KONGUNADU ARTS AND SCIENCE COLLEGE

(AUTONOMOUS)
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DEPARTMENT OF CHEMISTRY

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LAB MANUAL & SOP
(STANDARD OPERATING PROCEDURE)

CORE PRACTICAL – II

VOLUMETRIC AND ORGANIC ANALYSIS

Name : ……………………………………………………….

Class : ……………………………………………………….

Roll No. :……………………………………………………….

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Syllabus

I. Experiments in volumetric Analysis

(A) Acidimetry and Alkalimetry

Estimation of Na_2Co_3

(B) Permanganametry

1) Estimation of Ferrous sulphate
2) Estimation of oxalic acid
3) Determination of Iron in Ferric Alum
4) Estimation of calcium – Direct method

(C) Dichrometry

1) Estimation of ferrous Iron using internal indicator

(D) Iodimetry

1) Estimation of Arsenious oxide (AS_2O_3)
2) Estimation of copper

(E) Argentemetry (Demonstration Experiments)

1) Estimation of chloride – Fajans and Volhards method

II Organic Analysis

Systamatic analysis of an organic compound. Preliminary tests, detection of elements present, Aromatic Or Aliphatic, Saturated or unsaturated, nature of the functional group, confirmatory tests and preparation of derivatives-- Aldehydes, ketones, Amines, Amides, Diamides, Carbohydrates, phenols, Acids, Esters and nitro compounds.

VOLUMETRIC ANALYSIS

Introduction

Quantitative chemical analysis is ordinarily done by two methods namely volumetric and gravimetric methods. Volumetric analysis involves estimation of a substance in solution by neutralisation, reduction, oxidation or precipitation by means of another solution of accurately known strength. Gravimetric analysis involves estimation of a substance by the process of weighing. Of the two methods of analysis, the volumetric analysis is much more rapidly carried out. Due to simplicity, accuracy and wide applicability, volumetric analysis is preferred to gravimetric analysis.

Volumetric analysis depends on measurements of the volumes of solutions of the interacting substances. A measured volume of the solution of a substance 'A' is allowed to react completely with the solution of definite strength of another substance 'B'. The volume of 'B' is noted. Thus we know the volumes of the two solutions used in the reaction and the strength of solution 'B'. From this data, we can find the strength of the solution 'A'.

Titration

The process of finding out the volumes of reagents required to bring out a definite reaction just to completion is termed as titration.

End Point

The end point of a reaction is the stage at which complete reaction takes place between two solutions. The end point is determined by an indicator which shows a marked colour change at the completion of the chemical reaction.

Standard Solution

Volumetric analysis depends on the use of one standard solution; i.e. a solution of known strength or concentration. A standard solution is prepared by dissolving an accurately weighed amount of a substance called primary standard substance in a definite volume of the solution. The primary standard substance should fulfil the following characteristics:

a. It should be available in a high degree of purity.
b. It should be stable and unaffected by the atmosphere.
c. It should not be efflorescent or deliquescent.
d. It should be readily soluble in water and
e. Its solution in distilled water should not deteriorate on keeping.

Examples of primary standard substances are crystalline oxalic acid, anhydrous sodium carbonate, potassium dichromate, Mohr's salt, sodium chloride etc. If a substance does not conform to one or more of the above characteristics, its standard solution is prepared indirectly. i.e. by preparing a solution of approximately higher concentration than the required one and subsequently determining its exact concentration by titrating it against a solution of a suitable primary standard substance. The solution is then diluted to such an extent so as to get the required concentration. Solutions of potassium permanganate, inorganic acids, caustic alkalies etc. are prepared by indirect method.

Normality

The concentration of solutions is generally expressed in terms of normality. A normal solution is a solution which contains one gram equivalent mass of the substance dissolved in one litre of the solution. Thus a normal (N) solution of sodium hydroxide contains 40 g of sodium hydroxide in one litre of the solution. 2N solution of sodium hydroxide contains 80 g of sodium hydroxide in one litre of the solution. A decinormal solutions (0.1N) of sodium hydroxide contains 4 g sodium hydroxide per litre of the solution.

$$\text{Normality} = \frac{\text{Mass in grams per litre of solution}}{\text{Gram equivalent mass of the substance}}$$

(or) $$\text{Normality} = \frac{\text{Mass in grams}}{\text{Gram equi.mass x Volume in litre}}$$

CLASSIFICATION OF VOLUMETRIC REACTIONS

Volumetric reactions are classified under the following heads.

1. Acidmetry and Alkalimetry

Acidmetry is the estimation of alkali solution using standard acid solution. Alkalimetry is the estimation of an acid solution using standard alkali solution.

e.g. $HCl + NaOH \rightarrow NaCl + H_2O$

2. Oxidation - Reduction Titrations.

Here an oxidising agent is estimated by titrating it with a standard reducing agent and vice-versa. In this type of reaction oxidation and reduction take place simultaneously.

e.g. $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$5H_2C_2O_4 + 5[O] \rightarrow 5H_2O + 10CO_2$

3. Iodimetry and Iodometry

Estimations using standard iodine solution are called iodimetry and those involving iodine liberated from potassium iodide solution by a chemical reaction is iodometry.

Example for iodimetry

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

Example for iodometry

$2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + Cu_2I_2 + I_2$

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

4. Precipitation Titrations

In this type of titration, the strength of a solution is determined by its complete precipitation with a standard solution of another substance.

e.g. $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

5. Complexometric Titrations

This type of titration depends upon the concentration of ions (other than H^+ and OH^-) to form a soluble ion or compound.

e.g. $Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$

The common complexing agent used in complexometric titration is ethylene diamine tetra acetic acid (EDTA).

EQUIVALENT MASSES OF COMPOUNDS

In volumetric analysis a knowledge of the equivalent mass of substances to be estimated and whose standard solutions are to be prepared should be known.

1. Equivalent mass of an acid.

Equivalent mass of an acid is the number of parts by mass of it which contains 1.008 parts by mass of replaceable hydrogen.

$$\text{Equivalent mass of an acid} = \frac{\text{Molecular mass of the aci}}{\text{Basicity of the acid}}$$

Acid	Molecular mass	No. of replaceable H atoms (Basicity)	Equivalent mass
HCl	36.5	1	36.5
HNO_3	63.0	1	63.0
H_2SO_4	98.0	2	49.0
$H_2C_2O_4.2H_2O$	126.0	2	63.0

2. Equivalent mass of a base

Equivalent mass of a base is the number of parts by mass of it which will completely react with one equivalent of an acid.

$$\text{Equivalent mass of an alkali} = \frac{\text{Molecular mass of the alka}}{\text{Acidity of the alkali}}$$

Acidity is meant the number of hydrogen ions which react with one molecule of alkali.

Alkali	Molecular mass	Acidity	Equivalent mass
NaOH	40.0	1	40.0
KOH	56.0	1	56.0
$NaHCO_3$	84.0	1	84.0
$KHCO_3$	100.0	1	100.0
Na_2CO_3	106.0	2	53.0
K_2CO_3	138.0	2	69.0
$CaCO_3$	100.0	2	50.0

3. Equivalent mass of an oxidising agent

Equivalent mass of oxidising agent is number of parts by mass of it which contains 8 parts of mass of available oxygen. Available oxygen means oxygen capable of being utilised for oxidation.

a. Equivalent mass of $KMnO_4$ in acid medium

In acid medium two molecules of potassium permanganate give 5 atoms of oxygen for oxidation.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

316 parts by mass of potassium permanganate give 80 parts by mass of oxygen for oxidation.

Therefore equivalent mass of potassium permanganate in acid medium

$$= \frac{316 \text{ x } 8}{80} \text{ x } 31.6$$

b. Equivalent mass of $K_2Cr_2O_7$ in acid medium

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

294 parts by mass of potassium dichromate give 48 parts by mass of oxygen.

Therefore equivalent mass of potassium dichromate in acid medium

$$= \frac{294 \text{ x } 8}{48} = 49$$

c. Equivalent mass of MnO_2 in acid medium

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + [O]$$

87 parts by mass of manganese dioxided give 16 parts by mass of oxygen.

