Engineering Chemistry

First Year Engineering

(Sem- II)

Syllabus

Course Code	Course Name	Examination Scheme								
		Theory					Term Work	Pract. /oral	Total
		Internal Assessment			End Sem. Exam.	Exam. Duration (in Hrs)			
		Test1	Test 2	Avg.					
FEC201	Engineering Mathematics-II	20	20	20	80	3	25	--	125
FEC202	Engineering Physics-II	15	15	15	60	2	--	--	75
FEC203	Engineering Chemistry-II	15	15	15	60	2	--	--	75
FEC204	Engineering Graphics	15	15	15	60	3	--	--	75
FEC205	C programming	15	15	15	60	2	--	--	75
FEC206	Professional Communication and Ethics- I	10	10	10	40	2	--	--	50
FEL201	Engineering Physics-II	--	--	--	--	--	25	--	25
FEL202	Engineering Chemistry-II	--	--	--	--	--	25	--	25
FEL203	Engineering Graphics	--	--	--	--	--	25	50	75
FEL204	C programming	--	--	--	--	--	25	25	50
FEL205	Professional Communication and Ethics- I	--	--	--	--	--	25	--	25
FEL206	Basic Workshop practice-II	--	--	--	--	--	50	--	50
Total		--	--	**90**	**360**	--	**200**	**75**	**725**

Topics

- 1) Principles of Spectroscopy
- 2) Applications of Spectroscopy
- 3) Concept of Electrochemistry
- 4) Corrosion
- 5) Green Chemistry and Synthesis of drugs
- 6) Fuels and Combustion

Topic- 3 Concept of Electrochemistry

- **Introduction**
- **Electrochemistry is the branch of chemistry which studies reactions which takes place in solution at interface of electron conductor (electrode) and ionic conductor (electrolyte)**

Topic- 3 Concept of Electrochemistry

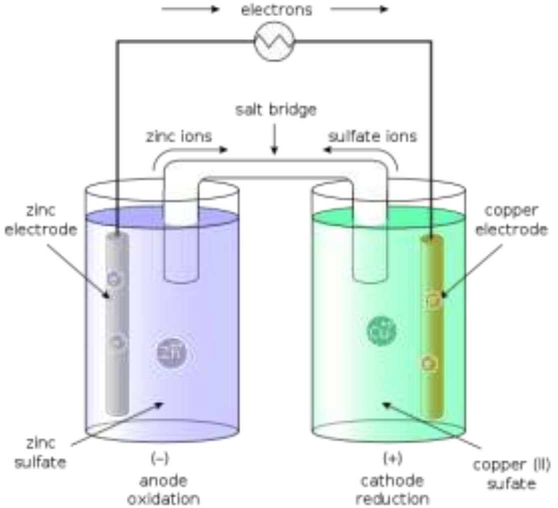
- **Electro Chemical Cell**
- **A cell consisting two electrodes in contact with solution of its own ions and transforms free energy change of redox reaction at electrodes into electrical energy.**
- **In short the device who produce electrical energy through spontaneous redox reaction takes place at electrodes by free electrons change.**
- **In redox reaction, the energy is released due to movement of charged particles gives rise to potential difference.**
- **The maximum potential difference is called electromotive force (EMF)**
- **Cell potential is more positive, the greater is the tendency for the reaction to proceed spontaneously.**

Topic- 3 Concept of Electrochemistry

- **Classification of Electro Chemical Cell**
- **1) Voltaic cell (Galvanic cell)**
- **2) Electrolytic cell**
- **3) Concentration cell**
- **4) Fuel cell**

