

PC-2(B):ELECTROCHEMISTRY-1(Contd...)

LESSION-2

Electrode

1. **STANDARD ELECTRODE** : To determine electrode potential

2. **STANDARD CELL** : To determine Cell EMF

(i) **Weston saturated standard cell**

Anode (+ve)

Cathode (-ve)

Cd (12.5%) -**Hg** , **3.CdSO₄.8H₂O(s)** , **CdSO₄ (aq)** , **Hg₂SO₄ (s)** , **Hg** , **Hg** ; E = 1.0183 V

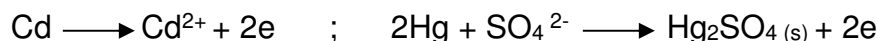


Fig (Weston cell)

(ii) **Weston unsaturated standard cell** : It will not have **3.CdSO₄.8H₂O(s)**

3. **MESUEMENT OF EMF- POTENTIOMETER- USE OF STANDARD CELL. c.f-**

Voltmeter

4. **THERMODYNAMICS OF ELECTROCHEMICAL REACTIONS**

- Nernst equation (E as a function of T & conc)
- $\Delta G = - nFE$; $\Delta G^\circ = - nFE^\circ$
- Temperature coefficient of EMF , $(\partial E/\partial T)_p$; The sign of $(dE/dT)_p$ can be +ve or -ve
- $\Delta S = nF(\partial E/\partial T)_p$
- $\Delta H = \Delta G + T\Delta S$
- $\Delta G^\circ = - nFE^\circ = -RT \ln K$; Hence , $nFE^\circ = RT \ln K$

5. **PROMLEM:**

The EMF of the saturated Weston-Cadmium cell at temperature , t (°C) varies as follows: $E_t = 1.018300 - 4.06 \times 10^{-5}(t-20) - 9.5 \times 10^{-7}(t-20)^2 + 1 \times 10^{-8}(t-20)^3$

Determine the following quantities

- (i) EMF at 300 °C ; (ii) ΔG° ; (iii) ΔS at 300 °C ; (iv) ΔH° and (v) K

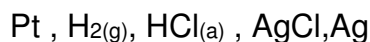
6. CLASSIFICATION of Galvanic CELLS

(a) Chemical cells (*Diff types of electrodes-Chemically different*)

(i) **Without transference**-No direct transfer of ions in the electrode from one to the other



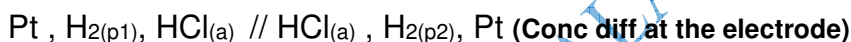
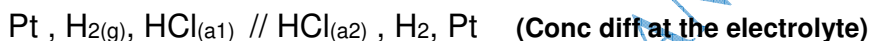
(ii) **With transference**-Direct transfer of ions in the electrode from one electrode to the other



Weston Cd Cell

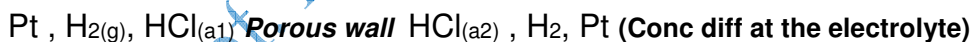
(b) Concentration cells (*Same type of electrodes- Chemically identical*)

(iii) **Without transference**- No direct transfer of ions in the electrode



$$E_{\text{wot}} = \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \text{Electrode reversible to cation}$$

(iv) **With transference**-Direct transfer ions in the electrode



$$E_{\text{wt}} = 2t_+ \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \text{Electrode reversible to anion.}$$

$$\text{NB : } E_{\text{wt}} / E_{\text{wot}} = 2t_+$$

(c) Liquid junction potential, E_{LJP}

If the ions don't migrate with equal velocity across a liquid junction, the junction gets polarized, this polarization occurring at the junction introduces a potential called Liquid Junction Potential (**LJP**)

This can happen in the salt bridge also if the ions don't migrate with equal velocity. Salt bridge gets polarized at the junction contributing to Liquid Junction Potential (**LJP**)

NB : $E_{wt} / E_{wot} = 2t_+$ (Measurement of transport number)

$$E_{LJP} = E_{wt} - E_{wot} = 0 ; \text{ if } E_{wt} = E_{wot} ; E_{wt} / E_{wot} = 1 ; t_+ = 1/2$$

KCl , KNO₃ ..etc., have $t_- = t_+ = 1/2$ and are used to minimize LJP.

