Name of the Teacher- Sutapa Chakrabarty Subject: Chemistry Class: Semester-2 Paper: C3T: Inorganic Chemistry Topic: Redox and Precipitation Reaction PART 4

Comments: Go through the whole lesson as much as possible for conception.But some topics such **formal potential**, **application of formal potential**, **Z-R solution,problems of latimer diagram** " are very important for preparation of examination.Also complete the assignment given below.

[**N.B**.- Acknowledgement of indebtedness to Mr. Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry]

W Betentiometric determination of PH
The fundamental run for Ingdrogen electrode is
H⁺ + 2
$$\Rightarrow \frac{1}{2}$$
 H₂(1).
This single electrode potential at 1 atm hydrogen pressure
is, $E_{H} = E_{H}^{o} + \frac{R}{H_{H}} \frac{C_{H}+}{P_{H_{2}}^{1}}$
Where $E_{H}^{o} = \frac{R}{H_{H}} \frac{R}{H_{H}} \frac{C_{H}+}{P_{H_{2}}^{1}}$
Electrode = 0, At 1 atm hydrogen pressure $p_{H_{2}}^{1} = 1$.
For dilute soft H can be written as
 $E_{H} = 2.303 \frac{R}{F} \log C_{H}+$ Where,
 $= 0.059 \log C_{H} + at 25^{\circ}$. $R = molar gas constant$
 $T = absolute tamp?$
 $n = No.08 electrong$
 $imolves = 1$
 $for This, hydrogen electrode is dipped into the soft and
combine with a calement electrode Throngs a walt bridge
 $O_{R} (M) \log O_{R} (m) + C_{R} (m) = 1$.
 $R + E_{R} (G, 1 atm) / solt (P^{H} = x) || 1(N) (alomet electrode g)$
The EMF of The cell is measured with a potentiometer. The
Potential of the 1(M) calomet electrode = 0.280 volt$

600 Hence, Ecell = Ecal - EH = 0.280 - (-0.059ph) : Ecel = 0.280+0.059 pH $PH = \frac{E_{CEU} - 0.280}{0.059}$ 0.059. From This equation the PH of the unknown solution can be calculate easily. V) Relative Stability of Oxidation states and dispropertiona tion. The relative stability of different opidation states of an element may be predicted from the knowledge of istandard Potentials. a) The disproportionation of Aut takes place according to the equation -3 Au+ 2 Au+ Au3+ This is explained as follows, 2A4++2e ≠ 2A4; E° = +168 V, 46° = -2F(1.68) .3 $Au^+ \Rightarrow Au^{3+} + 2e^{2}; E^{\circ} = -i(41V, 46^{\circ}) - 2F(-1) + 10^{\circ}$ Adding $3Au^+ \rightleftharpoons 2Au + Au^{3+} = 0.27 v, 4G^{\circ} = -0.54FJ$ This gives a positive of E° = 0.27 v for the total rxn. and the free energy change of the Process is negative (-0.54 F.J). Hence Aut disproportionates to Au and Aut The potentials in The series Aut +1.41V Au +1.68V Au increases from Rest to sight, The species in The middle (Aut) in such a case is unstable and disproportionates. b) For the run 2 cut = cu+ cu²⁺ The half runs are $cu^{+}+e \rightleftharpoons cu \in 20.521V$, $4G^{\circ}=-F(0.521)$ Joule. $c_{11}^{+} \rightleftharpoons c_{12}^{+} + e = E^{\circ}_{2} - 0.153^{\circ}_{, 4G^{\circ}_{, 2}} - F(-0.153)$ Joule Adding 2 cu+ = cu+ cu2+, 6°= 0.368V; dG°= - 0.368F. Jou This gives a positive EMF of 0368 v for the overall Let sun and The Bree energy change of the Process is neg-Hence the disproportionation of cut to cu and cy21 takes place spotaneously. the potential in The series --Cy2+ 0.1533V ; Cut 0.521V ; Cu. increases from left to right, This makes The cut in the middle is unstable and hence it Species disproportionate.

