipitate is ignited at red heat for 15 minutes, cooled in a desiccator and weighed. Heating, cooling and weighing repeated until constant mass is obtained.

A duplicate experiment is conducted. From the mass of ferric oxide, the mass of iron in the whole of the solution is calculated knowing that 159.68 g of ferric oxide contains 111.68 g of iron.

Calculation:

Mass of crucible (a) =__________g

Mass of crucible + ferric oxide (b) =__________g

Mass of ferric oxide (b-a) =__________g

159.68 g of Fe_2O_3 contains 111.68 g of Fe

Mass of Fe in (b-a) g of Fe_2O_3 = 111.68 × (b-a) / 159.68g

Mass of Fe in the whole of the given solution

= 111.68 × (b-a) × 5 / 159.68g

Result:

Mass of Fe in the whole of the given solution =__________g

Exp. No: 7 Estimation of Al as Aluminium oxide (Al_2O_3)

Aim:

To estimate the amount of Al in the whole of the given aluminium sulphate solution.

Principle:

The given aluminium sulphate solution is made up to a definite volume. Aluminium present in a definite volume of the made up solution is precipitated as aluminum hydroxide by ammonium hydroxide. The white gelatinous precipitate obtained is ignited and weighed as aluminum oxide.

$Al_2(SO_4)_3 + 6\ NH_4OH \rightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$

$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

From the mass of the precipitate, the mass of the Al in the whole of the solution is calculated knowing that one molecular mass of aluminium oxide contains two atomic mass of Al.

Procedure:

The given aluminium sulphate solution is made up to 100 ml in a standard flask. 20 ml of the made-up solution is pipetted out into a 250 ml beaker provided with a cover glass and a glass rod. Dilute the Solution with about 100 ml of distilled water and add about 5 g A.R. ammonium chloride and a few drops of 0.2% alcoholic solution of methyl red indicator. The solution is heated to boiling. The beaker is removed from the flame and the Al is precipitated as $Al(OH)_3$ by the addition of a (1:1)ammonia solution slowly with constant stirring. Addition of the ammonia solution is continued until the colour of the solution becomes distinct yellow. The contents of the beaker ais boiled for about 2 minutes and then the precipitate is allowed to settle. Then the supernatant liquid is then decanted through a quantitative filter paper (Whatman No.41 and size 11 cm) keeping as much of the precipitate as possible in the beaker.The precipitate is washed with 2% NH_4Cl or NH_4NO_3 solution. Washing is continued till the filtrate is free from chloride and sulphate ions (negative tests with $AgNO_3$ and barium chloride solution respectively) precipitate is transferred to the funnel and dried as usual. The precipitate is ignited along with the filter paper in a previously weighed silica crucible. In the beginning, the heating is done on a low flame till all the carbon of the filter paper has been burnt away. Now the crucible is strongly heated by means of a flame to while heat about 1200°c or preferably in a muffle furnace at this temperature for about half an hour. It is then cooled in a desiccator and weighed. Heating, cooling and weighing are repeated until constant mass is obtained.

A duplicate experiment is conducted. From the mass of Al2O3, the mass of aluminium in the whole of the solution is calculated knowing that 101.94 g of Al2O3 contains 53.94 g of Al.

Calculation:

Mass of crucible (a) =__________g

Mass of crucible + aluminium oxide (b) =__________g

Mass of aluminium oxide (b-a) =__________g

101.94 g of Al_2O_3 Contains 53.94 g of Al

Mass of Al in (b-a) g of Al_2O_3 = 53.94 × (b-a) / 101.94 g

Mass of Al in the whole of the given solution

= 53.94 × (b-a) × 5 / 101.94 g

Result:

Mass of Al in the whole of the given solution =__________g