

LECTURE NOTES  
ON  
ELECTROCHEMISTRY  
**ENGINEERING CHEMISTRY**

B.Tech 1<sup>st</sup> year

By

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## Contents

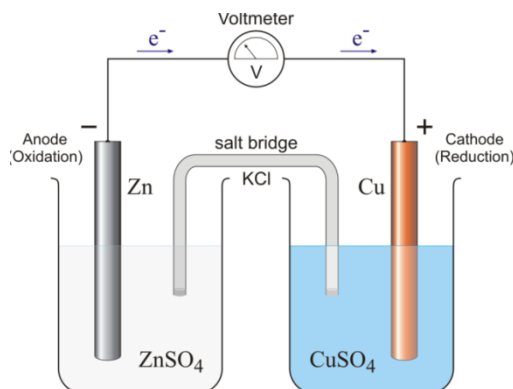
1. Introduction
2. Galvanic cell
3. Electrode potential
  - i) Single electrode potential
  - ii) Standard electrode potential
4. Factor affecting electrode potential
  - i) Nature of electrode
  - ii) Concentration of ionic solution
  - iii) Temperature
5. Electrochemical series
  - i) Application of electrochemical series
6. Electromotive force (EMF)
7. Nernst equation
8. Battery
  - i) Primary batteries
  - ii) Secondary batteries
9. Lead storage battery

## Introduction

“Electrochemistry is defined as the branch of chemistry which deals with inter-conversion of chemical energy to electrical energy and vice versa”. For example, in a battery, chemical energy is converted to electrical energy whereas in electroplating / electrolysis electrical energy is converted to chemical energy.

## Galvanic cell

Chemical energy is converted into electrical energy by Galvanic cell. These cells are known as electrochemical cells or voltaic cells. The best example of galvanic cell is Daniel cell. This cell is formed by combination of two half cells. One is oxidation half cell or anodic half cell and other one is reduction half cell or cathodic half cell. The oxidation half cell consists of ‘Zn’ electrode dipped in  $\text{ZnSO}_4$  solution and reduction half cell consists of ‘Cu’ electrode dipped in  $\text{CuSO}_4$  solution. Both the half cells are externally connected by metallic wire and internally connected by ‘salt bridge’. Salt bridge is a U shaped tube containing solution of  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$ ,  $\text{KCl}$  or  $\text{NH}_4\text{NO}_3$  in agar-agar gel contained porous site. It maintains the electrical neutrality between two solutions.



The following reactions take place in the cell.

At anode:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$  (oxidation)

At cathode:  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  (Reduction)

The movement of electrons from Zn electrode to Cu electrode produces a current in the reverse direction.

The overall cell reaction is:



The galvanic cell can be represented by



Presentation of galvanic cell:



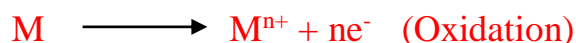
### Electrode potential

#### Single electrode potential:

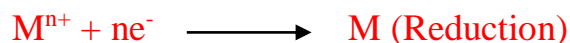
In galvanic cell, two electrodes are presented; at one electrode oxidation takes place and at other electrode reduction takes place.

“The tendency of an electrode (M) to get oxidized or reduced when it is contact with its own ionic ( $\text{M}^{n+}$ ) solution, known as single electrode potential”. It is represented by  $E_{(\text{M}/\text{M}^{n+})}$  or  $E_{(\text{M}^{n+}/\text{M})}$ .

If metal rod or electrode (M) loses electrons and change into metal ions ( $\text{M}^{n+}$ ) then metal get oxidized (oxidation potential,  $E_{(\text{M}/\text{M}^{n+})}$ ).



If metal ions ( $\text{M}^{n+}$ ), on collection with metal rod by gain electrons and change into metal atom (M), then metal ions get reduced (Reduction potential,  $E_{(\text{M}^{n+}/\text{M})}$ )



During oxidation negative charge developed on the metal electrode and during reduction positive charge develops on the metal electrode.

#### Standard electrode potential:

If the metal electrode is suspended in a ionic solution of 1M (molar) concentration or unit activity and temperature is kept at 25°C under 1atm pressure, then potential develop between electrode and ionic solution is known as standard electrode potential. It is represented by  $E^{\circ}$ . The standard electrode potential of two half cell are represented by  $E^{\circ}_{(\text{M}/\text{M}^{n+})}$  or  $E^{\circ}_{(\text{M}^{n+}/\text{M})}$ .

#### Factors affecting electrode potential:

##### Nature of electrode

Ability of an element to lose or gain an electron depends on it properties like ionization energy, electro affinity, size etc. For example, the oxidation potential of Li atom is higher than Na, therefore it release electron easily and get oxidized.