Therefore mass of manganese dioxide in acid medium

$$= \frac{87 \text{ x } 8}{16} = 43.5$$

4. Equivalent mass of a reducing agent

Equivalent mass of a reducing agent is the number of parts by mass of it which can be oxidised by 8 parts (one equivalent) by mass of oxygen.

a. Equivalent mass of crystalline ferrous sulphate, $FeSO_47H_2O$

In the presence of dilute sulphuric acid, iron(II) sulphate is oxidised as follows.

$$2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$$

Therefore, the equivalent mass of crystalline ferrous sulphate is the same as its molecular mass i.e. 278.

b. Equivalent mass of Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$

$$2FeSO_4.(NH_4)_2SO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + 2(NH_4)_2SO_4 + H_2O$$

Therefore the equivalent mass of Mohr's salt is the same as its molecular mass i.e. 392.

c. Equivalent mass of oxalic acid, $H_2C_2O_42H_2O$.

$$H_2C_2O_4 + [O] \rightarrow H_2O + 2CO_2$$

One equivalent of oxygen oxidises half the molecular mass of oxalic acid. Therefore, the equivalent mass of oxalic acid is

$$\frac{H_2C_2O_4.2H_2O}{2} = \frac{126}{2} = 63$$

d. Equivalent mass of sodium oxalate, $Na_2C_2O_4$

$$Na_2C_2O_4 + H_2SO_4 + [O] \rightarrow Na_2SO_4 + 2CO_2 + H_2O$$

Therefore equivalent mass of sodium oxalate is half its molecular mass i.e., 67.

5. Equivalent masses of metal halides

$$\text{Equivalent mass of metal halide} = \frac{\text{Molecular mass of halide}}{\text{No. halogen ions furnished by a molec}}$$

Thus

$$\text{Equivalent mass of NaCl} = \frac{58.46}{1} = 58.46$$

$$\text{Equivalent mass of KCl} = \frac{74.46}{1} = 74.46$$

a. Equivalent mass of silver nitrate

$$AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl$$

Therefore, the equivalent mass of silver nitrate $= \frac{AgNO_3}{1} = \frac{170}{1} = 170$

b. Equivalent mass of sodium thiosulphate and iodine

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

Therefore equivalent mass of sodium thiosulphate is its own molecular mass, i.e. $Na_2S_2O_3.5H_2O$, i.e. 248 and that of iodine is its own atomic mass i.e. 127

c. Equivalent mass of copper sulphate

$$2CuSO_4 + 4Kl \rightarrow Cu_2l_2 + 2K_2SO_4 + l_2$$

Therefore, the equivalent mass of crystalline copper sulphate is its own molecular mass, $CuSO_4.5H_2O$, i.e. 249.5.

d. Equivalent mass of arsenious oxide

$$As_2O_3 + 2H_2O + 2l_2 \rightarrow As_2O_5 + 4Hl$$

Therefore, the equivalent mass of arsenious oxide $= \frac{As_2O_3}{4} = 49.5$

PRINCIPLE OF VOLUMETRIC ANALYSIS

When two solutions completely react with each other, the product of volume and normality of one solution will be equal to the product of volume and normality of the other solution

$$V_1 \times N_1 = V_2 \times N_2$$

where, V_1 and N_1 are the volume and normality of the first solution and V_2 and N_2 are the volume and normality of the second solution. Thus, if the volumes of the two solutions which completely react with each other are determined, and if the normality of one of the solutions is known, the normality of the other solution can be calculated. By multiplying the normality factor by the equivalent mass, the mass of the substance in one litre of the solution is found out.

Normality x Equivalent mass = Mass per litre of the solution.

APPARATUS USED IN VOLUMETRIC ANALYSIS

1. Weighing Bottle and Standard Measuring Flask.

Weighing bottle consists of a cylindrical glass vessel with an accurately ground stopper in which the material can be weighed out of contact with the open atmosphere. The weighing bottle is usually heated in an oven at 100 to 105°C before use to ensure dryness and is then allowed to cool in a desiccator. It should be handled in a dry cloth to avoid contamination with moisture and grease from the fingers. The substance may be weighed in a weighing bottle as follows. The weighing bottle containing an amount of the substance (known to be roughly suitable for the purpose) is accurately weighed by using a chemical balance. It is then transferred very carefully into a funnel placed over a standard measuring flask. (Standard measuring flask is a long narrow-necked flask fitted with tight fitting glass stopper and constructed to contain a given volume of liquid when filled to a mark scratched on the neck of the flask). The mass of the weighing bottle is again determined after the substance has been transferred. The substance in the funnel is washed down into the flask by a jet of distilled water from a wash bottle. The funnel and its stem are then rinsed down into the standard flask and the funnel removed. By carefully giving the flask a rotating motion, the substance is dissolved. Water is then added to the solution till the lower meniscus of the water level coincides with the mark on the neck of the standard flask. The flask is then closed with the stopper and the solution is shaken till it gets uniform concentration.

2. Pipette

When a definite quantity of a liquid (5 ml, 10 ml, 20 ml etc.) is to be delivered a pipette is usually used. It consists of a long tube with an elongated bulb ending in a jet at one end. The capacity of the pipette is marked on the bulb. There is a mark scratched on the stem.

How to use a pipette?

Wash the pipette thoroughly and finally rinse it with distilled water. Then dip the drawn out end of the pipette in the liquid to be measured and suck in a few ml of the liquid. Rinse the pipette with the liquid. Then hold the pipette in the right hand; keeping the fore-finger free. Then again suck in the liquid. When the liquid level reaches a little above the mark, take, the pipette from the mouth and close the top immediately with the fore-finger. The pipette is then raised so that the mark is at eye-level and by controlled release of the finger from the stem, the liquid is allowed to fall slowly until the bottom of the meniscus is at the mark. The lower tip of the pipette is then introduced into a clean conical flask. By removing the finger from the stem, the liquid may be delivered from the pipette into the flask. When the liquid has drained off, touch the side of the conical flask with the jet of the pipette. A little liquid will be retained in the tip and no attempt should be made to expel it as the pipette will already have delivered the specified volume of the liquid.

3. Burette

Burette is an accurate devise usually having a capacity of 50 ml and graduated to 0.1 ml. The graduation begins from zero at the top and proceeds downwards. Burette is used for adding measured volumes of solutions during a titration.

How to use a burette?

The burette is washed thoroughly by using tap water at first and then with distilled water. The burette is then rinsed (washed out with a small quantity of the solution it is to contain, the washings being allowed to run away through the nozzle), so as to eliminate completely any impurities sticking to it. It is then filled above the zero mark with the solution and the nozzle is also filled by opening the stop-cock for a second or two. The reading of the bottom level of the meniscus is adjusted to zero. A white sheet of paper held behind the liquid may be employed to see the position of the meniscus more clearly.

The burette is clamped vertically, while using the burette, the stop-cock is kept on the right side. The stop-cock is held by the left hand by passing the thumb before and the other fingers behind the burette. The stop-cock is held by thumb and the fore-finger. This keeps the stopper pressed inwards thus avoiding the risk of its coming out. The flask containing the solution is held in the right hand. During titration, the solution from the burette is added slowly and the flask is whirled with right hand, so that the two solutions get mixed thoroughly. When the end point is reached, the final burette readings is noted. The difference of the two burette readings will give the volume of solution used for titration of solution contained in the flask.

Precautions to be taken in using a burette

1. Before using the burette, see that the glass stop-cock does not leak and works properly.
2. No air bubble should be present in the nozzle of the burette.
3. While noting the initial burette reading see that there is no drop of liquid hanging at the nozzle. If there is any, remove it by touching with a piece of paper.
4. The reading should always be taken at eye level.

5. Read the bottom of the meniscus in case of colourless and transparent liquids.
6. Read top of the meniscus in case of highly coloured liquids.
7. Do not keep the funnel over the burette while adjsuting the liquid level in the burette.
8. It is not necessary to have the initial reading always at zero.
9. Before taking the final burette reading allow about 30 seconds to let the liquid sticking to the walls of the burette slip down.
10. The burette after use should immediately be emptied and thoroughly washed with water.
11. The burette stopper should be greased as follows: Clean and then thoroughly wash it with distilled water. Then wash it a number of times with a little chromic acid to remove any adhering grease from the inner surface and again wash it with water. Then apply a little grease on the stopper and insert the stopper into the cavity, rorate and see that the stopper moves quite freely.

4. Titration flask

Titration flask is a special type of flask having a wide neck, belly and a flat bottom. The wide neck, allows the direct fall of the liquid from the burette even when the flask is being swirled. The big belly avoids the risk of liquid going up along the sides while the flask is in swirling motion during titrations.

Note: Titration flask, before using, is washed thoroughly with water and then rinsed with distilled water. It must never be rinsed with liquid to be titrated.

The Analytical Balance

The accuracy of a quantitative analysis depends on a number of factors among which the sample has been weighed is of primary importance. For weighing a substance accurately an analytical balance is used. An analytical balance consists of the following parts:

1. *Beam*. The beam is made from a light and rigid aluminium alloy. It is graduated from the centre towards the ends.
2. *Central Agate*. The beam is mounted at the centre on an agate, prism-like edge.
3. *Central Pillar*. Central pillar supports the central agate.
4. *Terminal Knife Edges*. At equal distances from the central knife edge on the beam are placed two terminal knife edges.
5. *Stirrups*. Each of the terminal knife edges support a stirrup.
6. *Adjusting Nuts*. The two ends of the beam are provided with two adjusting nuts. By screwing these in or out, the effective mass can be changed.
7. *Pans*. Pans are hung from the two stirrups.