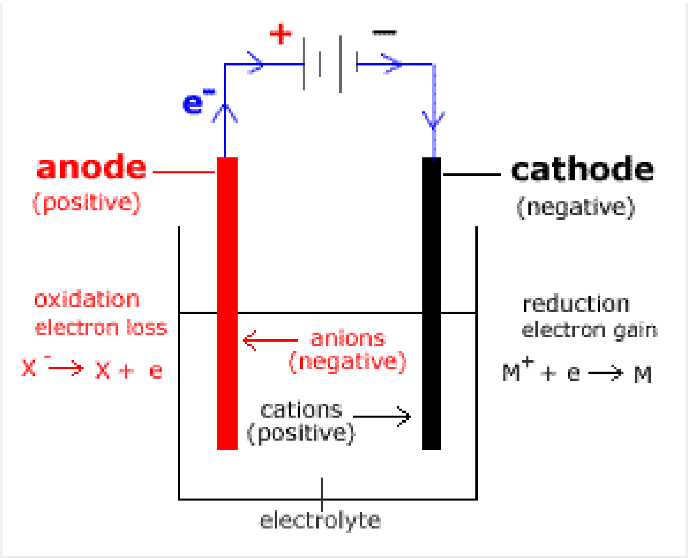
Topic- 3 Concept of Electrochemistry

- **Classification of Electro Chemical Cell**
- **1) Voltaic cell (Galvanic cell)**
- **Free energy change in galvanic cell is negative and potential difference is positive.**
- **Energy is released by spontaneous redox reaction.**
- **In this cell free energy change is converted into electrical energy ($\Delta G = -nFE$).**
- **Examples- Dry cell (irreversible cell) and Lead acid storage cell (reversible cell)**



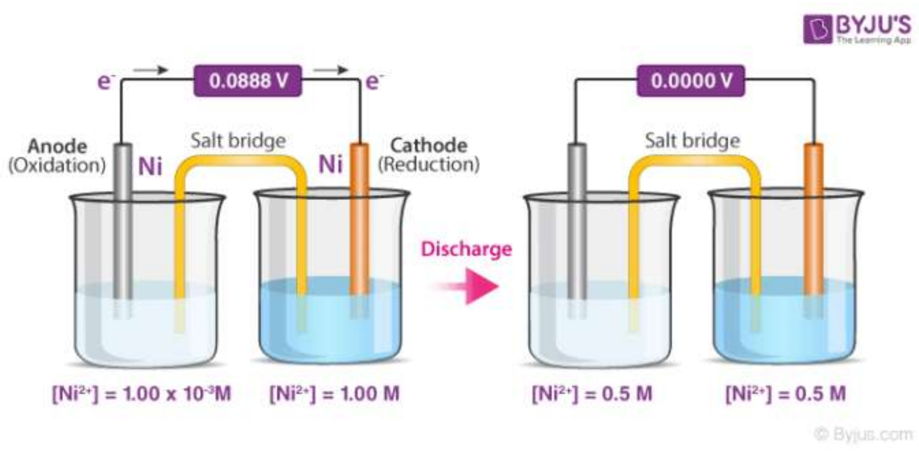
Topic- 3 Concept of Electrochemistry

- **Classification of Electro Chemical Cell**
- **2) Electrolytic cell**
- **In this cell electrical energy is used from external source to produce chemical reaction.**
- **Energy is absorbed for non spontaneous redox reaction.**
- **This cell free electron change is positive.**



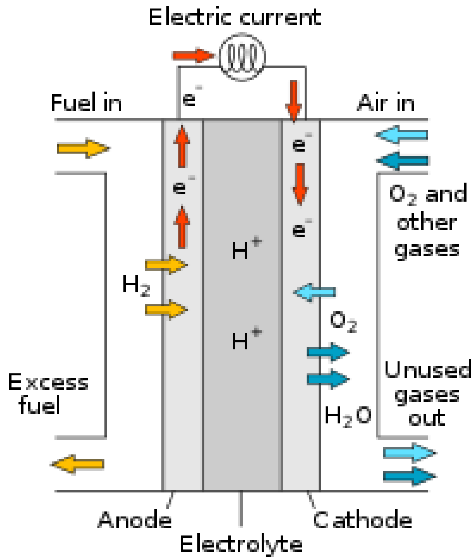
Topic- 3 Concept of Electrochemistry

- **Classification of Electro Chemical Cell**
- **3) Concentration cell**
- **It is electrochemical device which generate electrical energy by using chemical energy.**
- **Same metal electrodes are in contact with solution of different concentration.**
- **In this cell free energy change of electrode reaction is converted into electrical energy.**



