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PAPER-II

UNIT-III

* OXIDANT SYSTEMS - PRINCIPLES AND APPLICATIONS IN ANALYSIS

⇒ Oxidant systems

1) **Oxidation**:- Loss of electrons ($e^\ominus$) (or) increasing Positive ion species is known as oxidation.

Eg: $Fe^{+2} \longrightarrow Fe^{+3} + e^\ominus$

$V^{+2} \longrightarrow V^{+3} + e^\ominus$

$Cr^{+2} \longrightarrow Cr^{+3} + e^\ominus$

2) **oxidant**:- [oxidising agent] (O.A)

It self reduce (or) increasing other species of ions (or) oxidise the other species of ions is known as oxidant.

Eg: $Ni + \underset{(O.A)}{Cu^{+2}} \longrightarrow Ni^{+2} + Cu^{+}$

3) **Reduction**:- Gain of electrons (or) decreasing Positive ion species is known as Reduction.

Eg: $Fe^{+3} + e^\ominus \longrightarrow Fe^{+2}$

$V^{+3} + e^\ominus \longrightarrow V^{+2}$

4) **Reductant** :- [Reducing agent] (R.A)

It self oxidise (or) decreasing other species of ions (or) Reducing other species of ions is known as Reductant.

Eg: $Fe^{+2} + Cr^{+6} \longrightarrow Fe^{+3} + Cr^{+3}$
(R.A)

5) **Electrode** :- A metalwire (or) metal plate used for passing of electricity through it, it is known as electrode.

6) **Conductor** :- Electricity is passes through a substance is known as conductor.

7) **Conductivity** :- The mobilite of ions (or) transformation of ions in a solution by applying electricity is known as conductivity.

8) **Potential** :- Changing of current in any two solutions is known as potential. (difference between current in a solutions)

* Electrode Potential :-

when a metal is immersed in a Solution Containing it's own ions i--e, zinc in zinc sulphate solution (or) Copper in Copper sulphate solution.

A Potential difference is established between the solution.

the electrode reaction can be written as

i--e, $\boxed{M^{+n} + ne \longrightarrow M}$

the Potential difference (E) for an electrode reaction is given by the expression is equal to i--e,

$$\boxed{E = E_0 + \frac{RT}{nF}\left(\ln a_m^{+n}\right)} \longrightarrow ①$$

Here, R is Gas Constant

T is Absoulte temperature

F is Faraday function

n is no. of electrons transfer

a_m^{+n} is activation of ions in the Solution

E_0 is Constant depend upon the Nature of the metal.

In terms of Concentration equation ① Can be written as

$$\boxed{E = E_0 + \frac{RT}{nF} \overset{+}{e} \ln Con^{+n}}$$

The reversible reaction system is,

$$\text{oxidant} + ne^{\ominus} \rightleftharpoons \text{Reductant}$$

For the system electrode Potential is,

$$E = E_0 + \frac{RT}{nF} \ln \frac{[oxi]}{[Red]}$$

$$\simeq E = E_0 + \frac{RT}{nF} \log \frac{[oxi]}{[Red]} \longrightarrow ②$$

If the concentration of oxidant and Reductant are equal (unit concentration) then equation ② can be written as,

$$E = E^{\circ} \text{ at } 25^{\circ}C$$

The Potential is known as standard Potential. For spontaneous reaction the redox Potential should be positive.

Standard electrode Potential:-

It is defined as Potential difference in at 25°c developed in a cell Consisting at two electrodes. The electrode made up of Pure metals which is in Constant with the electrolite of more concentration containing same metalic ions and reference electronic normal hydrogen electrode having zero volts (0V).

At $E = E^\circ$ at 25°C and various atmosphere the electrode Potential is known as Standard electrode Potential, and it is containing different volts.

At $E = E^\circ$ at 25°C, one atmosphere Pressure zero volts the electrode Potential is known as normal electrode Potential.

* Formal Potential:-

The Potential of system having equal formal concentration of oxidant and reductant, which cover the effect of complex formation of Precipitation, concentration change in p^H of the medium is known as Formal Potential.

$$Cu^{+2} + e^{\ominus} \rightleftharpoons Cu^{+}, \quad E_0 = 0.15V \rightarrow ①$$

$$I_2 + 2e^{\ominus} \rightleftharpoons 2I^{\ominus}, \quad E_0 = 0.54V \rightarrow ②$$

E_0 system suggested that Cu^{+2} should not formation of Precipitation with $I^{\ominus}$.

In these system Cu^+ ions to form a Precipitation with Iodide ion $(I^{\ominus})$

$$Cu^+ + I^{\ominus} \longrightarrow CuI \downarrow$$

In a equilibrium constant,

$$\boxed{K = \frac{\{Cu^+\}\{I^-\}}{\{CuI\}}}$$

According to solubility product the above equation can be written as,

$$K_{sp} = \{Cu^+\}\{I^-\}$$

$$\boxed{\{Cu^+\} = \frac{K_{sp}}{\{I^-\}}}$$

Here,
$$\boxed{\{Cu^+\} = \frac{10^{-12}}{\{I^-\}}}$$

Redox Potential of giving system is,

$$E = E^0 + \frac{RT}{nF} \log \frac{[oxid]}{[Redu]}$$

From reaction ①,

$$E = E^\circ + \frac{RT}{nF} \log \frac{[Cu^{+2}]}{[Cu^{+}]}$$

$$E = E^\circ + \frac{RT}{nF} \log \frac{[Cu^{+2}]}{\frac{10^{-12}}{[I^{-}]}} \qquad \left(\because [Cu^{+}] = \frac{10^{-12}}{[I^{-}]}\right)$$

$$E = 0.15 + 0.0591 \log [Cu^{+2}][I^{-}] - \log(10^{-12})$$

$$\boxed{E = 0.858 + 0.0591 \log [Cu^{+2}][I^{-}]}$$

due to the formation of precipitation copper Iodide (CuI), the formal potential of $(Cu^{+2})/(Cu^{+})$ coupled system. It is Jumps to 0.858. this is the greater than the standard potential value of I_2/I^- system.

then the oxidising $I^{\ominus}$ by possible with Cu^{+2}.