8. *Pointer*. The upper end of this is attached to the centre of the beam, while the pointed lower end swings against the index plate.
9. *Index Plate*. Index plate is a scale at the lower end of the supporting pillar.
10. *Lever*. Lever is a knob provided at the base of the balance. This is directly linked with the central agate. By turning this clockwise/counter-clockwise, the pans are set in swing or brought to rest.
11. *Beam Arrest*. Beam arrest offers a support to the two ends of the beam, while the balance is at rest.
12. *Levelling Screws*. The balance is provided at the base with 3 levelling screws. By running these clockwise or anti-clockwise, the balance is brought to the correct level.
13. *Rider Rod*. This is a rod provided at the top of the balance. This carries a rider hook for the purpose of carrying a rider.
14. *Rider*. Rider is a U-form of platinum wire weighing 10 mg.

Graduation on the Beam and use of Rider.

The adjustments of masses lower than 10 mg are made by placing a rider over a suitable point on the graduated scale with the help of rider rod. If the rider is placed at the extreme end of the beam scale, it amounts to 10 mg effective mass on the pan of that side. The beam is divided into 50 small divisions from the centre to the end. Therefore 50 small divisions = 10 mg or I small division = 0.2 mg. If the rider is placed at the 24th small division from the centre of the beam on the right side, then the effective mass on the right pan due to rider is 24 x 0.2 = 4.8 mg.

Method of Weighing

The article to be weighed is carefully placed in the centre of the left pan and masses a little greater than estimated of the article are placed on the centre of the right pan, with the help of the forceps. Then carefully allow the pointer to swing freely, by turning the lever. See which way the pointer swings. If the pointer swings more to the left than to the right, it means the masses placed in the pan are heavier than the actual mass of the article. Now arrest the beam by turning the lever. If the masses in the pan are too heavy, then replace it by the next smaller mass. This process is continued until the difference of the masses is less than 1 g. Then fractional masses are added in a decreasing order. Adjustments below 10 mg is made by placing rider on a suitable point of the beam scale, by means of the rider controlling rod. When the pointer swings equally on either sides of the zero, the article is exactly counter balanced. Note the masses placed on the pan.

Precautions to be taken in using an Analytical Balance.

1. Balance should be levelled. This adjustment may be done with the aid of levelling screws.

2. When not in use, the balance should be arrested. The doors of balance should be kept closed whenever possible.

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EQUIVALENT MASSES OF COMMON COMPOUNDS

S.No.	Compound	Molecular Mass	Equivalent mass
1	Arsenious oxide, As_2O_3	197.82	49.45
2	Crystalline oxalic acid, $H_2C_2O_4.2H_2O$	126.00	63.00
3	Calcium carbonate, $CaCO_3$	100.00	50.00
4	Hydrochloric acid, HCl	36.46	36.46
5	Hydrated ferrous sulphate, $FeSO_4.7H_2O$	278.00	278.00
6	Hydrogen peroxide, H_2O_2	34.02	17.01
7	Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$	392.00	392.00
8	Potassium hydroxide, KOH	56.00	56.00
9	Potassium permanganate, $KMnO_4$	158.00	31.60
10	Potassium dichromate, $K_2Cr_2O_7$	294.24	49.04
11	Sulphuric acid, H_2SO_4	98.00	49.00
12	Sodium hydroxide, $NaOH$	40.00	40.00
13	Sodium carbonate, Na_2CO_3	106.00	53.00
14	Sodium thiosulphate, $Na_2S_2O_3.5H_2O$	248.00	248.00
15	Sodium arsenite, Na_3AsO_3	191.90	95.95

VOLUMETRIC ANALYSIS

ACIDIMETRY AND ALKALIMETRY

Acidimetry : Acidimetry is the estimation of alkali solution using standard acid solution.

Alkalimetry : Alkalimetry is the estimation of an acid solution using standard alkali solution.

The object of titrating an alkaline solution with a standard solution of an acid is to determine the amount of acid which is exactly equivalent to the amount of base present. The point at which this is reached is the theoretical end point. If both the acid and base are strong electrolytes, the resultant solution will be neutral and have a p^H of 7. But if either the acid or the base is a week electrolyte, the salt will be hydrolysed, and the solution at the equivalent point will be either slightly alkaline or slightly acidic.

Acid-base Indicators : Acid-base indicators possess different colours according to the H^+ concentration of the solution. However the colour change is not sudden or abrupt, but takes place within a small interval of p^H . All acid-base indicators are very weak organic acids or bases.

Colour change and p^H range of indicators

Indicator	p^H range	Colour in acid solution	Colour in alkaline Solution
Methyl orange	3.1 to 4.4	Red	Orange
Methyl red	4.2 to 6.3	Red	Yellow
Phenolphthalein	8.3 to 10	Colourless	Red

The common indicators used in acidimetry and alkalimetry are phenolphthalein and methyl orange.

1. Phenolphthalein is used when: (a) A strong acid like hydrochloric acid, nitric acid or sulphuric acid is titrated against a strong base such as sodium hydroxide or potassium hydroxide. (b) A weak acid like oxalic acid is titrated against a strong base like sodium hydroxide or potassium hydroxide.

2. Methyl orange is used when: (a) Strong acids like hydrochloric acid, nitric acid or sulphuric acid are titrated against a strong base such as sodium hydroxide or potassium hydroxide. (b) Strong acids are titrated against weak bases like sodium carbonate, potassium carbonate, ammonia etc.

Preparation of Indicator Solutions :

1. **Phenolphthalein :** 5 g of phenolphthalein is dissolved in 500 ml of alcohol. Then 500 ml of water is added with constant stirring. Any precipitate formed is filtered off and the clear filtrate is used.

2. **Methyl orange :** Methl orange is available either as the free acid or sodium salt. 0.5 g of the free acid or the sodium salt is dissolved in a litre of cold water. Any precipitate formed is filtered off and the clear filtrate is used.

3. **Methyl red :** 1 g of the free acid is dissolved in 600 ml of alcohol. The 400 ml of water is added with stirring. This is used as indicator.

ESTIMATION OF SODIUM HYDROXIDE

AIM :

To estimate the mass of sodium hydroxide present in 1250 ml of the given solution. You are given a standard solution of sodium carbonate containing 8 g in 1.5 litre of the solution and a decinormal solution of hydrochloric acid.

PRINCIPLE :

The estimation depends on the reactions between sodium carbonate and hydrochloric acid and that of sodium hydroxide and hydrochloric acid as given below.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

From the above equation, it is clear that, the

$$\text{Equivalent mass of anhydrous sodium carbonate} = \frac{\text{Molecular mass of } Na_2Co_3}{2} = \frac{106}{2} = 53$$

$$\text{Equivalent mass of sodium hydroxide} = \frac{\text{Molecular mass of NaOH}}{1} = 40$$

A definite volume of standard sodium carbonate solution is titrated with approximately decinormal hydrochloric acid using methyl orange as indicator which is golden yellow in alkaline medium and pale red orange in acid medium.

The unknown sodium hydroxide solution is then standardized using standardized hydrochloric acid solution with phenolphthalein as indicator. From the titre values the mass of sodium hydroxide can be calculated.

PROCEDURE :

(i) Standardisation of hydrochloric acid solution

Exactly 20 ml of the standard sodium carbonate solution is pipetted out into a clean conical flask. 2 drops of methyl orange indicator solution are added. The golden yellow coloured solution is titrated with hydrochloric acid solution taken in a clean burette after rinsing it with the same solution. At the point the solution changes from golden yellow to pale red orange. The titration is repeated for concordant values. From the titre value, the concentration of hydrochloric acid solution is calculated.

(ii) Estimation of sodium hydroxide

Exactly 20 ml of the unknown sodium hydroxide solution is pipetted out into a clean conical flask. 2 drops of phenolphthalein indicator solution are added. The pink coloured solution is titrated against hydrochloric acid until the end point is reached. The end point is just disappearance of pink colour. The titration is repeated for concordant titre values.

From the titre value the concentration of sodium hydroxide solution and hence the mass of sodium hydroxide present in the given solution is calculated.

REPORT :

Mass of sodium hydroxide present in 1250 ml of the given solution = ………..g

$$\text{Concentration of sodium carbonate solution} = \frac{\text{Mass of anh. Sodium carbonate}}{\text{Gram equivalent mass x Volume in litre}}$$

=

= ……….N.

