Name of the Teacher- Sutapa Chakrabarty Subject: Chemistry Class: Semester-2 Paper: C3T: Inorganic Chemistry Topic: Redox and Precipitation Reaction PART 3

Comments: Go through the whole lesson as much as possible for conception.But some topics such as "standard electrode potential, Nerst equation and calculation of EMF of some cells, calculation of free energy, equilibrium constant and application of standard redox potential values" 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]

· Galvanic Cell

The driving force of a sum can be measured in terms of EMF of a Jaivannie eeu indivance cell is a device in Duich oridation and reduction run, takes place in two separate containers and electrical energy is produced during This run. It is an arrangement of two electrodes and electrolyte in two separate containers. This Chemical energy is converted into electrical energy in a Galvanie cell.

When shep a cell is connected in services with an ammeter and the circuit is closed, There occurs a deflection in the ammeter indicating a flow of current Through the circuit due to existance of a pot.

ential disservere between the two electrodes. ential dibberence between me ponsible box the this ential dibberence phich is responsible box the total current brow the electrode of higher potential to one of the lower potential, is known as the electron motive borce or EMP of the cell and is expressed in volts.

· Cell Rxm and EMF

1

by taking the example of Daniell cell. This cell consists ob two beakers, one of Duich contains I(M) solution of Enso, and The other beaker contains ICM solutions ob cusoq. A zinc rod is dipped into FINSOA sol " While a Cu rod is dipped into cusof solution. These metallie rods are Called electrodes.

The electrodes are connected with an ammeter. A key is also inserted in the excuit. The solutions of The two beakers are called electrolyte solutions. These somitions are connected together by an inverter U tube containing saturated sociution of an inest electrolyte like Kcl, (KNO3 etc. The Utube is called sait bridge. When the circuit is completed by inserting the key in the circuit, the middle of the ammeter sh--ows a deflection. The deflection of the middle indicates that electric current is blowing in the external circuit.

Fellowing observations are made, U Zn (s) is oxidised to Zn 2+ (aq) ions. i.e, Zn(s) Oxidation Zn2+ (aq)+2e

Ar or

As a result, In 2+ ion obtained by the oxidat. ion of In, go into The solution of InSog and hence The concentration of En2+ ions in Insog soln, increases Due to the conversion of In into In2+ jous, En rod. losses it's weight.

i) Electrons released at In electrodes lowards in electrodes Through the order exercit. These electrons are accepted by en2+ ions of ensor soin. Which

en 2+ caq) + 2e seduction, en (s)

As a result, since cu2+ ious of cusog soph are reduced to cu, The concentration of cuiztions in cusod sol decreases. Cu obtained by reduction ob cultions gets deposite on cu rod and hence cu xod govins weight.

12 Flow of electrons. Ð. (anode) xci - Cu (cathode) salt bridge Fusoa ensoy soin IM. SOINIM Fig: working of a Daniell cell. · working of a Daniell Cell In The external circuit electrons Blow Brow Zn rod to en rod. These fore by convention électric entrent Blows in the opposite discetion. i.e; electric current from cu rod to Fn rod. 810005 Zn electrode where oxidation takes place is anode while in electrode at which reduction takes called place is called Cathode. oxidation xxn taking place at In electrode is Called oxidation half cell in and the reduction own taking place at en electrode is called reduction Rate cell rxn. The sum of These two that's cell run is called cell rxn. Thus, 0 kid ation half cell rks.; tri(5) -> 2n2+ cas) + 2e Reduction that's cell men; cu2+ cag) + 2e - en(s) Total cell rxn 2n (s) + cu²⁺ (as) - 2n²⁺ (ag) + (4 (5) In a simplified way, Daniell cell can be represented as Bollows; Blow of electrons

 $\overline{Zn}(s)/2n^{2+}(aq), I(M) // en^{2+}(aq), I(M) / en(s)$ \overline{I} sait bridge.