Redox indicators:- In a solution, one component is oxidised and another component is reduced, Then the titrations are known as Redox titrations. which indicators are used in redox titrations is known as redox indicators.

A redox indicator whose Potential range of Colour change of false with in the Potential Jump at equililent of titration is Suitable for that titrations for an indicator to be suitable for redox titrations.

It's standard Potential should be higher than that of the redox Potential and lower than that of the oxidant.

For the reason, in the titration of Fe(II) with dichromate (Cr(VI)), Barium diphenyl Sulphonate in the Presence of Phosphoric acid.

i.e $Cr_2O_7^{2-} + 14H^+ + 6e^\ominus \rightleftharpoons 2Cr^{+3} + 7H_2O$, $E_0 = 1.33V$

$Fe^{+3} + e^\ominus \rightleftharpoons Fe^{+2}$, $E_0 = 0.77V$

oxidant $+ ne^\ominus \rightleftharpoons$ Reductant

$E_0 = 0.83V$

To get sharp endpoint, the E_0 of the

Fe(III)/Fe(II) Coupled is lower by addition of Phosphoric acid (or) then E_0 of Fe(III)/Fe(II) Coupled is reduced to 0.61v by removing of Fe(III) ie,

$(Fe(H_3PO_4)^+)$

diphenyl amine is also used in presence of phosphoric acid but barium diphenyl sulphonate is better results.

Ferroin is also used for titration between Fe(II) and Ce(IV) Cerium in these titration without used Phosphoric acid.

i.e, $Fe^{+3} + e^{\ominus} \rightleftharpoons Fe^{+2}$, $E_0 = 0.77v$

$Ce^{+4} + e^{\ominus} \rightleftharpoons Ce^{+3}$, $E_0 = 1.44V$

$$\{Fe(C_{12}H_8N_2)_3\}^{+3} + e^{\ominus} \longrightarrow \{Fe(C_{12}H_8N_2)_3\}^{+2}$$

$E_0 = 1.14v$

Problem:-

10^{-3} moles Cr(VI) and 10^{-2} moles Cr(III) present in the solution medium of pH = 2, then find out half cell Potential.

Solution:- From data, the Equation as follows

$$Cr_2O_7^{2-} + 14H^+ + 6e^{\ominus} \rightleftharpoons 2Cr^{+3} + 7H_2O, \quad E_0 = 1.33V$$

$$E = E^\circ + \frac{RT}{nF} \log \frac{[Red]}{[oxi]}$$

$$= 1.33 + \frac{0.0591}{6} \log \frac{\{Cr^{+3}\}^2}{\{Cr_2O_7^{2-}\}\{H^+\}^{14}}$$

$$= 1.33 + \frac{0.0591}{6} \log \frac{[10^{-2}]^2}{10^{-3} \times (10^{-2})^{14}}$$

$$= 1.33 + \frac{0.0591}{6} \log \frac{10^{-4}}{10^{-3} \times 10^{-28}}$$

$$= 1.33 + \frac{0.0591}{6} \log 10^{-4} \times 10^{+31}$$

$$= 1.33 + \frac{0.0591}{6} \log 10^{27}$$

$$= 1.33 + \frac{0.0591}{6} \cdot 27 \log (10)$$

$$= 1.59595 \, V$$

oxidant systems

Inorganic systems

- Mn (VII)
- Mn (III)
- Ce (IV)
- V (V)
- Cr (VI)
- Iodate / Iodite

organic systems

- Chloramine -"T"

Manganese (VII) System :-

* General discussion :-

1) Mn (VII) is a Powerful (or) strong oxidising agent.
2) Mn (VII) is Prepaired by F. Margurite by titration with Fe (II)
3) The standard Potential value is 1.51V.

Merits :-

1) It is a strong oxidising agent
2) It is avaliable modest cast
3) It act as self indicator

Demerits :-

1) It is easily oxidised with chlorine
2) It ~~is~~ produce multiple products
3) It have low stability.

* Specious responsible for oxidant system :-

In acidic medium Permongerate is converted to manganese. It can be written as

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

when the solution is titrate with by useing Permanganate mostly we are used sulphuric acid than compaired to hydrochloric acid. If we are used hydrochloric acid, the stability is decrease by liberating chlorine.

$$2MnO_4^{\ominus} + 10Cl^{\ominus} + 16H^{\oplus} \longrightarrow 2Mn^{+2} + 5Cl_2 + 8H_2O$$

* Stability :-

1) Potassium permonganate is one of the secondary standard solution. So that it has low stability.
2) In presence of HCl medium, it is most avaliable and in liberating chlorine and

have low Stability.

3) Potassium Permonganate is avaliable in impure form so that the stability is decrease.