Topic- 3 Concept of Electrochemistry

- **Classification of Electro Chemical Cell**
- **4) Fuel cell**
- **It is an electrochemical device.**
- **It operates continuous replenishment of fuel, hence no charging required.**
- **In this cell. Free energy change of electrode redox reaction is converted into electrical energy.**



Topic- 3 Concept of Electrochemistry

- **Applications of Electro Chemical Cell**
- It is used in electro refining of metals.
- Electroplating, electrotyping etc.
- Extraction methods of metals.
- Some electrochemical cell are used to generate electrical energy. i.e. in vehicle batteries used to start engine.
- Fuel cell is used as source of clean energy.

Topic- 3 Concept of Electrochemistry

- **Difference between Galvanic cell & Electrolytic cell**

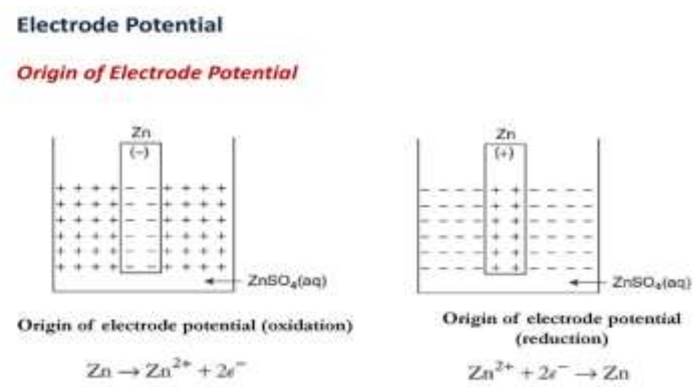
Sr. No.	Particulates	Galvanic cell	Electrolytic cell
01	Function	It convert chemical energy to electrical energy	It convert electrical energy to chemical energy
02	Anode and Cathode charges	Anode- negatively charged and cathode- positively charged.	Anode- positively charged and cathode- negatively charged.
03	Electrons origin	Electrons originates from undergoes oxidation	Electrons used from external source
04	Electrodes	Electrodes are of dissimilar metals	Electrodes are of similar or dissimilar metals

Topic- 3 Concept of Electrochemistry

- **Electrode Potential**
- **A piece of metal is immersed in solution of its own ions.**
- **A potential difference is created at electrode and solution.**
- **The magnitude of potential difference is a tendency of electrode to undergo oxidation or reduction or loose or gain electrons.**
- **The immersed metal is an electrode and the potential due to reaction at the interface of the electrode and the solution is called electrode potential.**

Topic- 3 Concept of Electrochemistry

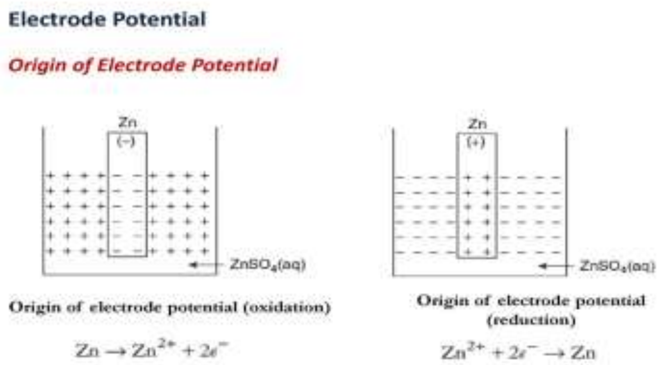
- **Origin of Electrode Potential**



- **Consider Zn rod is placed in $ZnSO_4$ solution, Zn has two tendencies- oxidation or reduction.**
- **Oxidation tendency, looses the electrons and Zn acquire Zn^{++} ions.**
- **Zn rod become negatively charged and positively charged metal ions accumulate around the Zn rod.**
- **$Zn \rightarrow Zn^{++} + 2e^-$**