The EMF is the sum of the single electrode potential corresponding to the actual xxn occurring at each electrode and is positive. Then the cell EMF. = Oxidation potential of the In electrode + Reduction potential of cu electrode.

i.e; " Ecell = Eox (208+) + Exed (xight) = Exed (xight) - Exed (208+) = Eox (108+) - Eox (xight)

Let us consider, a metal; metal ion electrede · Single electrode Potential 01 Which is obtained by immersing a metal rod in it salt solution i.e; sol containing metal Carifors. In This electrode There exist a separation of charges between The metal and it's sall solution. This separation of charges results That a met negative separation of charges is developed on the metal with or positive charge. is developed on the metal with respect to it's solution. The negative or positive charge developed on the metal produces electrical potential difference between the metal and it's solution. This electrical potential difference is called single electrode potential. Thus single electrode potential is a measure of the tantance of an electrode in a a measure of the tendency of an electrode in a half cell to gain or loss electrons. · Origin of electrode Potential How The electrode potential is generated, has been explained by Nerist. By This Theory Winiehis called Nernst Theory, Let us consider The Boliowing two: examples. a) Zn metal place placed in a sol " containing Zn^{2†}ions. when a Zn metod is placed in a soll, containing Zn2+ ions, Zn atoms loss electrons and are oxidised to Zn2+ ions, i.e. tammag En (s) -> En 2++2e Electrons Thus generated get accumulated on The metal and hence make The Zn plate negatively そい charged. In order to neutrolised The negative hang created on the surface of the metal plate, a larger of \$12+ ions is bormed round the surbace of Fn plate. In This way an electrical layer is generated between The metal plate and the solution. This electrical layer developed a debinite potential dibber. ence between The metal and metal ions of the soly This potential difference is called electrode potent. ion on In(s) / In2+ caq) electrode. > -ve changed plate > Zu2+ BOIN OB ZUSOA (I.M).

Fig: origin of wingle electrode potential of Zu(s)/ Zn2+ (aq) ele.

cu metal plate placed in a sol Containing cu2+ When a Cu metal plate is placed in a solution containing cu2+ ions, cu plate becomes positively charged and in order to neutralise The positive charge on The plate, alayer of supporter ions is formed round The surface of the positively charged plate. In This case an electrical layer is generated between The metal plate and the solution, containing Cu²⁺ ions. Thus electrical larger gives rise to a potential dibberence between the metal and metal ions in solution. This potential difference is called electrode potential ob "en(s) / cu2+ (aq) electrode:

Negatively charged soft usod soll 1(M) Fig: Origin of single electrode potential of (12+(0a)/cu(5)

-> + ve charaged cu plate

electrode. Standard electrode potential

The standard electrode potential of a metalmetal ion electrode is The EMF of a cell made by coupling a normal hydrogen electrode, with the a metal-metalion electrode obtained by immersing The metal in it's salt solutions of I (M) concentration and 25°c. The potential of normal H electrode is taken as zero.

The standard reduction potential gives a measure ob the tendency ob metal ions (at unit cone-entration) to get reduced by gain ob electrons.

Metalions + electrons = metal

2.9; 2.1 + 2 E = cu ; Ecu2+/cy = 0.3.4 volt The standard ordation potential measured The capacity of a metal to 1055 electrons in a solution.

Metal = Metalions + electrons

e.g: $Zn \implies Zn^{2+} + 2e$; $E_{Zn/Zn^{2+}}^{c} = 0.763V$. Reduction potential = - Oxidation potential

· Sign convention

According to the present convention, the vary ob electrode potential is expressed as reduction electrode potential, Thus is we say that the value of standard electrode potential of Zn(s) / Zn2+ (az) electrode is -0.763 volt, This means That the given value is the value of standard reduction potential of In electrode.

i.e; Egn2+/ Fn 2 -0.763 Volt

· Negative Reduction potential and positive Reduction Potential.

According to The present convention The value of the electrode potential is expressed as reduction electrode potential. This reduction potential many have a negative value or positive value; depending on whether the given electrode acts as an anode or as a cathode of the Galvanic cell obtained by coupling The given electrode with a normal hydrogen electrode (NHE ON SHE). When the given electrode act as an anode, The électrode has a negative value for its standard reduction potential. On the other hand when the given electrodes acts as a Cathode, The electrode has a positive value Bor its standard reduction potential.

98 two electrodes are complied together to get galvanic een, Then The electrode having less value of its standard reduction potential will con stitude The anode of the resulted cell and the electrode having more value of its reduction (Standard Potential will constitude The Cathode of the cell.