4) permonganate is reduced to manganese oxides by hydrolysis it can be written as,

$$2mno_4^{\ominus} + 3mn^{+2} + 2H_2O \longrightarrow 5mno_2 + 4H^{\oplus}$$

Indicators:-

Commonly used indicators are

1) Ferroin
2) DPA
3) N-Phenyle Anthronilic acid
4) It act as self indicator

*** Preparation of Standard Solution:-**

Preparation of 0.02M Permonganate Solution:-

Accurately weight out 3-3.25 gms of Potassium permonganate is taken in a 1 liter flask. first it is diluted with water. The containing sample solution is heat upto 15-30min and it is Filter.

After filteration the filterate sample is taken in required volume of flask. and it is diluted with water until required volume is obtained.

Preparation of Sodium Oxalate Solution:-

Accurately weight out 3gms of sodium oxalate and it is taken in a 250ml flask. First it is dissolve by useing 12.5ml Con. H_2SO_4 and then it is diluted with water until required volume is obtained.

Standardisation of Potassium permonganate by useing Sodium oxalate:

10ml of acidified Sodium oxalate solution is taken in a conical flask, the containing sample solution is boiled for little bit time and it is titrate with by useing Potassium permonganate solution in presence of a suitable indicator until to get a pale pink Colour. The Process is repeated until to get same values. Then we are Calculate unknown molarity of Potassium permonganate by useing the following formula.

$$\boxed{M_1V_1 = M_2V_2}$$

$$2Na^+ + C_2O_4^{2-} + 2H^{\oplus} \rightleftharpoons H_2C_2O_4 + 2Na^+$$

$$2MnO_4^{\ominus} + 5H_2C_2O_4 + 16H^{\oplus} \rightleftharpoons 2Mn^{+2} + 10CO_2 + 8H_2O$$

* **Applications** :-

1) **Analysis of Hydrogen peroxide :- (H_2O_2)**

When Potassium Permonganate solution is added to hydrogen peroxide solution with dilute H_2SO_4 then the reaction as follows.

i.e $2mnO_4^{\ominus} + 5H_2O_2 + 6H^{\oplus} \longrightarrow 2mn^{+2} + 5O_2 + 8H_2O$

2) **Determination of Nitrites ($NO_2^{\ominus}$)** :-

Nitrites can be estimated by useing back titration of permonganate. To the solution containing Nitrites, acidified permonganate solution is added it and unreacted. Potassium permonganate is titrate with by useing ferrous ammonium sulphate. Then the equation as follows.

i.e $2mnO_4^{\ominus} + 5NO_2^{\ominus} + 16H^{\oplus} \longrightarrow 2mn^{+2} + 10NO_3^{\ominus} + 8H_2O$

3) **Determination of Fe(II)** :-

Required volume of mohr's salt is taken and it is acidified by useing Concentration H_2SO_4 then it is titrate with Potassium Permonganate inpresence of suitable indicator. Then equation as follows.

$$Mn(VII) + Fe(II) \longrightarrow Mn(III) + Fe(III)$$

4) Determination of Alcohols :-

In acidic medium at a room temperature ethyl alcohol is oxidised to acetic acid. Take 10ml of ethyl alcohol and add it 10ml of 4N H_2SO_4 and again add it 25ml of 0.1N Permonganate and it is mix well and allowed to 24 hours then it is titrate with by useing Mohr's Salt Solution. Then equation as follows.

i.e

$$4KMnO_4 + 5C_2H_5OH + 6H_2SO_4 \longrightarrow 5CH_3COOH + K_2SO_4 + 4MnSO_4 + 6H_2O.$$

* Manganese (III) Systems :-

* General discussions :-

1) It is a strong oxidising agent than compare to Mn(VII)
2) Mn(III) is Protect from sunlight otherwise the stability is decrease.
3) The standard Potential value is 1.4V.
4) In acidic medium Mn(III) is reduced to Mn(II)

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* Stability :-

Mn(II) is also have less stability. This stability of Mn(III) is increase by addition of diphosphate and to form manganese diphosphate.

* Indicators :

The following indicators used as

1) DPA
2) Ferroin
3) 1,10 - Phenanthanilic acid
4) BDPS (Barium diphenyl sulphonate)

* Preparation of Standard Solution :-

The standard solution of Mn(III) is prepaired by oxidation of Mn(II) and Reduction of Mn(VII).

By oxidation Mn(II) :-

Required amount of Mn(II) is taken and add it Bromate and ortho phosphoric acid. The Containing solution is allow to stand for until to form violet and Bromin is liberated. In these Process Mn(II) is converted to Mn(III) by the equation.

$$10Mn^{+2} + 2BrO_3^{\ominus} + 12H^{\oplus} \longrightarrow 10Mn^{+3} + Br_2 + 6H_2O$$

* Reduction of Mn (VII):

By useing hydrogen Peroxide, is taken and oxidising agent Mn (VII) is added. It self reduce and oxidise the other specious and the containing solution is mix well until to get colourless solution.

usage $H_2O_2 + Mn(VII) \xrightarrow{Con.\, H_3PO_4}$ Colourless solution

* Standardisation of Mn(III) :-

Mn (III) is standardised by Potentiometrically with hydrogen peroxides (or) Mohr's salt (or) hydroquinones.