For the $r x h 2 A g^{\dagger} \rightleftharpoons A g + A g^{2+}$, the two half runs are. $A g^{\dagger} + e \rightleftharpoons A g = 6^{\circ} = 0.799 V$; $A 6^{\circ} = -0.799 F$ $A g^{\dagger} \rightleftharpoons A g^{2+} + e = F^{\circ} = 1000 V$; $A 6^{\circ} = -0.799 F$

Ag⁺ = Ag²⁺+e E[°] = -1.980V; △G[°] = + 1.980F Adding 2Ag⁺ = Ag + Ag²⁺; E[°] = -1.18V; △G[°] = +1.181F This gives an overall cell potential of E[°] = -1.181 voltand. consignently Ag⁺ will not disproportionate. The bree energy change in the overall process is also positive and hence The 'TXM CAMMOT takesplace spontaneously.

The potentials in The series -

Ag2+ +1:98v Ag+ +0.799v Ag decreases lebt to right and hence Ag+ shows no tendency to disproportionate

· Formal Potential

In The process OX + ne = Red, according to Nernet equation The potential is given by

 $E = E^{\circ} + \frac{0.059}{17} \log \frac{a_{0X}}{a_{red}} \text{ at } 25^{\circ}c$

when aox = ared, Then E= E°

Here it is believed that all the involved species will remain in Their simple forms and The activity equals to concentration. Such a situation may only exist in a very dilute condition. In practice, The solution is subficiently concentrated to disallow The condition activity = concentration. Besides This, The ions may not exist in simple forms in The presence of Their delectrolytes. Under These conditions, The activity and concentration widely differ. In Buch cases, The concept of standard potential is of mo Practical use and it requires another porameter called formal Potential Duich takes care The actually situation existing in solution.

The effects of the concentration of the system is The experimentaing observed potential of The system in solution where the formal concentration (formality) of The oxidised and o reduced forms are The same. The formal potential covers The effects of the conc. of The species, pt of The solution The possibility of complexation and other factors.

The modified form of the Nexust equ is given by $E = E^{\circ} + \frac{\circ \cdot C \cdot 5 \cdot 9}{n} \log \frac{E \circ X}{E \cdot Red T} \quad \text{out } 25^{\circ} C \cdot C$ where E° is the stormod potential.

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Ethin.

• The Utility of Formal Potential. The standard potentials of Ferringanide (Ferro yanide couple and Iodise (godide couple are;

cyanide couple and toange [9000000 0001 $[Fe(w)_{6}]^{3-} + e \implies [Fe(w)_{6}]^{4-}, F_{e(w)_{6}}^{0} + 2 + 2e \implies 2I^{-}; F_{e(w)_{6}}^{0} + 1 + 2e^{-36} \sqrt{2}$ Since The iodiste | Iodiste Couple has a greates the potential Than $[Fe(w)_{6}]^{3-} / [Fe(w)_{6}]^{4-}$ couple, The I_{2} is a better oridant than $[Fe(w)_{6}]^{3-}$ ion. There have it would be expected that I_{2} would tridised $[Fe((w)_{6}]^{3-}]$

 $2 \left[\operatorname{Fe}(\operatorname{CN})_{\mathcal{L}} \right]^{4-} + \mathbb{I}_{2} \longrightarrow 2 \left[\operatorname{Fe}(\operatorname{CN})_{\mathcal{G}} \right]^{3-} + 2\mathbb{I}^{-}$

In reality, it is the [Fe (cw) of ³⁻ion that oxidises I- to bree I2 in acid medium. It is explained in terms of formal potential.

The expression for Redors potential of [Fe (W)] [Fe (CN) 5]⁴⁻ couple can be written as according to Nerrost equation as follows.