& standard . EMF of a Galvanie cell.

When all reactants and The products involved in the cell reaction of a Galvanie cell are at unit concentration (IM), The EMF of The cell is called standard EMF of The cell Dhich is represented as Feell. It is also called standard cell potential. Rel" between Bree energy and Cell EMF

We know That requiradent of any substance Corresponds to 1 Faraday or F. Confombs ob electricity. Suppose n'equivalents ob The reactants in a chemical cell are present per mole. Then for

7

v

V

14 each mole of the reactant converted to products, I MF coulombs of electric charge pass through the cell. 98 E is The EMF developed by the cell ren, The net-electrical Pork available Pould be MFE Jowle. When This Pork is equal to the decrease The cell operates, This work is equal to the decrease in Bree energy per mole of the reactant. Denoting This by - 46, we obtain the relation. -AG= MFE Or AG = - HFE. For Thermodynamic principles, we know that at constant temps and pressure 4 G is i) Negative Bor any spontaneous process. ii) Positive for any non-spontaneous process. iii) Equat to zero for any system at equilibrium. Since, 4G = - nFE, we may readily conclude That The EMF of cell will be, i) Positive when the cell rxn is spontaneous. i) Negative ahen The cell rxm is non spontaneous. iii) Equal to zero When The cell own reaches equily At standard state, i.e. when the activities of all species appearing in electrode rxn are unity. $AG^{\circ} = - nFE^{\circ}$ Where, 46° = standard Bree energy change E° > Standard EMF ob The cell. · Derive Nernst equation for an electrochemical cell and establish The relation between istandard Sree energy change and equilibrium constant for given cell rxn. Let us consider an electrochemical cell rxn A + BB ≓ VC + 6D where the activities of all species undrogo change. For species A bree energy change bor a mole is AGA = GA + ARTINOA = GA + RT In aA Similarly The expression for species B, C and D are

 $\mathbf{A} \mathbf{G}_{\mathbf{B}} = \mathbf{G}_{\mathbf{B}}^{\circ} + \mathbf{R} \mathbf{T} \mathbf{M} \mathbf{G}_{\mathbf{B}}^{\mathbf{B}}$ $\mathbf{A} \mathbf{G}_{\mathbf{C}} = \mathbf{G}_{\mathbf{C}}^{\circ} + \mathbf{R} \mathbf{T} \mathbf{M} \mathbf{G}_{\mathbf{C}}^{\mathbf{C}}$ $\mathbf{A} \mathbf{G}_{\mathbf{D}} = \mathbf{G}_{\mathbf{D}}^{\circ} + \mathbf{R} \mathbf{T} \mathbf{M} \mathbf{G}_{\mathbf{D}}^{\mathbf{C}}$

The change in Bree energy box the overall cell my is expressed on 4 G = EGproduct - EGReactant $= AG' + RT m \frac{ac' \cdot ab}{a' \cdot a} - 0$ Where 16° = (standard free energy change. DE KNOW AG = - NFE and AG = - NFE, Where E. is the istandard GMF of the cell. Thus equ " () become $- nFE = -nFE^{\circ} + RT \ln \frac{\alpha_{e}^{\vee} \cdot \alpha_{p}^{\vee}}{\alpha_{A}^{\vee} \cdot \alpha_{B}^{\vee}}$ $\Rightarrow E = E^{\circ} - \frac{RT}{nF} \ln \frac{\alpha_{e}^{\vee} \cdot \alpha_{p}^{\vee}}{\alpha_{A}^{\vee} \cdot \alpha_{B}^{\vee}} - \frac{\alpha_{e}^{\vee}}{\alpha_{A}^{\vee} \cdot \alpha_{B}^{\vee}}$ This is known as Nexust equation. From equation (ii) $E = E^{\circ} - 2.303 \frac{RT}{nF} \log \frac{q_c^{\circ} \cdot q_b^{\circ}}{q_A^{\circ}} \frac{q_c^{\circ} \cdot q_b^{\circ}}{q_b^{\circ}}$ $= E^{\circ} - \frac{0.059}{n} \log \frac{q_c^{\circ} \cdot q_b^{\circ}}{q_A^{\circ}} \frac{q_c^{\circ} \cdot q_b^{\circ}}{q_b^{\circ}} \text{ at } 25^{\circ}c.$ This is also the another borm of Nervist equation. Where 2.303 RT = 0.059 of 25°C. For ainte sol" equation (i) can be written as $E = E^{\circ} - \frac{RT}{NF} In \frac{c_{e}^{\vee} c_{b}^{\circ}}{c_{e}^{\vee} c_{b}^{\circ}} - (ii)$ ٤. At equilibrium, since the cell could not perform any work as EMF will be zero, hence equation (ii) becomes E° = <u>RT</u> Inkeq [Keq = Equilibrium Constant] > NFE° = RT MKeq => $-AG^{\circ} = RT \ln keq$ => $[AG^{\circ} = -RT \ln keq]$ (iv)

