PC-2(A): ELECTROCHEMISTRY-1

LESSON-I

Introduction

1. **ELECTROCHEMISTRY-** Subject of Chemistry involving electricity
2. **ELECTROCHEMICAL REACTIONS-** Chemical reactions related to electricity
3. **ELECTRODE** – *It is a system in which the element is present in two different oxidation states*- **Electrode reaction** – Oxidation or Reduction

   a) Cu | Cu^{2+}(aq.) ; **Cu : 0 & +2 oxidation states**

   b) Zn | Zn^{2+}(aq.) ; **Zn : 0 & +2 oxidation states**

   c) Chlorine electrode

   Pt, Cl_2, Cl^-, Here Pt acts as an inert electrode.

   d) Pt, Mn^{2+}, MnO_4^- - Manganous-permanganate electrode

   An electrode will have two possible tendencies namely i) Oxidation; ii) Reduction

   Displacement reactions

   $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$; Hence, reactivity: Zn > Cu

   Reactivity order: Na > Mg > Zn > Cu > Ag ……for ***metals***

   F > Cl > Br > I ……for ***non-metals***

4. **CELL-System in which an electrochemical reaction occurs-***similar to* ***system in thermodynamics***

   A **cell** is a combination of **two electrodes**.

   (i) **Electrolytic cell** - Electrical ⟶ Chemical

   Anode **–** Positive; ***Cathode***- Negative

   (ii) **Galvanic (Voltaic) cell** - Chemical ⟶ Electrical

   Anode-Negative; ***Cathode***- Positive

   But, in both cases **anode**= oxidation; **cathode** = reduction

5. **DANIEL CELL : Zn / $ZnSO_{4(aq)}$ // $CuSO_{4\,(aq)}$ / Cu ;** E^o_{cell} = 1.1V .

   Zinc dipped into a solution of **$ZnSO_4$** and **copper** dipped into a solution of **$CuSO_4$**. The two electrodes are connected internally by a **salt bridge** (solution of

KNO_3 or KCl , **they have almost same mobility & transport number**) and externally by a metallic wire.

Zinc electrode,

$Zn \longrightarrow Zn^{2+} + 2e$ (*Oxidation*) **Anode -ve**

Copper electrode,

$Cu^{2+} + 2e \longrightarrow Cu$ (*Reduction*) **Cathode +ve**

Zn leaves as Zn^{2+} .Hence Zn carries a negative charge. Electrons travel towards copper electrode which is positively charged because of the accumulation of Cu^{2+} from the solution.

The weight of Zn will decrease while the weight of Cu will increase.

Electrons migrate through the metallic wire to copper electrode where Cu^{2+} accepts the electrons and gets deposited. Hence, **electron flow** is from **zinc to copper & current flow** is from **copper to zinc.** Ions in the salt bridge migrate suitably to maintain electro neutrality. There is a migration of $2Cl^-$ ions to the zinc solution while $2K^+$ ions migrate to the copper sulphate solution for every Zn^{2+} formed and Cu^{2+} discharged.

6. **POTENTIAL**(***Electrode of an electrode with reference to a standard electrode,SHE***)- **POTENTIAL DIFFERENCE, emf (*Cell*) –** Difference in potential of the electrode ; Unit is **volt** for both
7. **ELECTRODE - Standard electrode** (1 atm, 298K , a =1)
8. **ELECTRODE & Standard electrode POTENTIAL** *(Reduction potential & Oxidation potentials)* – **SRP -** Single electrode potential can not be determined
9. **STANDARD CELL –** Definition-NB , $E_{cell} = E^o_{cell}$ **does not mean Std. cell**
10. **REFERENCE ELECTRODES (Primary & Secondary)**

(i) SHE *(**Primary** reference electrode)*; $E^o = 0$ V

SHE = Pt , H_2 (1 atm , 298K) , H^+(1M) **– Fig**

Difficulties which may be involved in the construction of SHE

- Pressure of H_2 should be maintained exactly at 1 atm.
- When a gas is bubbled into a solution the solution will undergo evaporation leading to increase in concentration.

- The electrode surface should be completely coated with Pt .

(ii) SCE *(**Secondary** reference electrode)*

SCE = Hg, $Hg_2Cl_{2\,(s)}$, Cl^- (satd) ; **E^o = 0.2422 V (w.r.t SHE)**

11. TYPICAL SRP DATA

Electrode	Std. Potential, V
(i) Li^+ / Li	-3.045
(ii) Na^+ / Na	-2.714
(iii) Mg^{2+} / Mg	- 2.37
(iv) Zn^{2+} / Zn	-0.76
(v) Fe^{2+}/ Fe	- 0.44
(vi) I^- , AgI , Ag	-0.151
(vii) SHE	**0.00**
(viii) Br^- , AgBr , Ag	0.071
(ix) Cu^{2+} / Cu^+	0.153
(x) Cl^- , AgCl , Ag	0.222
(xi) NCE	0.2676 ; **(SCE = 0.2422 V)**
(xii) Cu^{2+} / Cu	0.34
(xiii) Cu^+ / Cu	0.52
(xiv) Pt , Q , QH_2 , H^+	0.6996
(xv) Pt , Fe^{2+} , Fe^{3+}	0.77
(xvi) Ag^+ / Ag	0.80
(xvii) Pt , $Cr_2O_7^{2-}$, Cr^{3+} , H^+	1.33
(xviii) Pt , Cl_2 / Cl^-	1.36
(xix) Pt, MnO_4^- , H^+ , Mn^{2+}	1.51