## Concentration of ionic solution

If concentration of ions is increase the equilibrium shift towards the metal site



In this case, metal have lower tendency to lose electron (Oxidation potential)

## Temperature

The equilibrium between ions and the pure metal is also affected by the temperature. If reaction is exothermic then an increase in the temperature will make the equilibrium move more to the left hand side making the electrode potential more negative. If reaction is endothermic then an increasing in the temperature makes the electrode potential more positive.

## Electrochemical series

Series in which elements are arranged in increasing order of their standard electrode potential is known as electrochemical series.

Electrode	Half cell reaction	$E^0$ volts (standard reduction potential)
$Li^+/Li$	$Li^+ + e^- \rightarrow Li$	-3.04
$K^+/K$	$K^+ + e^- \rightarrow K$	-2.9
$Ca^{+2}/Ca$	$Ca^{+2} + 2e^- \rightarrow Ca$	-2.8
$Na^+/Na$	$Na^+ + e^- \rightarrow Na$	-2.7
$Mg^{+2}/Mg$	$Mg^{+2} + 2e^- \rightarrow Mg$	-2.3
$Zn^{+2}/Zn$	$Zn^{+2} + 2e^- \rightarrow Zn$	-0.76
$Fe^{+2}/Fe$	$Fe^{+2} + 2e^- \rightarrow Fe$	-0.4
$H^+/H_2, Pt$	$H^+ + e^- \rightarrow \frac{1}{2}H_2$	+ 0
$Cu^{+2}/Cu$	$Cu^{+2} + 2e^- \rightarrow Cu$	+0.15
$Ag^+/Ag$	$Ag^+ + e^- \rightarrow Ag$	+ 0.7
$Pt, Cl_2/Cl^-$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.3
$Pt, F_2/F^-$	$F_2 + 2e^- \rightarrow 2F^-$	+ 2.8

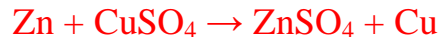
## Application of Electrochemical series

### i) Comparison of relative oxidizing and reducing power:

The greater the reduction potential, greater the tendency of the element or ions to get reduce. For example, the reduction potential of  $\text{Fe}^{2+}$  (-0.41 V) is higher than the  $\text{Li}^+$  (-3.04 V), therefore  $\text{Fe}^{2+}$  ion is easily reduce and  $\text{Li}^+$  ion is easily oxidized.

### ii) Relative reactivity of metals:

Greater the oxidation potential of the element, greater will be the tendency to lose electrons (greater tendency to get oxidized). A metal with higher oxidation potential can displace the metal with lower oxidation potential. For example, the oxidation potential of  $\text{Zn}^{2+}$  (-0.76 V) is higher than  $\text{Cu}^{2+}$  (0.34 V), therefore Zn replace Cu from its salt solution.



### iii) Spontaneity of reaction:

If EMF of the cell is positive then redox reaction is spontaneous and if EMF of the cell is negative then redox reaction is non-spontaneous.

**Electromotive force (EMF)** The force which causes the flow of electrons from one electrode to another electrode and thus results in the flow of current from electrode at higher potential to electrode at lower potential is called electromotive force.

### Calculation of EMF of the cell:

Standard EMF of the cell = [standard reduction potential of R.H.S. electrode] –  
[Standard reduction potential of L.H.S. electrode]

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

**Oxidation potential = - reduction potential**

### Question 1:

Write the half cell and net cell reactions for the following cell,

$\text{Zn} / \text{ZnSO}_4 (\text{aq}) // \text{CuSO}_4 (\text{aq}) / \text{Cu}$ .

Calculate the standard emf of the cell given,

$$E^{\circ}_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ v and } E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} = + 0.34 \text{ V}$$

Solution

Half cell reactions



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$= E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} - E^{\circ}_{\text{Zn}^{+2}/\text{Zn}}$$

$$= 0.34 - (-0.76)$$

$$= 1.1 \text{ V}$$

### Application of EMF:

i) **In determination of  $\text{H}^{+}$  ion concentration or pH of solution**

a) **Using Hydrogen electrode:**

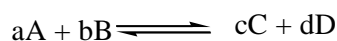
$$\text{pH} = - \frac{E^{\circ}_{\text{calomal}} - E_{\text{cell}}}{0.0591}$$

b) **Using Quinehydrone electrode:**

$$\text{pH} = \frac{E^{\circ}_{\text{Q}} - E^{\circ}_{\text{calomal}} - E_{\text{cell}}}{0.0591}$$