This is the relation between Blandard bree energy Change and equilibrium Louistant box a given cell rxn.

* For a rem

Oxidant + ne = Reductant

The Nernst Equation can be written as

$$E = E^{\circ} - \frac{FT}{ME} \text{ in } \frac{[Vectorization I]}{[Colidant]}$$

$$= E^{\circ} + \frac{RT}{ME} \text{ in } \frac{[\text{locidant}]}{[Colidant]}$$

$$= E^{\circ} + \frac{RT}{ME} \text{ in } \frac{[\text{locidant}]}{[Colidant]}$$

$$= \frac{E^{\circ} + \frac{RT}{ME}}{[Colidant]} \frac{[\text{locidant}]}{[Colidant]}$$

$$= \frac{E^{\circ} + \frac{RT}{ME}}{ME} \text{ in } \frac{[\text{locidant}]}{[Colidant]}$$

$$= \frac{2}{(Colidant)} \frac{1}{1} \frac{Colid}{Colid} \frac{1}{1} \frac{1}{(Colidant)} \frac{1}{1} \frac{1$$

•

ii) For the run
$$(2n_0 q^2 + 14 H^2 + 6e) = 2(n_0^{34} + 7190)$$
, by runses equation can be written as;
Normal equation can be written as;
Eurof [(n^{34} = E'_{03}0_7](n^{34} + \frac{6}{16}E_{m} - \frac{a(n_0 D_7^2)}{a'_{03}n^{34}} - \frac{a'_{100}}{a'_{100}}
 $\therefore E_{0n_0} f_1[(n^{34} = E'_{0n_0} D_7](n^{34} + \frac{6}{16}E_{m} - \frac{a(n_0 D_7^2)}{a'_{01}n^{34}} - \frac{a'_{100}}{a'_{01}n^{34}} - \frac{a'_{100}}{a'_{01}n^{34}}$
For dilute solution and at 25%, this equation (and be written ad -
 $E_{0n_0} f_1[(n^{34} = E'_{0n_0} D_7](n^{34} + \frac{6}{6}D_7) + 17g - \frac{c_{0n_0} D_7}{C_{0n_0}} - \frac{c_{0n_0} D_7}{D_7} - \frac{c_{0n_0} D_7}{D_7}$