Titration I : Std. aqueous sodium carbonate
Vs
Link aqueous hydrochloric acid
Indicator : Methyl orange
End point : Change of colour from golden yellow to pale red orange

S.No.	Volume of aqueous Na_2Co_3 (ml)	Burette reading		Volume of aqueous HCl(ml)
		Initial	Final	

Volume of aqueous sodium carbonate, V_1 =

Conc. of aqueous Sodium carbonate, N_1 =

Volume of aqueous hydrochloric acid, V_2 =

Conc. of aqueous hydrochloric acid, N_2 = $$\frac{V_1 \times N_1}{V_2}$$

=

=

Titration II : Link aqueous hydrochloric acid Vs Unknown aqueous sodium hydroxide
Indicator : Phenolphthalein
End point : Disappearance of pink colour

S.No.	Volume of aqueous Na_2Co_3 (ml)	Burette reading		Volume of aqueous HCl (ml)
		Initial	Final	

Volume of aqueous hydrochloric acid, V_1 =

Conc. of aqueous hydrochloric acid, N_1 =

Volume of aqueous sodium hydroxide V_2 =

Conc. of aqueous Sodium hydroxide, N_2 = $\frac{V_1 \text{ x } N_1}{V_2}$

=

=

$\left.\begin{array}{l}\text{Mass of sodium hydroxide present in}\\ \text{1250 ml of the given solution}\end{array}\right\}$ = G. Eqt. mass x Nor.xVol. in litre

=

=

ESTIMATION OF SODIUM CARBONATE

AIM :

To estimate the mass of Sodium carbonate present in the whole of the given solution, being supplied with Analar Sodium carbonate and an approximately decinormal HCl acid solution.

PRINCIPLE :

The estimation depends on the reaction between sodium carbonate and hydrochloric acid.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

Since the carbonate reacts with two equivalents of HCl, equivalent mass of carbonate is half its molecular mass.

i.e. The equivalent mass of $Na_2CO_3 = \frac{\text{Molecular Mass}}{2} = \frac{106}{2} = 53$.

For this acid-base reaction , methyl orange is used as the indicator.

PROCEDURE :

Titration I : Standardisation of HCl Acid Solution

About 1.25 g of analar sodium carbonate is accurately weighed in a chemical balance and transferred into a 250 ml standard flask. The crystals are carefully washed down into the flask by a jet of distilled water. The funnel is well washed down into the flask. The sodium carbonate substance is dissolved and the solution made up to the mark and well shaken.

A clean burette is filled up with the given link Hydrochloric acid solution after rinsing it with the solution. Exactly 20 ml of the standard sodium carbonate solution is pipetted out into a clean conical flask. Two drops of methyl orange indicator are added to the solution. It is titrated against the Hydrochloric acid solution taken in the burette. At the end point, the solution will change from golden yellow to a red orange. The titrations are repeated until concordant values are obtained.

Titration II : Estimation of Sodium Carbonate

The given sodium carbonate solution is made upto 100 ml in a standard flask. It is thoroughly shaken to get a uniform concentrated solution. Exactly 20 ml of this solution is pipetted out into a conical flask. To the solution, two drops of methyl orange indicator are added. It is titrated against the standardised Hydrochloric Acid solution. The end point is the change from golden yellow to a red orange colour. From the concordant titre values, the strength of sodium carbonate solution and hence its mass is calculated.

REPORT :

$$\left.\begin{array}{l}\text{The mass of sodium carbonate present}\\ \text{in the whole of the given solution}\end{array}\right\} = \text{.........g.}$$

Mass of weighing bottle + Na_2CO_3 before Transfer = …………g

Mass of weighing bottle + Na_2CO_3 after Transfer = …………g

Mass of Na_2CO_3 = …………g

Concentration of Std.Na_2CO_3 solution = $\frac{\text{Mass of } Na_2CO_3}{\text{G.Eqt.Mass x Volume in litre}}$

=

= …..…….N

Titration I : Std. Na_2CO_3 Vs aqueous Link HCl acid

Indicator : Methyl orange.

End point : Colour changes from golden yellow to pale red orange.

S.No	Volume	Burette Reading		Volume of HCl

	Of Na_2CO_3(ml)	Initial Final	(ml)

Volume of aqueous Na_2CO_3 , V_1 =

Conc. Of aqueous Na_2CO_3 , N_1 =

Volume of aqueous HCl ,V_2 =

Conc. Of aqueous HCl, N_2 = $\frac{V_1 \text{ x } N_1}{V_2}$

=

= ……….N.

Titration II : Unknown Na_2CO_3 Vs aqueous Link HCl acid.

Indicator : Methyl orange.

End point : Colour changes from golden yellow to pale red orange.

S.No	Volume of Na_2CO_3(ml)	Burette Reading		Volumeof HCl

		Initial Final	(ml)

Volume of aqueous HCl, V_1 =

Conc. Of aqueous HCl, N_1 =

Vol of aqueous Na_2CO_3, V_2 =

Conc. Of aqueous Na_2CO_3, N_2 = $\dfrac{V_1 \times N_1}{V_2}$

=

= ……….N.

Mass of sodium carbonate present in the whole of the given solution } = G. Eqt. mass x Nor. x Volume in litre

=

= …………g.

PERMANGANOMETRY

Introduction :

Estimation using potassium permanganate is known as permanganometry. Potassium permanganate in acid medium is an oxidizing agent, two molecules of the substance giving 5 atoms of oxygen for oxidation. This oxygen oxidizes redusing agents such as oxalic acid, ferrous sulphate, and sodium sulphite. The reaction between oxalic acid and potassium permanganate may be represented by the following equations.

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$H_2C_2O_4 + [O] \rightarrow H_2O + 2CO_2$

Using a standard solution of potassium permanganate, solutions of reducing agents can be estimated.

Potassium permanganate solution is pink in colour and when reduced changes into potassium and manganous salts which are colourless in solution. Therefore reducing agents decolourise the pink solution. So no other indicator is required to denote the end point in the titrations with potassium permanganate.

ESTIMATION OF FERROUS SULPHATE

AIM :

To estimate the mass of crystalline Ferrous sulphate present in the whole of the given solution, being supplied with pure crystals of Oxalic acid AR and approximately decinormal $KMnO_4$ as the link.

PRINCIPLE :

In the presence of dil . H_2SO_4 , $KMnO_4$ oxidises $FeSO_4$ into $Fe_2 (SO_4)_3$

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSo_4 + 3H_2O + 5[O]$$
$$2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + 2CO_2$$

Two molecular mass of $FeSO_4$ reacts with 2 equivalents of oxygen.
Ionically the equations can be represented us

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^2 + 4H_2O$$
$$Fe^{+2} \longrightarrow Fe^{+3} + e$$

Since $FeSO_4 . 7H_2O$ gives up one electron,

$$\text{the equivalent of mass } FeSO_4 . 7H_2O = \frac{\text{Molecular mass}}{1} = \frac{278}{1} = 278$$

PROCEDURE :

Titration I : Standardisation of $KMnO_4$

Preparation of Standard Oxalic Acid (N/10) Solution :

Accurately about 1.6 g of AR quality oxalic acid is weighed in a chemical balance. It is transferred into 250 ml flask and the solution is made up to the mark. The solution is shaken well to get a homogeneous solution.

The given $KMnO_4$ solution is taken in a clean and rinsed burette. Exactly 20 ml of standard Oxalic acid solution is pipetted out into a clean conical flask by means of a washed and rinsed pipette. A test-tube full of (20 ml) dil. H_2SO_4 is added. Then the solution is titrated against $KMnO_4$ taken in the burette. The end point is the appearance of permanent pale pink colour. Titrations are repeated to get concordant values. From the titre values, the strength of $KMnO_4$ solution is calculated.

Titration II : Estimation of Ferrous Sulphate

The whole of the given Ferrous Sulphate solution is made upto 100 ml in a standard flask. The flask is shaken well to get uniform concentration.

Exactly 20 ml of Ferrous sulphate solution is pipetted out into a clean conical flask. A test-tube full of (20ml) dil H_2SO_4 is added. Then the solution is titrated against the standardised $KMnO_4$ taken in the burette. The end point is the appearance of permanent pale pink colour. Titrations are repeated to get concordant values. From the concordant titre values, the strength of Ferrous Sulphate and hence its mass is calculated.