1

 $E = E^{\circ} + \frac{0.059}{1} \log \frac{(F_{2} C_{N})_{6}}{[F_{2} C_{N}]_{6}} = 0.36 + 0.059 \log \frac{F_{2} C_{N}}{[F_{2} C_{N}]_{6}} = \frac{1.36}{[F_{2} C_{N}]_{6}} = \frac{1.36}{[F_{2} C_{N}]_{6}} = \frac{1.59}{[F_{2} C_{N}]_{6}} = \frac{1.59}{[F_$

In The sol of low pt (IMH+) [Fe (CN), 74- and [Fe (W)] iows combined with the bi more H+ ions to boxing ingdroderrocyanic acid and hydro berricyanie acid. [Fe (CW), 674- ion is a stronger base than [Fe (W), 73ion and hence the reactivity of [Fe (CN), 6]4- ions ion with H+ ions is more than the reactivity of [Fe (W), 73ion with H+ ion. Thus the concentration of [Fe (W), 74is appreciably diminished in acid medium. Hence the to +0.71 votif in 1M Her, H2SO4 or Helo4. The formas the oxidation of I- to T2 by [Fe (CN), 74take place by the Bollowing equation

Hence we may conclude gormal potential command

Tublinence of different bactors on Redox potential.
) Influence of PH of the medium.
and
$$f_2 | f^-$$
 systems are 0.56 v and 0.54 v respectively.
As $0q^{3-} + 2H^+ + 2f^- \Rightarrow As 03^{3-} + J_2 + H_20$
on the pH of the direction of the reaction depends
couple depends on pH.
As $0q^{3-} + 2H^+ + 2e^- \Rightarrow As 03^{3-} + J_2 + H_20$
on the pH of the solution of the reaction depends
couple depends on pH.
As $0q^{3-} + 2H^+ + 2e^- \Rightarrow As 03^{3-} + H_20$
Therefore,
 $E = E^0 + \frac{0.059}{2} \log \frac{[As 0q^{3-}]}{[As 03^{3-}]}$
 $= E^0 + \frac{0.059}{2} \log [H^+]^2 + \log [As 0q^{3-}]]$
 $= E^0 + \frac{0.059}{2} \log \frac{[As 0q^{3-}]}{[As 03^{3-}]}$

Here E° = Bormal potential.

Thus The bormal potential $(E^{\circ\prime})$ of The system decreases with increasing of PH. In presence of exceps Natton sol (PH = 8) $E^{\circ\prime}$ becomes 0.088 v. Which is less Than 0.54 volt (standard potential of T_2/T^- system) under The comparable condition. Thus at PH = 8, $A \ge 0q^{3-}$ can not 0ridised T^- to iodine (T_2) but T_2 can origined $A \le 0q^{3-}$.

ie $A = SO_3^2 + I_2 + H_20 \rightleftharpoons A = SO_4^2 + 2H^+ + 2T^$ b) The redox potential OB $Mm04^-/Mn^{2+}$ couple largely depends on The pH oB The Both.

 $Mn04^{-} + 8H^{+} + 5e \rightleftharpoons Mn^{2+} + 4H_{2}0$ $E = E^{0} + \frac{0.059}{5} \log \frac{IMn04^{-}]IH^{+}J^{8}}{IMn^{2+}J}$ $= E^{0} + \frac{0.059}{5} \log [H^{+}J^{8} + \frac{0.059}{5} \log \frac{IMn04^{-}J}{IMn^{2+}}]$

= 1.51 - 0.004PH + 0.059 log [Mn04] TM12+7 = E° + 0.059 log IMN04-] TMN2+]

Here E° = standard potential

E°' = bormas potentias

Though The istandard potential (E°) at PH = 0 is 1.51V, At $P^{H} = 6$, $E^{\circ} = 0.95V$, hence among the halides only I - can be oxidised = E° 12/I - = 0.54 volt. E° Br2/Br = 1.07V, E° C12/CF = 1.36V. At PH = 3, E° = 1.23V and Br - can be oxidised but ct cannot be oxidised. Thus to oxidised UT a much higher concentration 08 H+ is required (PH=1.5).

ii) <u>Instrucce</u> of precipitation on Redox potentias. a) The volumetric estimation of copper by an iodometric method is based on The reaction.