7. APPLICATIONS OF EMF MEASUREMENTS

a. Calculation of ΔG , ΔH , ΔS & K of electrochemical reactions at electrodes

b. Determination of valency of ions

Hg , Mercurus chloride (w_2 g)_(aq) // Mercurus chloride (w_1 g)_(aq), Hg

$$E_{\text{cell}} = \frac{RT}{nF} \ln \frac{w_2}{w_1} ; \text{ "n" can be calculated}$$

c. K_{sp} of a sparingly soluble salt (AgX , Ag₂CrO₄ , PbSO₄)

Ag , Ag⁺ // Cl⁻_(aq) (X⁻_(aq) , M) , AgCl , Ag



$$E_{\text{cell}} = 0.578 + 0.05915 \log K_{sp} ; \{\text{NB: } X^- \text{ will adjust with } E_{\text{cell}} \text{ to give the characteristic } K_{sp}\}$$

d. Determination of pH

(i) Hydrogen electrode

Pt, H₂, H⁺ (Expt Soln., pH = ?) // SCE

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.05915}$$

OR

$$\text{pH} = \frac{(E_{\text{SCE}}^0 \sim E_{\text{SHE}}^0) - E_{\text{cell}}}{0.05915}$$

(ii) Quinhydrone (Q + QH₂) electrodePt, Q, QH₂, H⁺ (Expt Soln., pH = ?) // SCE

$$\text{pH} = \frac{0.4574 - E_{\text{cell}}}{0.05915}$$

OR

$$\text{pH} = \frac{(E_{\text{SCE}} \sim E^{\circ}_{\text{Q.QH}_2}) - E_{\text{cell}}}{0.05915}$$

(iii) Glass electrode

Ag, AgCl, (0.1M, HCl) / glass/ Expt Soln ; pH = ? // SCE

$$E_g = E_g^{\circ} - \frac{RT}{F} \ln [H^+]; \text{ where } [H^+] \text{ is the concentration of the solution outside the glass electrode}$$

E_g^o must be determined by using a solution of known pH

$$\text{pH} = \frac{(E_{\text{SCE}} \sim E^{\circ}_{\text{GE}}) - E_{\text{cell}}}{0.05915}$$

NOTE: The difference “E_{SCE} ~ E^o_{TEST}” must be taken as +ve in all cases**e. Potentiometric titration****(a) Acid-Base titration** (*Ref., Determination of pH*)Pt, H₂, H⁺ (Expt Soln., pH = ?) // SCE

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.05915}$$

Pt, Q, QH₂, H⁺ (Expt Soln., pH = ?) // SCE

$$\text{pH} = \frac{0.4574 - E_{\text{cell}}}{0.05915}$$

Ag, AgCl, (0.1M, HCl) / glass/H⁺ (Expt Soln, pH = ?) // SCE

$$\text{pH} = \frac{(E_{\text{SCE}} \sim E^{\circ}_{\text{GE}}) - E_{\text{cell}}}{0.05915}$$

NB: pH vs V_{NaOH} will be a **decreasing curve in all acid base titrations**

8. RED-OX Titration : (Fe^{2+} vs Std $\text{Cr}_2\text{O}_7^{2-}$)Pt, Fe^{2+} , Fe^{3+} // SCE (Cell before END point)

SRP: 0.77 V 0.2422V

$$E = 0.5278 + 0.05915 \log (\text{Fe}^{3+} / \text{Fe}^{2+})$$

NB: The chemical tendency is Fe^{2+} to Fe^{3+} ; whereas the electrochemical tendency along with SCE is for Fe^{3+} to become Fe^{2+} .

➤ **During** the titration, the **EMF inc** with the added $\text{Cr}_2\text{O}_7^{2-}$

Pt, $\text{Cr}_2\text{O}_7^{2-}$, Cr^{3+} , H^+ // SCE (Cell after END point)

SRP: 1.33 V 0.2422V

$$E = 1.0878 + (0.05915/6) \log \{[\text{Cr}_2\text{O}_7^{2-}] [\text{H}^+]^{14} / [\text{Cr}^{3+}]^2\}$$

➤ **The inc in EMF with** the added $\text{Cr}_2\text{O}_7^{2-}$ **will be much high** at the end point

9. PRECIPITATION Titration : (X^- vs AgNO_3)Ag, AgX, X^- // SCEOrder of precipitation as AgX : AgI, AgBr, AgCl (cf K_{sp} values)

Electrode	SRP(V)	Cell emf
I^- , AgI, Ag	-0.151 ;	
Br^- , AgBr, Ag	0.071 ;	
Cl^- , AgCl, Ag	0.222 ;	
Solubility : AgI < AgBr < AgCl		

The **working electrodes & the cell emf** at different stages areAg, AgI, I^- // SCE ; $E = 0.3932 + 0.05915 \log [\text{I}^-]$ Ag, AgBr, Br^- // SCE ; $E = 0.3132 + 0.05915 \log [\text{Br}^-]$ SCE // Cl^- , AgCl, Ag ; $E = 0.0202 + 0.05915 \log [\text{Cl}^-]$

➤ **NB- EMF dec & changes sign** at time of Ag, AgCl, Cl^- as the working electrode
.Poles to be reversed.