REPORT :

The mass of Ferrous sulphate present in the whole of the given solution =……g

Mass of weighing bottle + $H_2C_2O_4$ before Transfer =

Mass of weighing bottle + $H_2C_2O_4$ after Transfer =

Mass of $H_2C_2O_4$ =

Concentration of Std. $H_2C_2O_4$ solution = $\dfrac{\text{Mass of } H_2C_2O_4}{\text{G.Eq. Mass x Volumein litre}}$

=

=

Titration I : Std. aqueous $H_2C_2O_4$ Vs Link aqueous $KMnO_4$

Indicator : Self Indicator

End point : Appearance of permanent pale pink colour

S.No	Volume of aqueous $H_2C_2O_4$ (ml)	Burette Reading		Volume of aqueous $KMnO_4$ (ml)
		Initial	Final	

Volume of aqueous $H_2C_2O_4$, V_1 =

Conc. of aqueous $H_2C_2O_4$, N_1 =

Volume of aqueous $KMnO_4$, V_2 =

Conc. of aqueous $KMnO_4$, N_2 = $\frac{V_1 \text{ x } N_1}{V_2}$

=

=

Titration II : Unknown aqueous Fe^{2+} Vs Link aq $KMnO_4$

Indicator : Self Indicator

End point : Appearance of permanent pale pink colour

S.No	Volume of aqueous Fe^{2+}(ml)	Burette Reading		Volumeof aq $KMnO_4$ (ml)
		Initial	Final	

Volume of aqueous $KMnO_4$, V_1 =

Conc. of aqueous $KMnO_4$, N_1 =

Volume of aqueous Fe^{2+} ,V_2 =

Conc. of aqueous Fe^{2+}, N_2 = $\frac{V_1 \times N_1}{V_2}$

=

=

Mass of Ferrous sulphate present in the whole of the given solution } = G. Eqt. mass x Nor. x Volume in litre

=

=

ESTIMATION OF OXALIC ACID

AIM :

To estimate the mass of Oxalic acid present in the whole of the given solution, being supplied with approximately decinormal solution of Potassium permanganate and pure Oxalic acid crystals of AR equality.

PRINCIPLE :

The estimation is based on the reaction between $KMnO_4$ and oxalic acid. Potassium permanganate oxidises Oxalic acid in the presence of acid and while hot.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSo_4 + 3H_2O + 5[O]$$

$$H_2C_2O_4 + [O] \longrightarrow H_2O + 2CO_2$$

Since one molecule of oxalic acid reacts with 2 equivalents of oxygen, its equivalent mass is half its molecular mass.

The above redox reactions can also be represented by ion-electron equation.

$$MnO_4 + 8H^+ + 5\ e \longrightarrow Mn^{+2} + 4\ H_2O$$

$$C_2O_4^{-2} \longrightarrow 2CO_2 + 2e$$

Since a molecule of oxalic acid loses two electronics,

$$\text{its equivalent mass} = \frac{\text{Molecular mass}}{\text{electronics lost Number}}$$

$$\text{i.e., Equivalent mass of } H_2C_2O_4 \cdot 2H_2O = \frac{\text{Molecular mass}}{2} = \frac{126}{2} = 63$$

Potassium permanganate itself acts as the indicator.

PROCEDURE :

Titration I : Standardisation of $KMnO_4$ Solution

About 1.5 g of oxalic acid crystals are accurately weighed and transferred into a funnel placed over a 250 ml standard flask. The crystals are then carefully washed down into the flask by a jet of distilled water. The funnel is well washed into the flask. The crystals are dissolved and the solution made up to the mark and well shaken.

Exactly 20 ml of the standard oxalic acid solution is pipetted out into a conical flask, about 20 ml of H_2SO_4 added the mixure heated to 60˚ C to 80˚ C on a wire gauze. The solution is then titrated with $KMnO_4$ solution taken in the burette. The first few drops of $KMnO_4$ take some time for decolorisation. But as the reaction proceeds, the manganous sulphate formed acts as catalyst and the reaction proceeds faster. The end-point is indicated by the appearance of a pale-pink colour in the solution. The titration is repeated to get concordant values.

Titration II : Estimation of Oxalic Acid

The whole of the given oxalic acid solution is made up to 100 ml in a standard flask and well shaken for uniform concentration.

Exactly 20 ml of this solution is pipetted out into a conical flask. To the solution, about 20 ml of dilute H_2SO_4 is added. It is then heated to 60˚ C to 80˚C on a wire gauze and the hot solution is titrated against standard $KMnO_4$ solution taken in the burette. The end point is the appearance of pink colour in the solution. The titration is repeated until the concordant values are obtained.

REPORT :

The mass of oxalic acid present in the whole of the given solution = ………..g

Mass of weighing bottle + $H_2C_2O_4$ before Transfer =

Mass of weighing bottle + $H_2C_2O_4$ after Transfer =

Mass of $H_2C_2O_4$ =

$$\text{Concentration of Std. } H_2C_2O_4 \text{ solution} = \frac{\text{Mass of } H_2C_2O_4}{\text{G.Eq. MassxVolume in litre}}$$

=

=

Titration I : Std. aqueous $H_2C_2O_4$ Vs Link aqueous $KMnO_4$

Indicator : Self Indicator

End point : Appearance of permanent pale pink colour

S.No	Volume of	Burette Reading		Volume of

	aqueous $H_2C_2O_4$ (ml)	Initial Final	aqueous $KMnO_4$ (ml)

Volume of aqueous $H_2C_2O_4$, V_1 =

Conc. of aqueous $H_2C_2O_4$, N_1 =

Volume of aqueous $KMnO_4$, V_2 =

Conc. of aqueous $KMnO_4$, N_2 $= \dfrac{V_1 \text{ x } N_1}{V_2}$

=

=

Titration II : Unknown aqueous $H_2C_2O_4$ Vs Link aqueous $KMnO_4$

Indicator : Self Indicator

End point : Appearance of permanent pale pink colour

S.No	Volume of aqueous $H_2C_2O_4$	Burette Reading		Volume of aqueous $KMnO_4$

	(ml)	Initial Final	(ml)

Volume of aqueous $KMnO_4$, V_1 =

Conc. of aqueous $KMnO_4$, N_1 =

Volume of aqueous $H_2C_2O_4$, V_2 =

Conc. of aqueous $H_2C_2O_4$, N_2 = $\frac{V_1 \text{ x } N_1}{V_2}$

=

=

Mass of Oxalic acid present in the whole of the given solution $\}$ = G. Eqt. mass x Nor. x Volume in litre

=

=

ESTIMATION OF FERRIC IRON IN FERRIC ALUM

AIM :

To estimate the amount of ferric iron in the whole of the given solution of ferric alum, being supplied with pure oxalic acid and approximately decinormal potassium permanganate solution.

PRINCIPLE :

The ferric salt is reduced to ferrous salt on heating with zinc and dilute sulphuric acid. The ferrous salt formed is then estimated by titration with standard potassium permanganate solution. The potassium permanganate solution is standardized using standard oxalic acid.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

$$Fe_2(SO_4)_3 + 2H \longrightarrow 2FeSO_4 + H_2SO_4$$

$$2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O$$

Since ferric sulphate on reduction gives two equivalents of ferrous sulphate, the equivalent mass of ferric sulphate is half its molecular mass. Since one atomic mass of iron is present in on equivalent of ferrous sulphate, the equivalent mass of iron is the same as its atomic mass.

A standard solution of oxalic acid is prepared. By using this solution potassium permangate is standardised. The given ferric alum is made up to definite volume. A known volume of this solution is reduced to the ferrous state which is then estimated by standard potassium permanganate solution. From the titre values the normality of the reduced ferrous iron solution and mass of ferric iron in the whole of the given solution can be calculated, knowing that the equivalent mass of iron is 55.84.

PROCEDURE :(a) *Preparation of standard oxalic acid solution*. 100 ml of decinormal solution of oxalic acid is prepard by weighing accurately abou 0.63 g of the A. R. quality crystals, dissolving in water and making up the solution in a standard measuring flask. The solution is well shaken.

(b) *Standardisation of potassium permanganate.* 20 ml of the made up oxalic acid is pipetted out in a conical flask, an equal volume of dilute sulphuric acid is added. The mixture is heated to 60°-70°C and titrated against potassium permanganate solution. The end point is the appearance of permanent pale pink colour. The titrations are repeated till concordant values are obtained.

(C) *Reduction of ferric iron to ferrous iron*. The given ferric alum solution is made up tot 100 ml in a standard measuring flask. While making up 20 ml of dilute sulphuric acid is added to the solution to prevent hydrolysis. The solution is then well shaken. 20 ml of the made up solution is pipetted out into a 250 ml breaker, provided with a cover glass. Ammonium hydroxid3e is added drop by drop stirring the solution continuously, till a faint permanent brown precipitate is formed. Dilute sulphuric acid is then carefully added tillthe precipitate is just redissolved. Then about 10 ml more of dil. Sulphuric acid is added. The solution is then heated but not boiled. About 1 g of zinc dust is added. The beaker is kept covered by a cover glass and gently shaken at intervals. Hydrogen reduces ferric to ferrous due to which the solution gets decolourised. Then it is tested for comp[lete reduction by withdrawing a drop of solution at the end of pointed glass rod, placing it on a porcelain tile and mixing it with a drop of ammonium thiocyanate solution. Absence of blood-red colouration indicates complete reduction.