 $2 \operatorname{Cu}^{2+} + 4 \operatorname{I}^{-} \rightleftharpoons 2 \operatorname{Cu} \operatorname{I} \downarrow + \operatorname{I}_{2}$ But the standard potential of the systems cu2+/cu+ $(E^{\circ}=0.15v)$ and $I_2/I^{-}(E^{\circ}=0.54v)$ suggest that reverse ron chould takes place. Now let us Lowider. The ebbect of precipitation of Cur on the cu2+/cut

 $E = E^{\circ} + 0.059 \log \frac{[C_{12}+]}{[C_{11}+]}$

TI-7

In presence of I, Cu+ is precipitated as CuE, have ing the now cohoility product 10-12 i.e Cut+ T= Cutt.

KSP = [Cu+][I-] = 10-12

Hence $[Cu+] = 10^{-12}$

Hence $E = 0.15 + 0.059 \log \frac{[Cu^{2+}][1^{-}]}{10^{-12}}$

= 0.15 + 12 × 0.059 + 0.059 log [Cu12+] [T-] = 0.86 + 0.059 log [cu 2+][I-]

Thus for the system Cu2+ + I - + e = CuI,; we get The standard Potential 0.86 v J. Now we used, though The Cu2+ jout Couple Cannot oxidise I- to I2 (EI2/I-=)

(.5AV). But in The presence of In, The oxidation , ecomes possible and in iodometric estimation of cupper, The Bollowing ron is utilysed. $2 \operatorname{Cu}^{2+} + 4\widehat{1}^{-} \rightleftharpoons 2\operatorname{Cu}^{-} \downarrow + 1_{2}$ up Let us consider The Bollowing system, $[Fe(w)_{6}]^{3-} + e \rightleftharpoons [Fe(w)_{6}]^{4-} E^{\circ} = 0.36 \text{ VOH.}$ I₂ + 2 e ≠ 2 I -E = 0.54 VOL from the above values it is expected that [Fe (cw);]3should not be able to oxidise I - to I2. But in presence of 212+ ion [Fe (cw)6]4- gets removed due to The formation of an insoluble precipitate k2 In3 [Fe(w)] $3 \mp n^{2+} + 2 \left[Fe(cN)_6 \right]^{4-} + 2k^+ \rightleftharpoons k_2 \mp n_3 \left[Fe(cN)_6 \right]_2$ ie Reduction potential of [Fe (cn) 6]3-/[Fe (cn) 6]1-expressed E = 0.36 + 0.059 log IFe (w) J3-[Fe (w) 6]4as Due to the removal of IFe CW)674- Though This precipitation The formal potential of the system [Fe (CN)6]3/ [Fe (CN)6] 4- increases and it exceeds that of I2/II- systems and it can liberate iodine by the bollowing you. $[Fe(CN)_6]^{3-} + 2I^- \rightleftharpoons [Fe(CN)_6]^{4-} + I_2$ iii) Induence of Complex bormation. Fe3+ ion normally oxidises I- ion to 22 in aquesolution, since the standard potential values of ous The two couples are $E^{\circ}F_{e^{2+}}/F_{e^{2+}} = 0.77$ volt and $E^{\circ}_{2_2/2}$ = 0.54 V. But in presence of excess F- 100, Fe3+ is removed as the complex in ion [FSF]2: and The radia IFP 3+7 licir endes. Fe3te fe2t [Fe2+] IN The system fest + e = Fe2+ $E = E^{\circ} + \frac{0.059}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$ = 0.77 + 0.059 log $\frac{[Fe^{3+}]}{[Fe^{2+}]} = 0$ $Fe^{3+} + F^- \rightleftharpoons [FeF]^{2+}; \quad keq = \frac{[FeF^{2+}]}{[Fe^{3+}][F^-]} = 10^5$ For $\therefore [Fe^{3+}] = \frac{[FeF^{2+}]}{10^5 \cdot [F^-]}$