* Applications:-

1) Arsenic (III), stanous chloride $SnCl_2$ can be titrated directly in acid medium, if the solution of diphosphate (or) Phosphate complex of trivalent Manganese (III).
2) the reaction of Mn(III) compound, α-hydroxy acids, aldehydes, alcohols can be determined by Mn(III).
3) By useing Mn (III) salt direct Potentiometric titration of organic compounds like oxalic acids, Hydroquinones, Phenols and 1° amines and isonicotanic acid.

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Cr(VI) System:

* General discussions:-

1) Potassium dichromate is a strong oxidising agent.
2) The standard potential value of Cr(VI) is 1.36V.
3) Dichromate is a less oxidising agent than Compaired to Mn(VII) and Ce(IV).
4) It is mostly avaliable in crystal and Pure form, so that it act as 1° standard solution.
5) Cr(VI) stability is doesn't change inpresence of by using Concentration. H_2SO_4 and HCl.
6) In this titration Process Cr(VI) is Converted to Cr(III) by the equation i.e,

$$Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{\ominus} \longrightarrow 2Cr^{+3} + 7H_2O$$

* Stability:-

Potassium dichromate is mostly avaliable in crystal and Pure form so that it act as a 1° standard solution and have higher stable.

* indicators:-

The following indicators used as

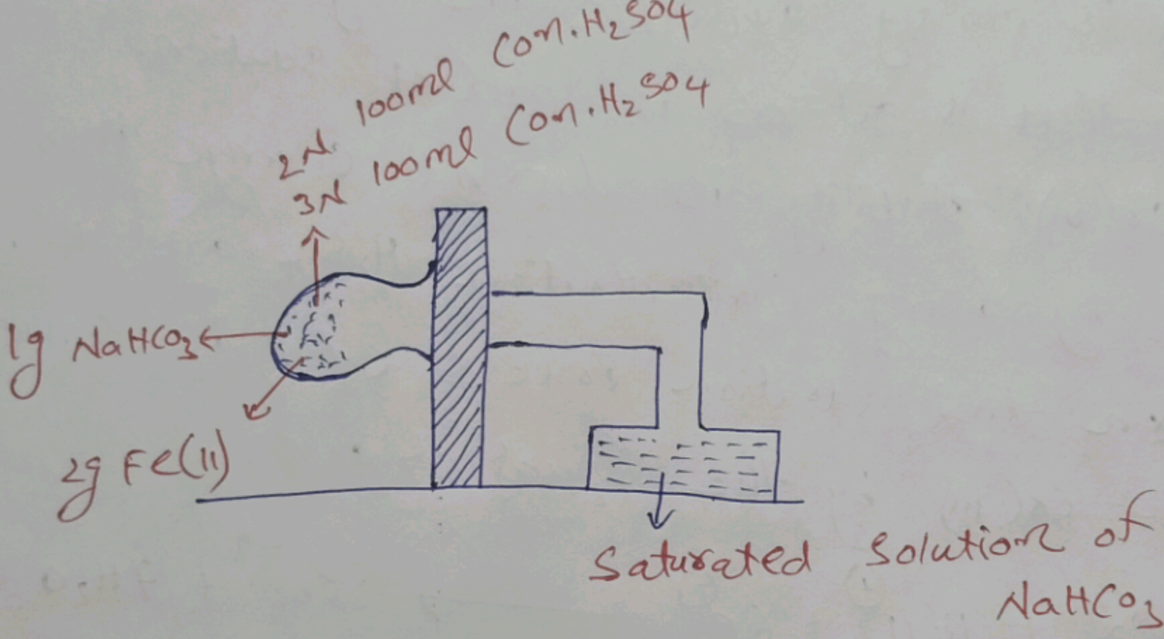
1) DPA (diphenyl amine)
2) BDPS (barium diphenyl sulphonate)
3) Potassium Ferrocynide

* Preparation of Standard Solution:-

Preparation of 0.05N dichromate solution:-

Required amount of pure dichromate is taken in a required volume of flask. the containing salt is dissolue by useing distilled water & dilute with water until required volume is obtain.

* Standardisation of Fe(II):-



Let take 2g of Fe(II) and it is saturated with 1g of sodium bicarbonate ($NaHCO_3$) and add it 3N Con. H_2SO_4 the containing solution is titrate with Potassium Permanganate inpresence of by useing BDPS indicator until to get a colourless to violet through greenish blue. The process is repeated until to get a same values. Then to calculate normality of Fe(II) by useing the following formula.

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$$\boxed{N_1V_1 = N_2V_2}$$

$$\boxed{1ml \text{ of } 0.01N\ Cr(VI) = 0.005585\ gm. \text{ of } Fe(II)}$$

The relationship between redox potential of permonganate and dichromate.

1) $MnO_4^- + 4H^{\oplus} + 3e^{\ominus} \longrightarrow MnO_2 + 2H_2O$, $E_0 = 1.69V$

2) $MnO_4^- + 8H^{\oplus} + 5e^{\ominus} \longrightarrow Mn^{+2} + 4H_2O$, $E_0 = 1.52V$

3) $Cr_2O_7^{2-} + 14H^{\oplus} + 6e^{\ominus} \longrightarrow 2Cr^{+3} + 7H_2O$, $E_0 = 1.36V$

* Applications:-

1) Determination of chlorides :- (ClO_3^-)

Chloride ion is reduced by Fe(II) ions in presence of high concentration of Sulphuric acid. The equation as follows,

$$ClO_3^- + 6Fe^{+3} + 6H^{\oplus} \longrightarrow Cl^- + 6Fe^{+3} + 3H_2O$$

Procedure:- Take 0.02 moles of Potassium chloride solution into 250ml volumetric flask, It is dissolve and dilute with water then take 25ml of Potassium Chlorate solution and add 25ml of 0.2 moles Fe(II) solⁿ and also add it 12ml of Concentration H_2SO_4, the containing solution is boil for a little time & cool, then add it Phosphoric acid. the unreacted Fe (II) sol^n is titrate with standard dichromate solution in presence of Barium diphenyl sulphonate and the colour changed from colourless to Purple by repeating the process by useing 25ml distill water in presence of chlorate solution.