When the reduction is complete the solution is filtered using a quantitative filter paper in which zinc dust is sprinkled. The filtrate is collected in a conical flask containing a little dil. Sulphuric acid and a pinch of sodium bicarbonate has been dropped. (carbon dioxide liberated provides an inert atmosphere). The unreacted zinc dust in the beaker is washed several times with water acidified with dil. Sulphuric acid. The washings are collected along with the filtrate.

Estimation of Iron. The filtrate containing ferrous sulphate is titrated

with potassium permanganate solution. The end point is the appearance of pale pink colouration. The experiment is repeated till concordant values are obtained.From the titre value, the normality of the iron solution is calculated. Knowing the normality, the mass of iron in the whole of the given solution is calculated.

REPORT : Mass of iron in the whole of the given solution = ………… g.

Mass of weighing bottle + $H_2C_2O_4$ before Transfer =

Mass of weighing bottle + $H_2C_2O_4$ after Transfer =

Mass of $H_2C_2O_4$ =

Concentration of Std. $H_2C_2O_4$ solution $= \dfrac{\text{Mass of } H_2C_2O_4}{\text{G. Eqt. Mass} \times \text{Volume in litre}}$

=

=

Titration I : Std. aqueous $H_2C_2O_4$ Vs Link aqueous $KMnO_4$

Indicator : Self Indicator

End point : Appearance of permanent pale pink colour

S.No	Volume of	Burette Reading	Volume of

	aqueous $H_2C_2O_4$ (ml)	Initial Final	aqueous $KMnO_4$ (ml)

Volume of aqueous $H_2C_2O_4$, V_1 =

Conc. of aqueous $H_2C_2O_4$, N_1 =

Volume of aqueous $KMnO_4$, V_2 =

Conc. of aqueous $KMnO_4$, N_2 = $\frac{V_1 \text{ x } N_1}{V_2}$

=

=

Titration II : Unknown aqueous Fe^{2+} Vs Link aq $KMnO_4$

Indicator : Self Indicator ($KMnO_4$)

End point : Appearance of permanent pale pink colour

S.No	Volume of aqueous Fe^{2+}(ml)	Burette Reading		Volume of aq.$KMnO_4$ (ml)
		Initial	Final	

Volume of aqueous $KMnO_4$, V_1 =

Conc. of aqueous $KMnO_4$, N_1 =

Volume of aqueous Fe^{2+} ,V_2 =

Conc. of aqueous Fe^{2+}, N_2 = $\frac{V_1 \text{ x } N_1}{V_2}$

=

=

Mass of Ferrous sulphate present in

the whole of the given solution = G. Eqt. mass x Nor. x Volume in litre

ESTIMATION OF CALCIUM

AIM :

To estimate the mass of calcium present in the whole of the given calcium chloride solution containing a little hydrochloric acid. You are supplied with approximately decinormal potassium permanganate solution and pure oxalic acid crystals.

PRINCIPLE :

The calcium chloride solution is made upto a definite volume. A measured volume of calcium chloride solution is precipitated as calcium oxalate. The precipitate is dissolved in dilute sulphuric acid and the equivalent amount of oxalic acid generated is estimated by titration with potassium permanganate solution., The potassium permanganate solution is standardised by standard oxalic acid solution prepared from quality oxalic acid crystals.

The reactions take place according to the following equation:

$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 + 2NH_4Cl$$

$$CaC_2O_4 + H_2SO_4 \rightarrow CaSO_4 + H_2C_2O_4$$

$$H_2C_2O_4 + [O] \rightarrow 2CO_2 + H_2O$$

$$CaC_2O_4 \equiv CaCl_2 \equiv H_2C_2O_4 \equiv 2Ca \equiv [O] \equiv 2 \text{ Equivalents}$$

Since calcium chloride ultimately given two equivalents of oxalic acid

$$\text{Equivalent mass of } CaCl_2 = \frac{\text{Molicular mass of } CaCl_2}{2}$$

$$\text{Equivalent mass of Calcium} = \frac{\text{Atomic mass of Calcium}}{2} = 20.04$$

PROCEDURE :

a. Standardisation of $KMnO_4$ Solution

About 1.25 g of pure oxalic acid crystals is accurately weighed, transferred into a 200 ml standard flask, dissolved in distilled water and made upto the mark.

20 ml of the oxalic acid solution is pipetted out into a clean conical flask. About 20 ml of dilute sulphuric acid is added and the solution is heated to bearable warm (about 60 to 70 ^{o}C). The hot solution is titrated against potassium permanganate in the burette till the just appearance of permanent pale pink colour. This is the end point . The titration is repeated for concordant titre values.

From the titre values the normality of potassium permanganate solution is calculated.

b. Precipitation and Estimation of Calcium

The whole of the given calcium chloride solution is transferred into a 100 ml standard measuring flask and made upto the mark and well shaken.

Exactly 20 ml of the made up solution is pipetted out into a 250 ml beaker and a drop of methyl orange is added to it. Ammonium hydroxide is then added drop by drop till the acid is neutralised and the solution just changes to yellow. About 5 ml of dil. HCl is then added and the solution is diluted to 150 ml. The beaker is covered with a watch glass and the solution is heated to boiling. To the boiling solution, about 10 ml of a hot freshly prepared 2% solution of ammonium oxalate is added slowly with constant stirring. Ammonium hydroxide is then added to the mixture drop by drop stirring continuously till the solution strongly smells of ammonia. The mixture is boiled for a few minutes more to made the precipitate granular. The precipitate is then allowed to settle for an hour to make sure that the precipitation is complete. A liquid along the sides of the beaker. If added to the supernatant liquid along the sides of the beaker. If the precipitation is incomplete, a turbidity will be seen in supernatant liquid as the drop of the reagent come into contact with it.

The precipitate of calcium oxalate is filtered by decantation through the quantitative (Whatmann 40) filter paper. The precipitate is washed with water containing a little ammonia, till the washings give no opalescence with nitric acid and silver nitrate (free from oxalate and chloride). The precipitate is then almost completely transferred to the filter paper. The beaker in which the precipitation is done is then placed under the funnel containing the precipitate. The apex of the filter paper is pierced with a pointed glass rod and the precipitate is washed down into the beaker with a jet of hot water. About 25 ml of hot dilute H_2SO_4 poured on the filter paper in small portions at a time taking care that the acid comes into contract with every part of the paper. Acid is also poured into the double fold of the filter paper to dissolve any precipitate that may be sticking there. The filter paper is again washed thoroughly with hot water. The sides of the beaker are also washed with dilute sulphuric acid. The sides of the beaker contained oxalic acid is heated to about 70 ^{o}C and titrated with standard potassium permanganate solution. The end point is the just appearance of permanent pale pick colour. A duplicate is also conducted.

From the results the mass of calcium present in the whole of the given solution is calculated.

REPORT :

The mass of calcium present in the whole of the given solution =

Mass of weighing bottle + $H_2C_2O_4$ before Transfer =

Mass of weighing bottle + $H_2C_2O_4$ after Transfer =

Mass of $H_2C_2O_4$ =

Concentration of Std. $H_2C_2O_4$ solution = $\dfrac{\text{Mass of } H_2C_2O_4}{\text{G.Eq. Mass} \times \text{Volume in litre}}$

=

=

Titration I : Std. aqueous oxalic acid Vs Link aqueous potassium permanganate

Indicator : Self-indicator($KMnO_4$)

End point : JustAppearance of pale pink colour

S.No.	Volume of	Burette reading	Volume of

	aqueous H_2C_2O (ml)	Initial	Final	aqueous $KMnO_4$ (ml)

Volume of aqueous oxalic acid, V_1 =

Conc. of aqueous oxalic acid, N_1 =

Volume of aqueous potassium permanganate, V_2 =

Conc. of aqueous potassium permanganate, N_2 = $\frac{V_1 \times N_1}{V_2}$

=

=

Titration II : Unknown aqueous $CaCl_2$ → $H_2C_2O_4$ Vs Link aqueous potassium permanganate
Indicator : Self-indicator($KMnO_4$)
End point : Just appearance of pale pink colour

S.No.	Volume of aqueous $CaCl_2$ (ml)	Burette reading		Volume of aqueous $KMnO_4$ (ml)
		Initial	Final	

Volume of aqueous potassium permanganate, V_1 =

Conc. of aqueous potassium permanganate, N_1 =

Volume of aqueous $CaCl_2$, V_2 =

Conc. of aqueous $CaCl_2$, N_2 $= \frac{V_1 \times N_1}{V_2}$

=

=

Mass of calcium present in the whole of the given solution } = G. Eqt. mass x Normality x Volume in lit.