Topic- 3 Concept of Electrochemistry

- **Origin of Electrode Potential**



- Consider Zn rod is placed in $ZnSO_4$ solution, Zn has two tendencies- oxidation or reduction.
- **Reduction tendency,** accept the electrons by Zn^{++} ions from metallic surface.
- Zn rod become positively charged and negatively charged ions accumulate around the Zn rod.
- $Zn^{++} + 2e^{-} \rightarrow Zn$

Topic- 3 Concept of Electrochemistry

- **Standard Electrode Potential**
- **It is defined as the potential exists between metal or the gas and its aqueous solution at temperature 298^0K when the sum of all partial pressure of all gaseous reactants and products is equal to 1 atm pressure.**
- **This value is considered to compare the relative abilities of different electrodes undergo oxidation or reduction.**

Topic- 3 Concept of Electrochemistry

- **Reference Electrode**
- **The potential of an electrode cannot be accurately measured.**
- **It may not connect to measuring device as lead to equilibrium with existing electrode.**
- **To overcome this, electrode is connected to another electrode of known potential is known as reference electrode.**

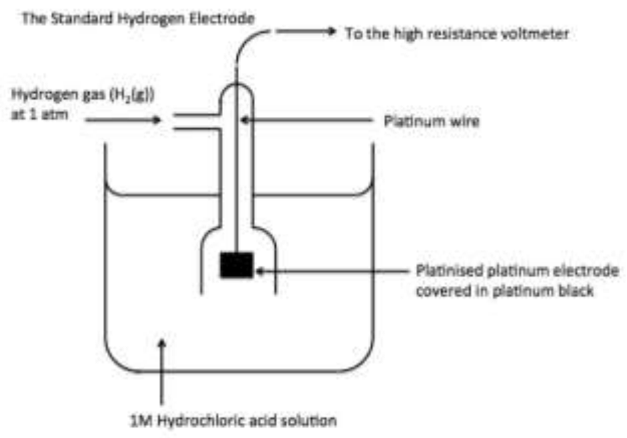
Criteria for selection of reference electrode;

- **1) Potential of reference electrode should be known.**
- **2) Its potential variation should be minimum with temperature variation.**

- **Most commonly used reference electrode is Hydrogen Electrode, because potential of other electrodes is measured w.r.t. hydrogen.**
- **Hydrogen electrode is also called as primary electrode.**
- **The electrodes standardizes by using hydrogen electrodes are called as secondary electrodes.**

Topic- 3 Concept of Electrochemistry

- **Reference Electrode**
- **1) Standard Hydrogen Electrode (SHE)**



- **a) It consists of Platinum foil is dipped in 1.0 m HCl.**
- **b) Platinum foil is enclosed by thick walled glass tube connected to external contact wire.**
- **c) Pure hydrogen is passed with 1 atm pressure, from top inlet which is absorbed by Pt foil and excess hydrogen leaves through outlet.**

Topic- 3 Concept of Electrochemistry

- **Reference Electrode**
- **1) Standard Hydrogen Electrode (SHE)**
- **d) It forms reversible electrode;**

  Pt, H_2(1atm) | (1.0M) HCl
- **e) The reduction occurs at the electrode, the reaction will be;**

  $$2H^+ + 2e^- \leftrightarrow H_2$$
- **As potential cannot measured directly, it can assumed to be zero at 298^0K.**
- **E^0 of SHE is assumed to be zero, the potential of second electrode is determined.**
- ***The potential of electrode is measured at standard condition is called as standard electrode potential.***
-

Topic- 3 Concept of Electrochemistry

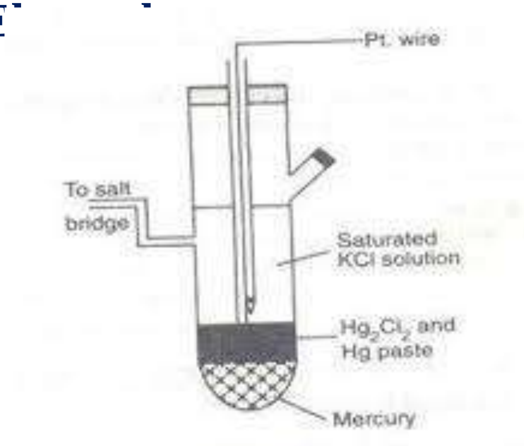
- **Reference Electrode**

*** Limitations of Standard Hydrogen Electrode (SHE)**

- **Cannot be used in presence of strong oxidizing and reducing agents.**
- **Difficult to maintain unit molar concentration of hydrogen and throughout pass 1 atm pressure of hydrogen.**
- **Pt foil get poisonous and get affected if arsenic compounds present.**