The different in titrate value is equal to the volume of Potassium chlorate solution is add it.

2) Determination of chromium in chromium salt:-

chromium (III) salts are oxidised to dichromate by boiling with excess of persulphate solution in presence of silver Nitrate used as catalyst.

$$Cr(III) \xrightarrow[S_2O_8^{-}\ \&\ AgNO_3]{(O)} Cr_2O_7^{2-}$$

After the oxidation the solution is boiled and resultant dichromate sol^n is determined by the addition of excess of standard Fe (II) sol^n. The excess of Fe(II) solution is titrated with by useing standard Potassium dichromate solution.

$$Cr^{+3} + S_2O_8^{2-} + H_2O \xrightarrow[AgNO_3]{} \underset{\text{Yellow}}{Cr_2O_7^{2-}} + 6HSO_4^{\ominus} + 8H^{\oplus}$$

the excess of $2S_2O_8^{2-} + 2H_2O \longrightarrow 4HSO_4^- + O_2\uparrow$

Procedure :- weigh accurately 0.25gr of chromium alum and dissolued in 50ml of distilled water to this add 20ml of 0.1 molar silver nitrate followed by 50ml of 10% Potassium per sulphate solution. ($K_2S_2O_8$).

Boil the solution for 20min and cool. then dilute 250ml volumetric flask from this 50ml of soln is taken and add it 50ml of Fe(II) soln, 40ml of 1 molar H_2SO_4 and 0.5ml of N-Phenyl anthrolinic acid. then titrate the excess of Fe(II) soln and the colour changed from green to violet.

> 1ml 0.1N Fe(II) solution is equal to 0.001734 gr of Cr(VI).

Ce(IV) system :-

General discussion :-

cerium oxidation state is +4. the example of cerium salts having oxidation state +4, are

1) cerium (IV) Ammonium nitrate
2) Ce(IV) Ammonium sulphate
3) Ce (IV) hydroxide

4) Ce (IV) sulphate.

⇒ The standard potential value of cerium is 1.43±0.05 volts at 25°c in 0.5 to 4 molar H_2SO_4.

⇒ Ce (IV) sulphate is a powerful oxidising agent.

⇒ The advantages of Ce(IV) sulphate as a standard oxidising agent are,

1) Ce (IV) sulphate solution is a stable for a long period of time for the need not protect from the light.

2) Ce (IV) sulphate solution may be boil for a short time without change in concentration.

3) Ce(IV) sulphate solution is used for the determination of reducing agents in presence of Con. HCl.

4) The solution has an intense yellow colour.

5) In acid solution with reducing agents. the following reaction occurs,

$$Ce^{+4} + e^{\ominus} \longrightarrow Ce^{+3}$$

The redox potential of Ce (IV), Ce (III) system depend on the nature and concentration of the acid presents of

H_2SO_4 - 1.4V

HNO_3 - 1.61V

$HClO_4$ - 1.70V

8% $HClO_4$ - 1.87V

* **Stability** :-

the solution of ce (IV) sulphate in dilute H_2SO_4 are stable even at boiling temperature hydrochloric acid solution used for the unstable of ce (IV) sulphate solution. It is reduced to ce(IV) to ce (III) by liberating chlorine.

$$2Ce^{+4} + 2Cl^{-} \longrightarrow 2Ce^{+3} + Cl_2$$

* **Indicators** :- The following indicators are used as

1) Ferroin
2) N-Phenyl Anthrolinic acid
3) 5,6-dimethyl ferroin

* **Preparation of Standard Solution** :-

weight out 21gr of ce(IV) hydroxide transfer to a beaker and add 100ml of Con. H_2SO_4 with stirring add 300ml of water slowly allow to stand over height. if any residue remains filter the solution and dilute up to the mark.

Standardisation of ce (IV) Solution:-

* Standardisation with Arsinate (III) oxide:-

when ce(IV) sulphate solution is standardised with Arcinate (III) oxide. The following reaction takes place,

$$2ce^{+4} + H_3ASo_3 + H_2O \longrightarrow 2ce^{+3} + H_3ASo_4 + 2H^{+}$$

Procedure:- weight out 0.2gr of Arcinate (III) oxide, which is heated at 105-110°c for 2 hours, transfer into a beaker and add 2 moles of NaoH solution warm the solution (or) mixture until Arcinate (III) oxide as completely dissolve and till the solution and water followed by 2.5V of H_2SO_4 acid, 3 drops of 0.5ml of N-phenyl. Anthralinic acid and indicator.

then titrate with standard ce(IV) solution.