## Nernst Equation

Lets us consider a hypothetical cell reaction



Applying Van't Hoff reaction isotherm

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (Q \text{ is the reaction co-efficient})$$

$$-nFE = -nFE^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \{-\Delta G = nFE\}$$

Both side is divided by  $-nF$

$$E_{cell} = E_{cell}^\circ - RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{cell} = E_{cell}^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T = 298\text{K}, F = 96,500 \text{ C}$$

$$E_{cell} = E_{cell}^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where,  $E_{cell}$  = single electrode potential

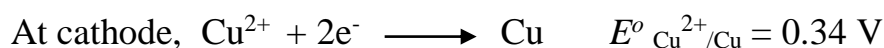
$E_{cell}^\circ$  = Standard reduction electrode potential

The above equations are the form of Nernst equation

### Question 2

Consider a cell Ni/Ni<sup>2+</sup> (0.01M) || Cu<sup>2+</sup> (0.5M)/Cu. The standard reduction potential of Ni and Cu are -0.25 and 0.34 V, respectively. Calculate the EMF of the cell.

Solution







therefore they can be use again and again. For example: lead storage battery (lead acid battery), Ni-Cd battery.

### iii) Fuel cell:

Fuel cell is a device, which produce electricity by the combustion of fuel.



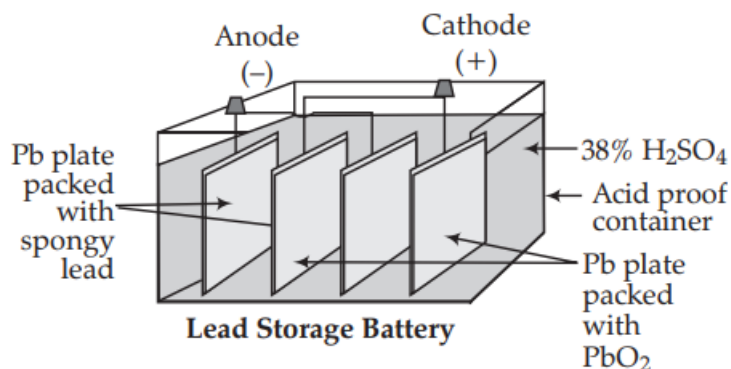
## Lead Storage Battery

Anode: spongy metallic lead

Cathode: Lead dioxide

Electrolyte: dil.  $\text{H}_2\text{SO}_4$

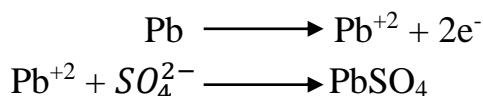
**Construction:** A number of spongy lead plates (anode) and a number of lead dioxide ( $\text{PbO}_2$ ) plates (cathode) are connected in parallel. The spongy lead plates are fit alternatively between lead dioxide plates. All the plates are separated from adjacent plates by insulators like wood strips, glass fiber etc. The entire combination is immersed in approximately 38 % dil.  $\text{H}_2\text{SO}_4$  of specific gravity 1.2 to 1.3  $\text{g/cm}^3$  solution.



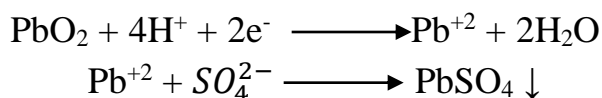
### Discharging:

Battery is said to be discharge when used for production of electrical energy. In this process the lead electrode loses electron and get oxidized into  $\text{Pb}^{+2}$  which react with  $\text{SO}_4^{2-}$  and form  $\text{PbSO}_4$ . The released electrons from anode are used up by cathode to reduce  $\text{PbO}_2$  into  $\text{Pb}^{+2}$  which react with  $\text{SO}_4^{2-}$  and form  $\text{PbSO}_4$ . In this process  $\text{PbSO}_4$  deposited on both the electrode and cell stop working.

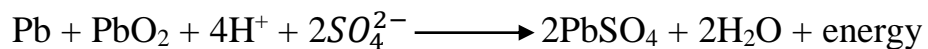
At anode:



At cathode:

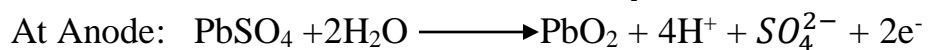
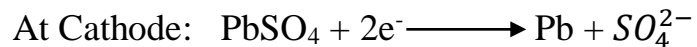


The net reactions



**Charging:**

A battery needs charging when the specific gravity of  $\text{H}_2\text{SO}_4$  falls below  $1.2 \text{ g/cm}^3$ . This can be achieved by applying external direct current so as to reverse the cell reaction.



The net reaction