Substituting the value of [fest] in equation ()
we get:

$$E = 0.77 + 0.059 \log \frac{[fest]}{[r^2+1]F^7]}$$

$$= 0.77 + 0.059 \log [rest] \frac{[Fest]}{[Fest]}$$

$$= 0.77 + 0.059 \log [rest] \frac{[Fest]}{[Fest]}$$
Therefore the system becomes,

$$[Fest]^{2+} + e \approx fest + f^-$$
As the reduction potential dereased, the oxidising
prover of fest decreases and it can no more oxidise
indice ion. On the other hand cured down with form
any such stable complex with friends.
The form the system liberated form with in presence
of fest decreases and it can no more oxidise
indice ion. On the other hand cured down with in presence
of fest decreases and it can be more oxidise
indice ion. On the other hand the system is the system
estimated celectively in a irren copper universe by
threating the indice liberated form with in presence
of fest.
• The fest value for (alw) is fired at eask
calculate the fire form form with the inpresence
Given stability constant for the species [form]]³
and [for (alw]] 4- are 1064 and to 20 respectively.
In the system (a³⁺, e = (a²⁺; fest 182 value
According to Nernst equation we can write
 $E = 1.82 + 0.059 \log [10.3^{3-1}] = 0$
On addition of CN- ion both (a³⁺ and (a²⁺ down
 $(a^{3+} + con^{-} \Rightarrow [co (cw)_{1}]^{3-}$
Given the stability constant of a cow d^{3-} for (k)
Hence $h_{1} = \frac{f(a(cw)_{2}^{3-1}]}{(a^{2+1}][cw]_{1}^{2}} = 1064$
 $ar, [fa^{3+1}] = \frac{f(a(cw)_{3}^{3-1}]}{(a^{2+1}][cw]_{1}^{3}}$
Similarly
 $(a^{2+} + 6 CN^{-} \Rightarrow [fo (cw)_{1}]^{4-}$
Given the ctability constant of Tex (w) of the form (k_{2}) = 10^{20}

Hence

$$\begin{split}
\begin{aligned}
& \chi_2 = \int_{(0,0^+)} f(x_0 - x_1^+) f(x_0 - x_0 - x_0$$

· Function of Z-R solution. * Role of Muson The redox potential of MNO, - / Mu2 + Couple is given by $E = E^{\circ} + \frac{0.059}{5} \log \frac{[Mn07][H+]^{8}}{[Mn^{2}+]}$ = $1.51 + \frac{0.059}{5} \log [H+]^8 + \frac{0.059}{5} \log \frac{[Mn0_{4}]}{[Mn^{2}+]}$ Under standard conditions, the concentrations of both Muoq and Mu2+ are IM, Their ratio being 1. On The addition of Z-R solution, There is also much Muzt present in The Fe2+ solution. So That The ratio [Mno4-]/[Mn2+] is considerably Nower Than one. The redox potential will be lower Than. The E° value of 1.51 volt and the formal potential becomes less Than 1.36 volt. Thus KMnog acts as a weaker obidant and Thereby tendency of the side rxn i.e. oxidation of c1 to c12 is prevented. * Functions of H2504 H2504 is used mainly control The H+ ion concentration i. e pH of The solution . (about 2N as which The titration is carried out). * Functions ob H_3Po_4 $E = E^\circ + 0.059 \log [fe^{3t}]$ [Fe2t] In presence of H3POA, Fe3+ complexes as Colour. less [Fe (HPOA)] + ion, effectively lowering The Loncentration ob bree Fe3+ in solution. Hence redox poten ob Fe3+ / Fe2+ Couple is also reduced so That Fe2+ turns out to be a stronger reducing agent Than it appears from it's E' value i.e oxidation of Fe2+ becomes These aynamicity bacilitated. Due to formation of colourless schuble complex, sharp detection of the end point becomes possible. · From The standard E values of The bollowing couples it is bound that Mnoz should not oxidise Hat to el2. But in back the ron is brought about in laboratory. Given E'MNO2/MN2+ = 1.23V, E'child = 1.36V. For The system MNO2 + 4H++2e = MN2++2H20; E=1.23V

and C12 + 2e = 201-; E° = 1.36 volt From the above to values of the complets it is clear mat cl2 showed oxidise MN2+ to MNO2. But in Back reverse is true i.e MNO2 Oridises di-ion to cl2. This is explained as bollows.