Applications:-

Determination of Nitrides:-

The following reaction as follows

$$2ce^{+4} + No_2^{\ominus} + H_2O \longrightarrow 2ce^{+3} + No_3^{\ominus} + 2H^{\oplus}$$

Procedure:- weigh out accurately 1.5 gr of Sodium Nitride dissolve and makeup with water in a required flask, take 50ml of ce(IV) solution in a conical flask add 10ml of 2 molar H_2SO_4 add 25ml of Nitride solution allow to stand for 5min and titrate the excess of Ce(IV) sulphate, with standard 0.1 molar Fe(II) sol^n useing ferroin as indicator.

Analysis of hydrogen Peroxide:-

$$2Ce^{+4} + H_2O_2 \longrightarrow 2Ce^{+3} + O_2 + H^+$$

Procedure:- the dilute solution of hydrogen Peroxide which may contain Hcl in the range of concentration 0.5 - 3 molar (or) H_2SO_4 in a range of 0.25 - 1.5 moles is titrate with standard Ce(IV) solution useing ferroin as indicator.

Iodate (IO_3^-)

$$KIO_3 \simeq IO_3^{\ominus}$$

General discussion:-

⇒ Iodate is a strong oxidising agent.

⇒ Standard Potential of Iodate is 1.23V.

⇒ It is used for the determination of Iodine (I_2).

i.e $IO_3^{\ominus} + 5I^{\ominus} + 6H^{\oplus} \rightleftharpoons 3I_2 + 3H_2O$

$IO_3^{\ominus} + 5H_3AsO_3 + 2H^{\oplus} \rightleftharpoons I_2 + 5H_3AsO_4 + H_2O$

The react with iodate with Titanium Chloride then the reaction as follows.

$$IO_3^{\ominus} + 6Ti^{+3} + 6H^{\oplus} \longrightarrow \underset{\substack{\downarrow \\ \text{Iodite (or) Iodide}}}{I^{\ominus}} + 6Ti^{+4} + 3H_2O$$

Iodate is titrate with no. of Substances inpresence of Hcl medium then to Produce different components, the reaction follows,

$$\underset{}{IO_3^{\ominus}} + 6H^{\oplus} + 6e^{\ominus} \rightleftharpoons \underset{\text{Iodide}}{I^{\ominus}} + 3H_2O$$

$$\underset{\text{Iodate}}{IO_3^{\ominus}} + 6H^{\oplus} + \underset{\text{Iodide}}{5I^{\ominus}} \rightleftharpoons \underset{\text{Iodine}}{3I_2} + 3H_2O$$

$$\underset{\text{Iodate}}{2IO_3^{\ominus}} + 6H^{\oplus} + \underset{\text{Iodine}}{2I_2} \rightleftharpoons 5I^{\oplus} + 3H_2O$$

In Hcl medium Iodine mono chloride ion react with Chlorine and to form Iodine dichloride

$$ICl^{\ominus} + Cl^{\ominus} \longrightarrow ICl_2$$

Stability:- The Iodate is higher stable at room temperature. The stability is decrease by increaseing of temperature.

Indicators:-

the following indicators are used

1) Amaranth indicator (red - colourless)
2) xylidine Pancean (orange - Colourless)
3) Napthalene Black 12B (green - Pink)
4) Para ethoxy chrysoldine (red - orange)

Preparation of Iodate $IO_3^{\ominus}$ solution:-

Required amount of KIO_3 is taken and is dried at 120°C for two hours and it is placed on desicators. Accurately weight of 5.350gr of Iodate in 1litre flask is taken and is dissolved in dilute water until required volume.

Standardisation of Iodine Solution:-

The reaction takes place between Iodine Solution and As(III) oxide then the reaction as follows,

$$H_3AsO_3 + I_2 + H_2O \longrightarrow H_3AsO_4 + 2H^+ + 2I^{\ominus}$$

0.2g of Ar(III) oxide is dried at 105-110°c for 1hour and it is transferred to Conical flask and then it is added 10ml of 1M NaoH Solution and the excess of dil. H_2SO_4 and 1gr $NaHCO_3$ in 50ml water, the containing solution is titrate with iodine in presence of starch indicator until to get colourless to blue colour.

* Applications :-

1) **Determination of hydrazine:-**

the reaction as follows

$$IO_3^{\ominus} + N_2H_4 + 2H^{\oplus} + Cl^{\ominus} \longrightarrow ICl + N_2 + 3H_2O$$

Procedure :- weight out 0.1g of hydrazine sulphate add mixture of 30ml Con. Hcl 20ml water and titrate with by useing 0.25 molar standard KIO_3 solution inpresence of 5ml CCl_4 (or) chloroform until organic layer is colourised.

2) **Determination of thalium salt :-**

the reaction as follows,

$$IO_3^{\ominus} + 2Tl^{+} + 6H^{\oplus} + Cl^{\ominus} \longrightarrow ICl + 2Tl^{+3} + 3H_2O$$

The solution should contain 0.25 - 0.30g of Tl^{+} salt in 20ml of Con. Hcl and 60ml of water and titrate with standard 0.25 molar KIO_3 solution.

⑯

5) Determination of Tin (II) Salt :- ($SnCl_2$)

the equation as follows,

$$IO_3^{\ominus} + 2Sn^{+2} + 6H^{\oplus} + Cl^{\ominus} \longrightarrow ICl + 2Sn^{+4} + 3H_2O$$

The solution should contain 0.15g of Tin chloride and take 20ml of prepaired solution then add it 30ml of Con. HCl and 20ml of water. Then it is titrate with by useing standard 0.25 molar KIO_3 solution.