Topic- 3 Concept of Electrochemistry

- **Reference Electrode**
- **2) Calomel E**



Calomel Electrode

- **a) It consists of thin layer of mercury at bottom.**
- **b) It is covered with paste of Hg, Hg_2Cl_2 and KCl with known concentration.**
- **c) Rest container (at upper side) filled with known concentration of KCl saturated with Hg_2Cl_2.**

Topic- 3 Concept of Electrochemistry

- **Reference Electrode**
- **2) Calomel Electrode**
- **Electrode can be represented as;**

Pt, $Hg_{(l)}$, $Hg_2Cl_{2(s)}$ | KCl(xM) saturated with Hg_2Cl_2

- **Potential of this electrode is depends on concentration of KCl.**
- **This is reversible electrode.**
- **If reduction occurs at this electrode, then reaction is;**

$$Hg_2Cl_{2(s)} \leftrightarrow 2Hg^{2+} + 2Cl^-$$

$$2Hg^{2+} + 2e^- \leftrightarrow 2Hg$$

$$Hg_2Cl_{2(s)} + 2e^- \leftrightarrow 2Hg + 2Cl^-$$

Topic- 3 Concept of Electrochemistry

- **Reference Electrode**
- **Nernst's equation for Calomel Electrode is**

$$E_{Hg/Hg_2Cl_2} = E^0 - \frac{2.303RT}{nF} \log [Cl^-]^2$$

- **Calomel electrode with saturated KCl and 1.0 M KCl have potential value is 2.2412 and 0.28 v respectively.**

- **Advantages of Calomel electrode:**
- **Used to corrosion studies.**
- **Easy to construct and transport.**
- **Provide constant potential value with varying temperature.**
- **Used in laboratories to measure potential of electrode.**

Topic- 3 Concept of Electrochemistry

- **Electro-Chemical Series**

- **The standard electrode potential for all metals can be obtained by preparing the cells in which standard hydrogen electrode is used as reference electrode and other metal electrode immersed in solution.**
- **The standard electrode potential is also known as standard oxidation potential.**
- **Metals can be arranged in increasing order of electrode potential.**
- **The elements arranged in the increasing order of their standard electrode potential constitute a series is called as electrochemical series.**
- **Electrochemical series according to electronegativity and electro positivity of metals.**
- **The elements occupying higher position in series, they have greater tendency to pass in the solution.**
- **The elements occupying lower position in series, they have lower tendency to pass in the solution.**

Topic- 3 Concept of Electrochemistry

- **Characteristics of Electro-Chemical Series**
- **1) Lithium is first member of series.**
- **Highly reactive metal which are good reducing agents are placed top of the series.**
- **Good oxidizing agents are placed at bottom of the series.**
- **Hydrogen system is at middle. All elements which displace hydrogen from dilute acids are placed above of it.**

Topic- 3 Concept of Electrochemistry

- **Applications of Electro-Chemical Series**
- **1) Higher of reduction potential, higher tendency to reduced. So relatively oxidizing and reducing ability of elements compared easily.**
- **2) Displacement reactions can be predicted.**
- **3) It helps the selection of electrode assemblies to construct the galvanic cell of desired EMF.**
- **4) The polarity of electrode system and electrode reaction can be easily predicted.**
- **5) Spontaneity and feasibility of the cell under construction can be easily predicted.**