The used HCI is meaning concentrated and it's molarrity is beyond IM. So The standard potentias of the couple (MNO2/MN2+ will tend to increase beyond 1.23 volt and exceeds 1.36 volt which is The standard Potential for ci2/ci couple. 98 we reduce The ci2 gas pressure below latin, by reeping the min ture boiling, The E° value of the chalce Couple will fall below 7.36 volf.

Thus MNO2 Can success fully oxidise Hel to cl2 according to the following ran.

MNO2 + 4H-CF = MNC12 + CP2 + 2H20

· Latimer Diagram.

Latimer diagram is a compact form of the different species of an element in varying oxidation states. The different species have arrows in betwthem and the standard potential involving two een species are written over The arrows. The oxidation states of the element concerned is specified under each species. The species with highest oxidation state is placed at The extreme left and The lowest is placed at the extreme right. Two examples are given below;

 $Mn04 \xrightarrow{0.56} Mn04 \xrightarrow{2.26} Mn02 \xrightarrow{0.45} Mn^{3+1.51} Mn^{2+7.18} Mn$ (∇I) (\widehat{W}) (\widehat{H}) (\widehat{H}) (\underline{n}) $(\sqrt{1})$ $clo_{4} \xrightarrow{l'20^{\vee}} clo_{3} \xrightarrow{l'18^{\vee}} Hclo_{2} \xrightarrow{l'65^{\vee}} Hoci \xrightarrow{l'67^{\vee}} cl_{2} \xrightarrow{l'36^{\vee}} ci$ (1) (0) (-1)(四) (\mathbb{Y}) (小下)

* Applications

The application of Latimer Diagram are given below; a) It is possible to predict whether a species will dis propostionate from an impection of the Latimer

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 $E_2 | \cdot 36 + 0 \cdot 0.59 | \cdot 09 [C12]$

in it

diagram covers The redox species. Is the potential to the right of the species is higher than the potential on the selft, Then the species will undergo disproport.

Let us consider The following case

The disproportionation rxn will be as,

Is we subtract The left hand side potential from The right hand side potential of the Latimer diagram we get The disproportionation ron. Whose standard potential is given by -

E° = (y-x) V

when (y-x) is positive, E° is positive and 46° is -ve and so the ron the spontaneous i.e the species will under go disproportionate

b) By using the Latimer diagram, The E° value of any step can be calculated. The basic principle is that AG° is a Thermodynamic state bunction. Hence the total change in The Gibbs free energy does not depend on The path Through which The process is carried out and it depends only on the final and initial states.

Let us calculate The potential tox Mn04 /Mn2 "couple

Mnoy= + 8+1+ + 4e = Mn2+ + 4+20

Thus The process may occure in two possible pathway

$$Mno_4 = \xrightarrow{2.26V} Mno_2 \xrightarrow{0.95V} Mn^{3+} \xrightarrow{1.51V} Mn^{2+}$$

$$E^{\circ}$$

$$E^{\circ}$$

As AGO for both the pathway are same Hence we can write

 $-AFE^{\circ} = -F(2 \times 2.26 + 0.95 + 1.51)$ $\Rightarrow E^{\circ} = (2 \times 2.26 + 1 \times 0.95 + 1 \times 1.51)$ $= 1.745 \quad \sqrt{2} \times t^{2+1+1}$

Solve the problems:

1. What is Z-R solution? What is the bunction of Z-R solution? 2. find out the standard electropotential bon Mnoy / Mnoz redox couple in acid medium. Given Emnoy /Mn2+ 21.51~ E"Hn 02/Mn2+=1.23V at 298K 3. What up Latimer Diagnamp 4. Why Aut disposoportionates to Au and Au3t vin solution? EAu3+1Aut 2141 V E Aut/Au = M68V