DICHROMETRY

Potassium dichromate in acid medium is an oxidizing agent and hence can be made use of for the estimation of reducing agents. One molecule of dichromate gives 3 atoms of oxygen (six equivalents) for oxidation and gets reduced to green chromic salt.

$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

The equivalent mass of pot. Dichromate $= \dfrac{\text{Molicular mass}}{6} = \dfrac{249}{6} = 49.$

Since the substance is obtained in a pure form, a standard solution of it may be prepared by taking a definite mass of the substance, dissolving in water and making up the solution to a definite volume. The end point in titrations with potassium dichromate is determined by two methods.

(1) With an external indicator and (2) With an internal indicator.

The use of potassium ferricyanide as external indicator is based on the reaction between Fe^{2+} ion and potassium ferricyanide to give an intense blue colour due to the formation of prussian blue.

$K_3 Fe(CN)_6 + Fe^{2+} \rightarrow KFe [CN)_6] + 2K^+$

The titration of Fe^{2+} against standard dichromate is continued until a drop of the solution does not give a blue colour with 1 drop of very dilute potassium ferricyanide solution.

N-phenyl anthranilic acid is used as internal indicator in the titration of ferrous iron against potassium dichromate solution. The colour change is from green to violet-red.

ESTIMATION OF FERROUS IRON

USING INTERNAL INDICATOR

AIM :

To Estimate the amount of ferrous iron in the whole of the given solution of ferrous sulphate, supplied with pure ferrous ammonium sulhate crystals and approximately decinormal potassium dichromate solution.

PRINCIPLE :

The estimation is based on the reaction of potassium dichromate in acid medium with ferrous sulphate. The dichromate oxidizes ferrous sulphate to ferric sulphate itself getting reduced to green chromic salt.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$2FeSO_2 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O$$

A standard solution of ferrous ammonium sulphate is prepared. Using this standard solution, potassium dichromate solution is standardized. The given ferrous salt solution is made up to a known volume and it is standardized using the standardized potassium dichromate solution. In both the titrations N-phenyl anthranilic acid is used as internal indicator. On the addition of the indicator, the solution becomes colourless. After adding a few millilitres of the dichromate solution, it becomes green and at the end point the colour changes from green to violet red.

PROCEDURE :

TITRATION : I

(a) *Preparation of standard ferrous ammonium sulphate solution.* 100 ml of the decinormal solution of Mohr's salt is prepared by weighing accurately about 3.92 g of A.R. quality of crystals, dissolving in water to which 40 ml of dilute sulphuric acid has been added (to prevent hydrolysis) and making up the solution in a standard measuring flask. The solution is well shaken.

(b) *Standardisation of potassium dichromate solution*. 20 ml of the standard ferrous ammonium sulphate solution is pipetted out into a conical flask. About 20 ml of 2N sulphuric acid is added followed by 10 drops of N-phenyl anthranilic acid as indicator. The solution is then titrated with vigorous shaking against the dichromate solution taken in the burette until green solution changes to violet red. The titration is repeated till concordant values are obtained.

TITRATION : II *Estimation of ferrous iron*

The Whole of the given ferrous salt solution is transferred to a 100 ml standard flask and made up to the mark and well shaken.

Exactly 20 ml of the made up solution is pipetted out into a conical flask. About 20 ml of 2N sulphuric acid is added followed by drops of N-phenyl anthranilic acid as indicator. The solution is then titrated with vigorous shaking against the standardized potassium dichromate solution until green solution changes to violet red. The titration is repeated till concordant values are obtained.

From the titre values, the mass of ferrous iron in the whole of the solution is calculated.

REPORT :

The mass of Ferrous iron present in the whole of the given solution = …...……g

Mass of weighing bottle + Mohr's salt before Transfer =

Mass of weighing bottle + Mohr's salt after Transfer =

Mass of Mohr's salt =

$$\text{Concentration of Std. Mohr's salt solution} = \frac{\text{Mass of Mohr's salt}}{\text{G.Eqt.Mass} \times \text{Vol.in lit.}}$$

=

=

Titration I : Std. aqueous Mohr's salt Vs Link aqueous potassium dichromate

Indicator : N- Phenyl anthranilic acid

End point : green solution changes to violet red colour

S.No.	Volume of Aqueous Mohr's salt (ml)	Burette reading		Volume of aqueous $K_2Cr_2O_7$ (ml)
		Initial	Final	

Volume of aqueousMohr's salt , V_1 =

Conc. of aqueousMohr's salt , N_1 =

Volume of aqueous $K_2Cr_2O_7$, V_2 =

Conc. of aqueous $K_2Cr_2O_7$, N_2 = $\frac{V_1 \times N_1}{V_2}$

=

=

Titration II : Unknown aqueous Ferrous sulphate Vs Link aqueous Potassium dichromate
Indicator : N- Phenyl anthranilic acid
End point : green solution changes to violet red colour

S.No.	Volume of aq,.Ferrous sulphate (ml)	Burette reading		Volume of aq.Potassium dichromate (ml)
		Initial	Final	

Volume of aqueous potassium dichromate ,V_1 =

Conc. of aqueous potassium dichromate , N_1 =

Volume of aqueousFerrous sulphate, V_2 =

Conc. of aqueousFerrous sulphate , N_2 = $\frac{V_1 \text{ x } N_1}{V_2}$

=

Mass of Ferrous iron present in the whole of the given solution } = G. Eqt. mass x Normality x Vol.in lit.

= ………….g

IODIMETRY AND IODOMETRY

The branch of volumetric analysis based upon the use of iodine as an oxidizing agent is called iodimetry or iodometry. Iodimetry is concerned with the titrations using a standard solution of iodine while iodometry deals with the titration of iodine liberated in chemical reactions.

There are two important sources of error in titrations involving iodine (1) loss of iodine owing to its volatile nature (2) acid solutions of iodine are oxidized by air.

1. It is found that in excess of potassium iodide, the volatility is markedly decreased. Hence, in all titrations involving iodine, an excess of potassium iodide, is used. Also the titration is done in conical flask and in cold solutions.
2. The error due to oxidation may be minimized by not keeping the solution containing excess of iodine and acid for long before it is titrated

Indicator : Starch is used as an indicator for titrations involving iodine. Starch reacts with iodine in presence of iodide to form a blue complex. This is a very sensitive colour reaction. But, starch forms a water insoluble complex with iodine. Hence, the indicator is added only at the very end of the reaction, when the colour of the iodine solution fades to pale yellow.

Preparation of Starch Indicator : A past of one gram of soluble starch is made with a little water. The paste is then added to 100 ml of boiling water with constant stirring. The resulting solution is boiled for a minute longer. It is then cooled.

About 2 ml of a freshly prepared 1% solution is used for each titration. It is essential that the same volume of starch is added for each titration.

ESTIMATION OF ARSENIOUS OXIDE

AIM :

The estimate the mass of arsenious oxide present in the whole of the given solution of sodium arsenite, being supplied with approximately decinormal iodine solution and pure arsenious oxide.

PRINCIPLE :

Arsenious oxide solution is used for the standardisation of iodine solution. Arsenious oxide reacts with iodine according the following equation.

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$$

$$Na_3AsO_3 + I_2 + H_2O \rightarrow Na_3AsO_4 + 2HI$$

$$As_2O_3 \equiv 2I_2 \equiv 4 \text{ Equivalents}$$

$$\text{Equivalent mass of } As_2O_3 = \frac{\text{Molecular mass of } As_2O_3}{4}$$

$$= \frac{197.82}{4} = 49.46$$

The reaction is reversible. But the reaction is quantitative if HI is removed as soon as it is formed. This may be done by the addition of sodium bicarbonate. Since sodium hydroxide and sodium carbonate react with iodine forming iodide, hypoiodate and iodate. The compete oxidation of arsenite occurs at pH 6.5 which is very close to the neutral point.. Buffer solutions are used to maintain the correct pH. Sodium bicarbonate saturated with CO_2 is used as the buffer solution. Since one molecule of arsenious oxide gives two molecules of sodium arsenite which react with 4 equivalents of iodine,

$$\text{Equivalent mass of } As_2O_3 = \frac{\text{Molecular mass of } As_2O_3}{4}$$

$$= \frac{197.82}{4} = 49.46$$

$$\text{Equivalent mass of sodium arsenite} = \frac{\text{Moleulcar mass of } Na_3AsO_3}{2}$$

$$= \frac{122.92}{2} = 61.46$$

A standard solution of arsenious oxide is prepared and iodine solution is standardised using starch solution as the indicator. The standardised of iodine solution is used to standardise the given arsenite solution. From this data, arsenious oxide present in the whole of the given solution is calculated.