Topic- 3 Concept of Electrochemistry

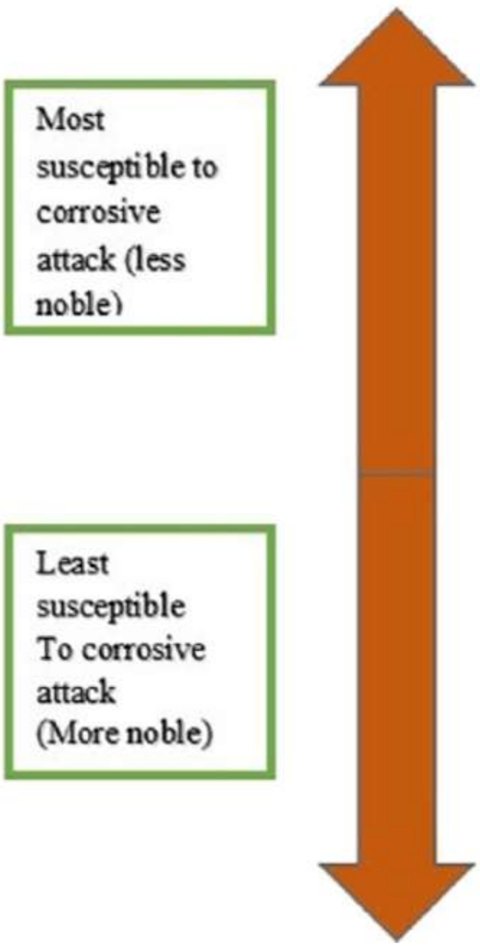
- **Electro-Chemical Series**

Element	Electrode potential
Li(lithium)	-3.050
K(potassium)	-2.925
Ca(calcium)	-2.870
Na(Sodium)	-2.714
Mg (magnesium)	-2.370
Al(aluminum)	-1.660
Zn(zinc)	-0.763
Fe(iron)	-0.440
Cd(cadmium)	-0.40
Ni(nickel)	-0.25
Sn(tin)	-0.136
Pb(lead)	-0.126
H_2(hydrogen)	0.0
Cu(copper)	+0.153
Hg(mercury)	+0.771
Ag(silver)	+0.789
Pt (platinum)	+1.188
Au(gold)	+1.520

Topic- 3 Concept of Electrochemistry

- **Galvanic Series**

Corrosion Susceptibility of metals



Magnesium and its alloys
Zinc and its alloys
Aluminum and its alloys
Cadmium
Mild Steel
Cast Iron
Stainless steel 13% Cr, type 410 (active)
Lead-tin solder, 50/50
Stainless steel, 18/18 type 304 (active)
Stainless steel, 18/18/3 Mo, type 316 (active)
Lead
Tin
Brasses
Aluminum bronzes
Copper
Copper-nickel alloys
Monel
Titanium and its alloys
Stainless steel, 18/18 type 304 (passive)
Stainless steel, 18/18/3 Mo, type 316 (passive)
Silver
Gold
Platinum

Topic- 3 Concept of Electrochemistry

- **Nernst Equation**

Consider an electrode assembly undergoing a spontaneous reaction.

$$M^{n+} + ne^- \leftrightarrow M$$

The equilibrium constant (K) for this system in equilibrium can be evaluated as

$$K = \frac{[M]}{[M^{n+}]}$$

Some amount of electrical work is done and is maximum at equilibrium referred to as W_{max}.

W_{max} = (Number of Coulombs of charge flowing across the HED) × (Energy available per Coulombs of charge)

$$W_{max} = nEF$$

As the reaction is spontaneous, there is decrease in the free energy. Also the decrease in free energy appears as work done (W_{max}).

Therefore,

$$-\Delta G = W_{max} = nEF$$

Under standard conditions, $-\Delta G^0 = nE^0F$

The decrease in free energy change for the above mentioned reaction can be expressed as,

$$\Delta G = \Delta G^0 + 2.303\ RT\ \log_{10} \frac{[M]}{[M^{n+}]}$$

Substituting the values of ΔG and ΔG^0,

$$-nEF = -nE^0F + 2.303\ RT\ \log_{10} \frac{[M]}{[M^{n+}]}$$

Dividing by $-nF$ we get,

$$E = E^0 - \frac{2.303RT}{nF} \log_{10} \frac{[M]}{[M^{n+}]}$$

For a Galvanic cell the EMF is given as,

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF} \log_{10}K$$

Where, K is the equilibrium constant for the reaction.