Significance of SRP *(Applications & Electro Chemical series)***:**

(i) The more reactive metal will undergo **oxidation** while the other metal electrode will undergo **reduction.**

(ii) Prediction of anode & cathode

(iii) Determination of cell emf

(iv) Feasibility of an electrode and cell reactions.

(v) Electrode with greater SRP will undergo reduction.

12. **ANODIC & CATHODIC REACTIONS** of an electrode **– CELL REACTION to cell formations.**
13. **REVERSIBLE Electrodes and Cells-Concepts**
14. **RELATION BETWEEN EMF & ΔG –** Derivation – Applications

w = Force x distance = ΔG

= EMF x Charge = = E x Q

= E x nF ; (F = $6.023 \times 10^{23} \times 1.6 \times 10^{-19} = 96485C$)

$\Delta G = -E \times nF = -nFE$; $\mathbf{\Delta G^o = -nFE^o}$

15. **CONVENTIONS Regarding SIGN OF EMF :** + ve spontaneous
16. **EMF & SPONTANEITY** of electrochemical reactions-PROBLEMS based on E^o_{cell} & ΔG
17. **NERNST EQUATION-**Derivation – Application to Electrode potential & Cell emf
18. **TYPES OF ELECTRODE –**Try Electrode reaction ,Electrode potential- Nernst Equation

(i) Metal- Metal ion electrode : **Cu/Cu^{2+}**

(ii) Amalgam electrode : **Na-Hg / Na^+**

(iii) Gas electrode : **Pt , Cl_2 , $Cl^-_{(aq)}$**

(iv) Metal insoluble salt electrode : **$AgCl_{(s)}$, $Cl^-_{(aq)}$, Ag**

(v) Oxidation-reduction electrode : **Pt , $MnO_4^-{}_{(aq)}$, $Mn^{2+}_{(aq)}$, $H^+_{(aq)}$**

(NB: All electrodes are red-ox systems)

PROBLEMS

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1. Calculate the reduction potential of hydrogen electrode at a
   (i) Pressure of 0.5 atm (ii) pH = 2 ; (iii) pH = 10
2. Calculate the emf of a Daniel cell at 298 K when the concentration of Cu^{2+} and Zn^{2+} are 0.1 M and 0.01M, respectively.
3. Write the cathodic reaction at the electrode : I^- , AgI , Ag
4. Calculate the cell emf when the SCE is combined with standard copper electrode. Write the electrode reaction, the overall cell reaction and predict anode & cathode and their algebraic sign.
5. Write the cathodic reaction at the electrode Pt , Q , QH_2 , H^+ ;
   $E^o = 0.6996V$
6. In an experiment to determine the SRP of an electrode using saturated calomel electrode as reference electrode, the cell potential was found to be 0.097V. Evaluate the SRP of the electrode.
7. Write the anodic reaction at the electrode Pt, MnO_4^- , H^+ , Mn^{2+} .
8. Calculate the EMF of the cell formed using the electrodes Pt , Q , QH_2 , H^+ (0.01M) (SRP = 0.6996V) and Cl^- (0.1), AgCl , Ag (SRP= 0.222 V)
9. Construct the cell in which the following overall reaction occurs. Determine its E^o_{cell} : $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$
10. Calculate the RP of Ag^+ / Ag at the concentration of X^- equal to the solubility of AgCl , AgBr , AgI (K_{sp} = 1.8 x 10^{-10} ; 5 x 10^{-13} ; 8.3 x 10^{-17} , respectively)
11. Formulate the cell corresponding to the following cell reaction. Determine its E^o_{cell} & ΔG^o : $Cd + 2Ag^+ \longrightarrow 2Ag + Cd^{2+}$
12. Calculate the SRP of Cu^+ / Cu electrode given the SRP of the electrodes Cu^{2+} / Cu^+ , E^o = 0.153 & Cu^{2+} / Cu ; E^o = 0.34 V .
13. Calculate the RP of the electrode at pH=3 Pt , MnO_4^- (0.1M), H^+ , Mn^{2+} (0.01M) if its SRP = 1.51V
14. Formulate a red-ox electrode involving (i) $Cr_2O_7^{2-}$ (ii) IO_3^- in acid medium.