PROCEDURE :

TITRATION : I

a. Preparation of Standard Solution of Sodium Arsenite

About 1.25 g of arsenious oxides is weighed accurately, transferred into a 250 ml beaker and dissolved in 20 ml of 10% sodium hydroxide solution. If arsenious oxide is not completely dissolved, the solution is warmed and stirred well, till arsenious oxide gets completely dissolved. It is cooled and then quantitatively transferred into a 250 ml standard flask. One drop of phenolphthalein is added and the solution is neutralised with 2N HCl. About 5 drops of HCl is added in excess. The solution is then made upto the mark.

b. Standardisation of Iodine Solution

Exactly 20 ml of iodine solution is pipetted our into a clean conical flask. About 2.5 g of sodium bicarbonate is added. It is then titrated against arsenite solution taken in the burette, till the solution attains pale yellow in colour. 2 ml of freshly prepared starch solution is added and the titration is continued slowly until the blue colour is just discharged. The titrations are repeated till concordant values are obtained.

TITRATION : II Estimation of Arsenious Oxide

The whole of the given sodium arsenite solution is transferred quantitatively with minimum quantity of water, into a 100 ml standard flask and a drop of phenolphthalein is added as indicator. The solution is neutralised with 2N HCl and 5 drops of HCl is added in excess. The solution is then made upto the mark. It is then taken in a burette.

Exactly 20 ml of the standardised iodine solution is pipetted out into a clean conical flask. About 2 g of sodium bicarbonate is added. It is then titrated with sodium arsenite solution until the solution attains a pale yellow colour. 2 ml of freshly prepared starch solution is added and the titration is continued till the discharge of blue colour which is the end point. The titrations are repeated till concordant values re obtained.

From the titre values the mass of arsenious oxide present in the whole of the given solution can be calculated, knowing that the equivalent mass of arsenious oxide is 49.46.

REPORT :

The mass of arsenious oxide present in the whole of the given solution = ……g

Mass of weighing bottle +As_2O_3 before transfer =

Mass of weighing bottle + As_2O_3 after transfer =

Mass of As_2O_3 =

Conc. of aqueous As_2O_3 = $\dfrac{\text{Mass of As2O3}}{\text{G. Eqt. mass x Vol. in litre}}$

=

=

Titration I : Std. aqueous As_2O_3 Vs Link aqueous I_2
Indicator : Starch solution
End point : Discharge of blue colour

S.No.	Volume of aq.I_2 (ml)	Burette reading		Volume of aq.As_2O_3 (ml)
		Initial	Final	

Volume of aqueous As_2O_3, V_1 =

Conc. of aqueous As_2O_3, N_1 =

Volume of aqueous I_2, V_2 =

Conc. of aqueous I_2, N_2 $= \frac{V_1 \times N_1}{V_2}$

=

=

Titration II : Link aqueous I_2 Vs Unknown aqueous As_2O_3
Indicator : Starch solution
End point : Discharge of blue colour

S.No.	Volume of aq.I_2 (ml)	Burette reading		Volume of aq. As_2O_3 (ml)
		Initial	Final	

Volume of aqueous I_2, V_1 =

Conc. of aqueous I_2, N_1 =

Volume of aqueous As_2O_3, V_2 =

Conc. of aqueous As_2O_3, N_2 = $\frac{V_1 \text{ x } N_1}{V_2}$

=

=

Mass of As_2O_3 present in the whole of the given solution $\Big\}$ = G. Eqt. mass x Nor. x Vol. in lit.

=

=

ESTIMATION OF COPPER

AIM :

To estimate the mass of copper present in the whole of the given solution. You are provided with pure potassium dichromate crystals and approximately decinormal solution of sodium thiosulphate.

PRINCIPLE :

The estimation is based on the reaction of potassium iodide with

i. copper sulphate
ii. acidified potassium dichromate

$$CuSO_4 + 2KI \rightarrow CuI_2 + K_2SO_4$$

$$2CuI_2 \rightarrow Cu_2I_2 + I_2$$

Potassium dichromate in acid medium liberates iodine from Kl, potassium dichromate getting reduced to green chromic salt.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$2KI + H_2SO_4 + [O] \rightarrow K_2SO_4 + H_2O + I_2$$

One molecular mass of copper sulphate liberates one equivalent of iodine. Hence the equivalent mass of cupric sulphate is the same as its molecular mass, i.e.

$$\text{Equivalent mass of Copper sulphate} = \frac{\text{Molicular mass of } CuSO_4.5H_2O}{1} = 248$$

$$\text{Equivalent mass of copper} = \frac{\text{Atomic mass of copper}}{1} = 63.54$$

The equivalent Mass of Potassium dichromate is 1/6 of its molecular weight, i.e. 49.04 since one molecular mass liberates 6 equivalents of iodine.

The given copper sulphate solution is made upto a definite volume. A definite volume of this solution is pipetted out and after destroying the mineral acid present, potassium iodide is added when an equivalent amount of iodine will be liberated.

PROCEDURE

TITRATION : I

a. Preparation of Standard Potassium Dichromate Solution

About 1.25 g of potassium dichromate is accurately weighed. It is then transferred into 250 ml standard measuring flask, dissolved in water and made upto the mark.

b. Standardisation of Sodium Thiosulphate Solution

Exactly 20 ml of the dichromate solution is pipetted out into a clean conical flask. About 3 ml of pure concentrated hydrochloric acid is added. About 10 ml of 10% of potassium iodide solution is added. It is then diluted to 100 ml and titrated against aqueous $Na_2S_2O_3$ taken in the burette. When the solution becomes straw yellow in colour about 2 ml starch solution is added and the titration is continued until the colour changes to green. The titrations are repeated till concordant values are obtained.

TITRATION : II Estimation of Copper

The whole of the given copper sulphate solution is made into 100 ml in a standard flask,made upto the mark and well shaken.

Exactly 20 ml of this solution is pipetted out into a clean conical flask. Aqueous ammonia is added drop by drop till a permanent pale blue precipitate is obtained. The precipitate is dissolved by adding required amount of acetic acid drop by drop. One or two drops of excess of acid as added. About 10 ml of 10% Kl solution is added and the solution is titrated against sodium thiosulphate solution taken in the burette. When the solution becomes pale brown in colour about 2 ml of starch solution is added. The solution becomes blue in colour. The titration is continued until the blue colour changes to dirty white. About 1 g of ammonium thiocyanate is added and if the solution becomes blue in colour the titration is continued till the blue colour changes to dirty white. The titration is repeated till concordant values are obtained.

From the titre value, the normality of copper sulphate solution and hence the mass of copper present in the whole of the given solution can be calculated.

REPORT :

The mass of copper present in the whole of given solution =

Mass of weighing bottle + $K_2Cr_2O_7$ before transfer =

Mass of weighing bottle + $K_2Cr_2O_7$ after transfer =

Mass of $K_2Cr_2O_7$ =

Conc. of aqueous $K_2Cr_2O_7$ = $\dfrac{\text{Mass of } K_2Cr_2O_7}{\text{G.Eqt.mass x Vol.in lit.}}$

=

=

Titration I : Std. aqueous $K_2Cr_2O_7$ Vs Link aqueous $Na_2S_2O_3$

Indicator : Starch solution

End point : Change of colour from blue to green

S.No	Volume of aq.$K_2Cr_2O_7$ (ml)	Burette reading		Volume of aq. $Na_2S_2O_3$ (ml)
		Initial	Final	

Volume of aqueous $K_2Cr_2O_7$, V_1 =

Conc. of aqueous $K_2Cr_2O_7$, N_1 =

Volume of aqueous $Na_2S_2O_3$, V_2 =

Conc. of aqueous $Na_2S_2O_3$, N_2 = $\frac{V_1 \times N_1}{V_2}$

=

=

Titration II : Link aqueous $Na_2S_2O_3$ Vs Unknown aqueous $CuSO_4$
Indicator : Starch solution
End point : Change of colour from blue to dirty white

S.No.	Volume of aq.$CuSO_4$ (ml)	Burette reading		Volume of q. $Na_2S_2O_3$ (ml)
		Initial	Final	

Volume of aqueous $Na_2S_2O_3$, V_1 =

Conc. of aqueous $Na_2S_2O_3$, N_1 =

Volume of aqueous $CuSO_4$, V_2 =

Conc. of aqueous $CuSO_4$, N_2 = $\frac{V_1 \times N_1}{V_2}$

=

Mass of copper(II) ions present in the whole of the given solution } = G. Eqt. mass x Nor. x Volu.in lit.

=