Topic- 3 Concept of Electrochemistry

- **Numericals on Nernst Equation;**

1) Calculate the electrode potential of copper, if the concentration of $CuSO_4$ is 0.206 M at 23.1^{0}C. Given that $E^0_{Cu^{++}/Cu} = +0.34V$.

- **Solution;**
- **CuSO4 = 0.206; T = 23.1^{0}C = 23.1 + 273 = 296.1^{0}K.**
- **Reaction taking place – $Cu^{++} + 2e^- \leftrightarrow Cu$; n = 2**

- **Nernst equation ;** $E_{Cu^{++}/Cu} = E^0_{Cu^{++}/Cu} - \frac{2.303RT}{nF} \log_{10} \frac{1}{[Cu^{++}]}$

- $$E_{Cu^{++}/Cu} = 0.34 - \frac{2.303x8.314x296.1}{2x96500} \log_{10} \frac{1}{0.206}$$

$$\boxed{E_{Cu^{++}/Cu} = 0.31984V}$$

Example 2:

- **Determine the emf of a Daniel cell at 25^0C , when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001M and 0.1 M respectively . The standard emf of the cell is 1.1 volt**
- Given : E_0 = 1.1 Volts , C_1 = 0.001, C_2 = 0.1
- The emf of the cell is given by

$$E_{cell} = E_0 + \frac{0.0591}{n} \log \frac{c_2}{c_1}$$

$$= 1.1 + \frac{0.0591}{2} \log \frac{0.1}{0.001}$$

= 1.1591 Volts

Example 3 :

- **Determine the emf of a concentration cell at 25^0 C consists of two Zn electrodes immersed in a solution of zinc ions of 0.1M and 0.01M concentration.**

Solution :

Given : n = 2 $C_1 = 0.01$ $C_2 = 0.1$

The reaction is

$$Zn^{2+} + 2e^{-} \rightarrow Zn$$

The emf of the cell is given by

$$E_{cell} = \frac{0.0591}{n} \log \frac{c_2}{c_1}$$

$$E_{cell} = \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

$$= 0.0296 \text{ Volts}$$

Example 4 :

- **Determine the reduction potential of Cu/Cu^{2+} is 0.5M at 25^0 C $E^0_{Cu/Cu^{2+}}$ = 0.337 V ..**

Solution :

E^0 = 0.337 Volts , $[Cu^{2+}]$ = 0.5

The reduction potential is given by

$$E = \frac{0.0591}{n} \log [Cu^{2+}]$$

$$E = \frac{0.0591}{n} \log [Cu^{2+}]$$

$$= 0.328 \text{ Volts}$$

Example 5 :

- **Determine the emf of the following cell**
- **$Zn \mid Zn^{2+} \parallel Ag^{+} \mid Ag$, $[Zn^{2+}] = 0.1$ M , $[Ag^{+}] = 0.1$M ,**
- **$E^0_{Ag} = +0.8$Volts , $E^0_{Zn} = -0.76$ Volts**

Solution :

Given :

$[Zn^{2+}] = 0.1$ M , $[Ag^{+}] = 0.1$M ,

$E^0_{Ag} = +0.8$Volts , $E^0_{Zn} = -0.76$ Volts

The emf of the cell is given by

$$E_{cell} = E_{cathode} - E_{anode}$$

$$(E_{Ag^{+}/Ag}) \qquad (E_{Zn^{2+}/Zn})$$

$$= E^0_{Ag} + \frac{0.0591}{1}\log 0.1 - E^0_{Zn} - \frac{0.0591}{2}\log 0.1$$

$$= (0.8 - (0.76)) - 0.02955$$

$$= 1.53045 \text{ Volts}$$

Example 6 :