The given cell is composed of two electrodes, which are
the (S) [fe²⁺(at, 0:001M) [amode] and H⁺(at, 0:001M)]^{[hz}(d)
[cathode] Rum. taking place at the two electrodes are.
Owild attom rum at anode; fe (S)
$$\rightarrow$$
 fe²⁺(as, 0:001M) + 2e
Reduction rum at (athode; 2H⁺(az, 1M) \neq fe²⁺(as, 0:001M)
Here n=2
Nernst equation of This run can be written as
Eccll = E^ocell + 0:057 log $\frac{a_{Fe}(y) \cdot a_{H^+}(az, 1M)}{a_{Fe}^{2+}(az) \cdot a_{H_2}(y)}$
 $= 0.44 + 0:057 log 1/001$
 $= 0.44 + 0:057 log 1/0001$
 $= 0.028 v$.
No the given cell is composed of two electrodes, which
are Mg (2) 1 Mg 2+ (car, 0:001M) [amode] and cu²⁺(ag, 0:001M) + 2e
Reduction run at anode, Mg (S) \rightarrow Mg 2⁺(ar, 0:001M) + 2e
Reduction run at (athode, cu²⁺(ar, 0:001M) + 2e + cu(S)
Tota? Cell rum; Mg (S + cu²⁺(ar) 0:001M) + 2e + cu(S)
Here N=2
New sinst equation for This cell can be written as, at
 $(af - b) 0.579 log 0 and cu both are solids. 0 ang2+(cap)
Now since Mg and cu both are solids. 0 ang2+(cap)
 $Eccll = Eocell + 0:059 log 0 ang2+(cap)
Eccll = Eocell + 0:059 log 0 ang2+(cap)
 $Eccll = Eocell + 0:059 log 0 ang2+(cap)
Eccll = Eocell + 0:059 log 0 ang2+(cap)
Eccll = Eocell + 0:059 log 0 ang2+(cap)
Eccll = Eocell + 0:059 log 0 and 2 cu2+(as)
 $Eccll = Eocell + 0:059 log 1/001 ang2+(cap)
Eccll = 0:84 - (-2:37)
 $= 2:71$
Eccll = 2:71 + 0:059 log 1001
 $= 2:71 + 0:059 log 1001
 $= 2:71 + 0:059 log 1001
 $= 2:6805$ volt:$$$$$$

in the

· Application of standard Redox Potential values i) prediction of Rons.

The oxidant of a couple with a more positive standovrd potential (red) volue will ingeneral, obidise the reductant of a couple with a less positive or negative standard (red) potential value.

considered the standard electrode potential of the bellowing couples,

 $cu^{2+} + 2e \neq cu'; E = 0.34 \text{ volt}$

Ag+ + e = Ag; E' = 0.79 VOH

The less positive potential of the couple, The more effective The metal is as a reducing agent. Since The cu2+/ cu louple has a less positive potential cu will serve as a better reducing agent. There fore Cu will pass into solution with greater case Than Ag metal.

These fore if a cu wire is dipped into an aqueous sol" of AgNO3, Cu will pass into solution as Cu2+ leaving electrons on its surface these electrons will react with Agt ions which will be reduced to Ag. Eddectively These with be a deposit of Ag on the cell were and the lotourless aqueous solution will assume a blue lolour due to CU2+ ions. On the contrary when a Ag wire is dipped into 1. 2+ solution Theirs will be no run.

similarly when a zir rod is dipped into a soluction containing cu2+ ions. There is a deposite of metallic cu on The In rod (E2n2+/2n = 0.763). On the other hand is a curred is immersed in a solution of Rol2+ BOTH NO YEM OCCUTS. ii) Colculation of Cell potentials.

Dith the help of Ered values, we can calculate the standard potential of a given galvanic cell. The value ob Ecell is given by -

Even = 5°xed (right) - 5'xed (left)
Let us consider the standard electrode potentials of the
pollowing two Cauples

$$2n^{2+} + 2e \neq \pin$$
 5° = -0.763 volt
 $Ag^{+} + e \neq Ag$ 5° = 0.799 volt
Thus for the cell $\pi / fen^{2+} \parallel Ag^{+} / Ag$;
The cell potential = 0.299 - (-0.763)
= 1.562 volt.
It is not hessessary to Consider the no. ob electrons:
Involved in the change.
11) Determination ob equivibrium (constant of a redor xm.
The relation between the standard force energy
by, $AG^{+} = -RT \ln Keq - G$)
Where $Keq = Equilibrium constant ob a redor xm.
 $R = molar gas constant$
 $AG^{+} = -RT \ln Keq - G$
Where, $E^{+} = Standard force energy (change obtice xm.
 $Again we Know, AG^{+} = -nFE^{+} - G$)
Where, $E^{+} = Standard Emf ob the cell.
 $n = No. ob electrons involved in this xm.
 $F = Faxadary.$
Comparing equⁿ(j) and (ij) we get,
 $nFE^{+} = RT \ln Keq = \frac{nFE^{+}}{RT}$
or, $10\pi keq = \frac{nFE^{+}}{RT}$
 $or, 10\pi keq = \frac{nFE^{+}}{RT}$
 $or, 10\pi keq = \frac{nFE^{+}}{RT}$$$$$

Thus Knowing 5° as well as n we may calculate the value ob equin constant of a redox xxu.

•