6) Vanadium (V) system :-

General discussion :-

⇒ vanadium is mostly avaliable in different forms like V(V), V(IV), V(III), and V(II).

⇒ vanadium (V) is a strong oxidising agent.

⇒ the standard potential value ~~is~~ of V(V) is 1volts.

⇒ It is used for oxidised for organic and inorganic substance.

⇒ vanadium is converted into vanadate ion in presence of concentration H_2SO_4, by the equation

$$2VO_3^{\ominus} + 8H^{\oplus} + 2e^{\ominus} \longrightarrow 2VO^{+2} + 4H_2O$$

⇒ The standard potential value of V(V) is changes inpresence of different concentration of sulphuric acid.

1N H_2SO_4 → 1.02 volts

2N H_2SO_4 → 1.07 volts

3N H_2SO_4 → 1.13 volts

4N H_2SO_4 → 1.30 volts

* **Stability** :- Vanadium is a one of the i° standard solution and it is stable for several months. this stability is increase inpresence of sodium carbonate (Na_2CO_3). The titration value of vanadium doesn't change even on boiling.

* **Indicators** :-

The following indicators used as

1) diphenyl amine
2) diphenyl benzoidine
3) diphenyl aminosulphate
4) N-Phenyl Anthralinic acid
5) ICl in CCl_4
6) chloroform

* **Preparation of standard solution** :-

Vanadium solution is prepaired by useing Ammonium metavanidate and sodium carbonate, sodium benidate, metavanadic acid and 1:1 H_2SO_4.

Required amount of Ammonium meta varidate is taken in a 250ml flask then add its required amount of Sodium carbonate by the increasing of stability. the Containing sample is dissolve in water and dilute with mark obtain. the containing sample is boil for 45min for Complete saturation and is Filter then the Filterate is taken in a another volumetrical flask then it is dissolve and dilute with by useing distilled water until the required volume is obtained.

* Standardisation of vanadium :-

Vanadium can be standardised by Potentiometrically with Fe(II) solution in Presence of a suitable indicator.

* Applications :-

i) Determination of Mercury :-

Mercury one ions are determined with V(V) in normal HCl the reaction Proceeds as follows by useing iodine mono chloride as indicator by the equation.

i.e $Hg_2^{\oplus} + 2VO_3^{\ominus} + 8H^{\oplus} \longrightarrow 2Hg^{2+} + 2VO^{+2} + 4H_2O$

In the indicator method the excess of meta varidate is titrate with Mohr's salt solution by useing N-phenyl anthralinic acid.

2) Determination of Hydrazine :-

Determination of Hydrazine proceede at room temperature in strong Hcl (or) H_2SO_4 medium.

By the equation,

$$N_2H_4 + 2VO_3^{\ominus} + 12H^{\oplus} \longrightarrow N_2 + VO^{+2} + 6H_2O$$

It ICl in carbon tetra chloride is used as indicator. It is catalyst for reductance, In H_2SO_4 solution. N-phenyl anthralinic acid is used as indicator. All hydrazine groups are quantatively oxidised to Nitrogen.

3) Determination of Iron :-

V(v) is used for determination of Fe (Iron) in presence of 4N H_2SO_4 and used N-phenyl anthralinic acid as indicator. By useing 7N HCl inpresence of ICl in CCl_4, as indicator for determination of Fe(II).

7) Periodide :- ($IO_4^{\ominus}$) Periodate

*** General discussions :-**

⇒ Periodide is an oxidising agent which is used mainly for the preparative organic chemistry. It was first introduced in the titrometric determinatio of some organic compounds.

⇒ The redox potential value of periodide is 1.375 volts.

⇒ In acid solution following reaction occurs.

$$IO_4^{\ominus} + 2H^{\oplus} + 2e^{\ominus} \longrightarrow \underset{\text{Iodate}}{IO_3^{\ominus}} + H_2O$$

⇒ In acid solution periodide is not only reduce to iodate. it can also be reduce to iodine mono chloride.

$$IO_4^{\ominus} + 8H^{\oplus} + 6e^{\ominus} \longrightarrow I^{\oplus} + 4H_2O$$

$$IO_4^{\ominus} + 8H^{\oplus} + 8e^{\ominus} \longrightarrow I^{\oplus} + 4H_2O$$

$$2IO_4^{\ominus} + 16H^{\oplus} + 14e^{\ominus} \longrightarrow I_2 + 8H_2O$$

⇒ the redox potential value of coupled IO_4/IO_3 = 1.4V.

* **Stability**:- Periodide is a higher stable at normal temperature and the stable is decrease by increaseing of temperature.

* **indicators**:-

The following indicators are used

1) Starch
2) ICl in CCl_4
3) $CHCl_3$

* **Preparation of Solution**:- Take required amount of Periodide salt such as ortho Periodic acid of 3° Sodium salt (or) Sodium (or) Potassium salt of meta Periodic acid and dissolve in H_2O upto the required volume, if the solution is impure then filter it.

* **Standardisation of Iodine Solution**:-

the reaction takes place between iodine solution and Ar(III) oxide then the reaction as follows.

$$H_3AsO_3 + I_2 + H_2O \longrightarrow H_3AsO_4 + 2H^{\oplus} + 2I^{\ominus}$$

0.20g Ar(III) oxide is dried at first 105-110°C for one hour and it is transfered to conical flask and then it is added 10ml of 1mole NaOH Solution and the excess of dil. H_2SO_4 and one gram $NaHCO_3$

in some water. the containing solution is titrated with iodine inpresence of starch indicator until to get blue colour.