- **Determine the emf of the cell at 25^0C concentration of $ZnSO_4$ and $CuSO_4$ are 0.01 M and 0.1 M respectively . The standard e.m.f of the cell is 1.1 volts .**
- **Solution:**

Given :

$[ZnSO_4]$ = 0.01 M , $[CuSO_4]$ = 0.1 M ,

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$$

$$= E^0_{Cu^{2+}/Cu} + \frac{0.0591}{2}\log 0.1 - E^0_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log 0.01$$

$$= E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn} + \frac{0.0591}{2}\log\frac{0.1}{0.01}$$

Example 6 :

- (We have $E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn} = 1.1$ volts)

$$\therefore E_{cell} = 1.1 + \frac{0.0591}{2}\log\frac{0.1}{0.01}$$

$= 1.129$ Volts

Example 7 :

Determine the emf of a concentration cell consisting of silver electrodes immersed in 0.01M and 0.1 M solutions of it's ions at 25^0 C .

Solution :

For the concentration cell with silver electrode ,

The electrical reaction involved is $Ag \rightarrow Ag^+ + e$

$n = 1$, $C_2 = 0.1$ M and $C_1 = 0.01$M

The emf of the cell is given by

$$E_{cell} = \frac{0.0591}{n} \log \frac{c_2}{c_1}$$

$$= \frac{0.0591}{1} \log \frac{0.1}{0.01}$$

$= 0.0591$ Volts

Example 8

- **The standard electrode potentials of lead and silver are**
- **–0.18V and + 0.8V respectively . Determine the emf .**
- **Solution :**

$$E^0_{Pb^{2+}/pb} = -0.18 \text{ V}$$

$$E^0_{Ag^{+}/Ag} = +0.8 \text{ V}$$

$$E_{cell} = E^0_{cathode} - E^0_{anode}$$

$$= +0.8 - (-0.18)$$

$$= 0.98 \text{ Volts}$$

Example 9

- **The standard electrode potentials of lead and silver are**
- **–0.18V and + 0.8V respectively . Determine the emf .**
- **Solution :**

$$E^0_{Pb^{2+}/pb} = -0.18\ V$$

$$E^0_{Ag^{+}/Ag} = +0.8\ V$$

$$E_{cell} = E^0_{cathode} - E^0_{anode}$$

$$= +0.8 - (-0.18)$$

$$= 0.98\ \text{Volts}$$

Example 10

- **The standard electrode potentials of lead and silver are**
- **–0.18V and + 0.8V respectively . Determine the emf .**
- **Solution :Determine the concentration of H^+ in the following cell .**
- **Pt, H_2 (P= 1 atm)│ H^+ (C = 10^{-6} M) ││ H^+ (C= ?)│**
- **H_2 (P = 1atm) Pt , E_{cell} = 0.118V at 25^0C**

The emf of the cell is given by

$$E_{cell} = \frac{0.0591}{n} \log \frac{c_2}{c_1}$$

$$0.118 = \frac{0.0591}{1} \log \frac{c_2}{10^{-6}}$$

$$\frac{0.118}{0.0591} = \log c_2 - \log 10^{-6}$$

$$C_2 = 1 \times 10^{-4} \text{ M}$$

Example 11

Find the potential of the cell in which the following reactions take place at 25^0C .

$$Zn(S) + Cu^{2+} (0.02\ M) \rightarrow Cu(S) + Zn^{2+} (0.4M)$$

- **Solution :**
- Given : $E^0 (Zn^{2+}/Zn) = -0.76\ V$
- $E^0 (Cu^{2+}/Cu) = 0.34\ V$
- $E^0_{cell} = E^0 (Cu^{2+}/Cu) - E^0 (Zn^{2+}/Zn)$
- $= 0.34 - (-0.76) = 1.10$ Volts
- According to Nernst equation

$$E_{cell} = E^0_{cell} - \underline{2.303\ RT} \quad \log \quad Zn^{2+}_{(products)}$$

- $= 1.1 - 2.303 \times 8.314 \times 298 \times \log (0.4/0.02)$
- $= 1.06$ Volts .