* Applications

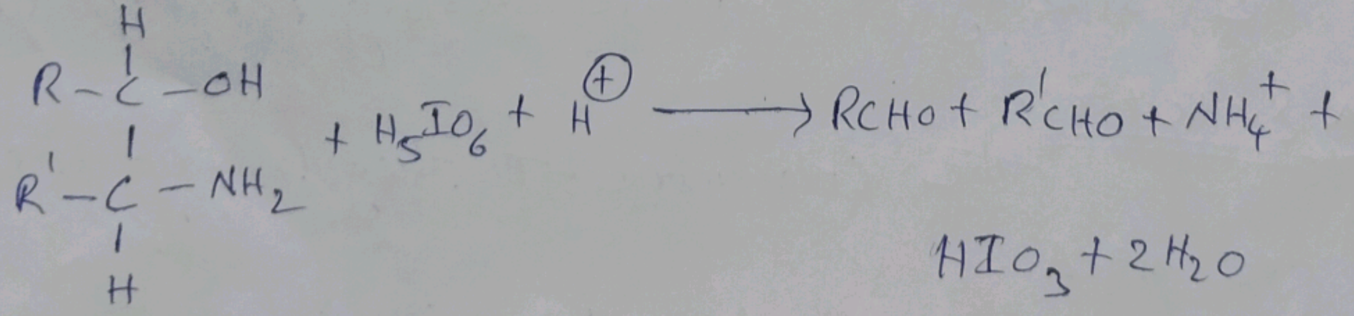
1) Determination of vanadium :-

The reaction between periodide proceeds in 1N H_2SO_4 in the determination of divalent vanadium periodate is reduced to iodate. The endpoint can be determined either potentiometrically (or) visually by useing starch as indicator.

2) Determination of Iron :-

The titration of Fe(II) salts carried out visually in 1N H_2SO_4 in presence of H_3PO_4 useing diphenyl amine as indicator and titrated with standard periodide solution.

3) Determination of α-amino hydroxide :-



$$R-\overset{H}{\overset{|}{C}}-OH \; (R'-\underset{H}{\underset{|}{C}}-NH_2) + H_5IO_6 + H^{\oplus} \longrightarrow RCHO + R'CHO + NH_4^{+} + HIO_3 + 2H_2O$$

8) Chloramine - T :-

⇒ It is called as Sodium salt of Paratoulene Sulpho chloramine is known as Chloramine "T".

⇒ Notation $(CH_3 - C_6H_5\, SO_2\, NaCl\, 3H_2O)$

⇒ It is one of the strong oxidising agent

⇒ It is used and strong oxidising agent is acid (or) base in alkali medium.

⇒ In acid medium the redox Potential value is acid (or) base in alkali medium.

⇒ In acid medium the redox Potential value is 1.53 volts.

⇒ In Neutral medium the redox Potential value is 0.92v.

⇒ It is used in iodometric titrations.

* **Stability :-** Chloramine -T is have higher stable, the solution is stored in ambeared Colour bottles. The stability is maintain overlong Period of time.

* **Indicators :-** The Chloramine -T, they following indicators are used.

1) The liberation of iodine by titrate inpresence

of starch indicator,

2) methyl red
3) Brilliant Carasine
4) Endigo Carasine

Preparation of standard Solutions:-

Required amount of Chloramine "-T" is placed on 1 liter flask and is dissolved in distilled water and dilute with required volume is obtained. May be it contain impurities then recrystalised with hot water.

standardisation:-

Required amount of Chloramine -"T" is taken and dissolved in suitable solvents and titrate with by useing 0.1 N Sodium thio sulphate solution inpresence of acidic medium and used as a suitable indicator.

Applications:

1) Determination of Aldehydes:-

Aldehydes are oxidised by useing chloramine "-T" in alkali medium then the raction as Follows,

$$2CHO + CH_3C_6H_5SO_2N.NaCl + NaOH \longrightarrow RCOONa + CH_3C_6H_5SO_2NH_2 + NaCl$$

2) Determination of Hydrazine :-

Hydrazine is also determine by useing chloramine "T". It is oxidised inpresence of sodium bicarbonate solution then the reaction as follows,

$$N_2H_4 + 2CH_3C_6H_5SO_2N.NaCl \longrightarrow N_2\uparrow + 2CH_3C_6H_5SO_2.NH_2 + 2NaCl$$

3) Determination of Fe(II) :-

Fe (II) is determine by titration with Chloramine "T" solution. Inpresence of HCl medium (high concentration of H_2SO_4 is interfear)

Procedure :- Take 25ml of 0.5N KI solution and add it 25ml of 1:4N HCl and also add it 40ml of 0.1N Chloramine "T" solution. The containing solution is mixed well. Then it is titrate with by useing standard sodium thiosulphate solution in presence of starch used as indicator.

㉑

UNIT - 3

Essays

1) Explain about the following oxidants a) Mn (VII) b) Ce(IV) c) Iodate.

2) write about the analytical chemistry of organic system of chloramine -T and Chromium (VI).

3) write a brief note on the following.
a) Mn (III) b) Per iodate c) V (V).

shorts

1) Explain the classification of redox indicators.

2) Explain the requirements of reductants standardization

3) Explain about Standard and normal Potentials in various media.

4) write about the Principles of oxidants in analytical chemistry.