ENGINEERING CHEMISTRY
COURSE CODE: 18CY1BSCHY/ 18CY2BSCHY

UNIT-2: Electrochemistry - Corrosion

Electrochemistry and Corrosion

Electrodes and cells – Introduction, classification of cells-primary, secondary and concentration cells, reference electrodes–calomel electrode and Ag/AgCl electrode, ion-selective electrode - glass electrode, determination of pH using glass electrode, determination of pKa of weak acids, numerical problems on concentration cells and pH determination.

Corrosion – Definition of chemical corrosion, electrochemical theory of corrosion, types of corrosion - differential metal, differential aeration (pitting and water line corrosion) and stress corrosion, factors affecting the rate of corrosion, corrosion control: inorganic coatings – anodizing and phosphating, metal coatings - galvanization, tinning and electroplating of
chromium, cathodic protection.

ELECTROCHEMISTRY

Introduction

"It is a branch of chemistry that deals with the inter conversion of chemical and electrical energies."

- The application of electrochemistry is found in many areas including chemistry, physics, engineering, biology, electronics, computers, metallurgy and material science.
- Electroplating (Metal finishing), extraction of metals (like Na, Al, Mg, etc), refining of metals (like Cu, Al, Au, etc), electronic and medical devices working on portable energy, batteries work on the principle of electrochemistry.

Electrochemical cells: The device which converts chemical energy to electrical energy or vice versa.

Electrode: An electrode is an electrical conductor used to make contact with a non-metallic part of circuit.

Anode: It is the electrode at which oxidation occurs.

Cathode: It is the electrode at which reduction occurs.

Redox reaction: A chemical reaction in which both oxidation and reduction reaction occur simultaneously.

Additional Info:

Conductors

Metallic Conductors	Electrolytic Conductors
– Allow electricity to pass through them Without undergoing chemical change	- pass electricity through them in their molten/aqueous solution
– Due to flow of electrons	- due to charged particles (ions)

Electrode Potential (E):

The potential developed at the interface between the metal and the solution when it is in contact with a solution is called electrode potential.

- When a metal is immersed in a solution of its own ions, two types of process take place.
- Metal may undergo oxidation, goes in to solution as ions losing electrons.

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

- Metal ions in the solution may undergo reduction and get deposited as metal atoms on the metal surface (electrode surface).

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

- When a metal undergoes oxidation, it loses positive ions in to solution leaving behind a layer of negative charges on its surface. This layer attracts positive charges and form electrical double layer, also called as Helmholtz electrical double layer.

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

- The resultant potential difference between the electrode (metal) and the solution is termed as electrode potential.

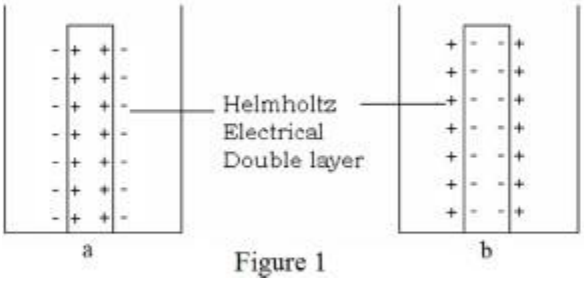


Figure 1

Standard electrode potential: The potential developed at the interface between the metal and the solution when it is in contact with a solution of unit concentration at 298 K at 1 atm pressure is called standard electrode potential.

Galvanic Cell: (For understanding: Not in the syllabus)

- Galvanic cell is an electrochemical cell which converts chemical energy in to electrical energy.
- It consists of two electrodes dipped in two electrolytic solutions.
- The two solutions are separated by a porous diaphragm called as salt bridge.
- Example for galvanic cell is Daniell cell. In the Daniel cell, zinc rod is dipped in zinc sulphate ($ZnSO_4$) solution and copper rod is dipped in copper sulphate ($CuSO_4$) solution. The two solutions are separated by salt bridge.
- The two metal rods are then connected externally through ammeter/voltameter by using wire, the following reactions are observed:
- At anode, Zinc undergoes oxidation as follows:

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

(Zn^{2+} ions go in to the solution and electron flow towards Cu rod)

- At cathode, Copper undergoes reduction as follows:

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

(Cu^{2+} ions present in the solution combine with the electrons forming Cu atoms, which are then deposited on electrode)

- The net chemical change taking place is,

$$\begin{array}{rcll} Zn & \longrightarrow & Zn^{2+} + 2e^- & \text{(oxidation)} \\ Cu^{2+} + 2e^- & \longrightarrow & Cu & \text{(reduction)} \\ \hline Zn + Cu^{2+} & \longrightarrow & Zn^{2+} + Cu & \text{Cell reaction} \\ \hline \end{array}$$

- This is a redox reaction where Zn undergoes oxidation and Cu undergoes reduction simultaneously.

Emf or Cell potential (E_{cell}):

The potential difference between the two electrodes of a galvanic cell which causes the flow of electrons (current) from one electrode to the other is called electromotive force (EMF).

- EMF of cell is also called as Cell potential.
- The emf of a cell is denoted by E_{cell}.
- E_{cell} depends on the nature of electrode, temperature and concentration of the electrolyte solution.
- **Standard emf** of a cell is defined as *"the emf of a galvanic cell when the reactants and products of the cell reaction are at unit concentration at 298 K and at 1 atm pressure"*. It represented as E^o_{cell}

$$E^o_{cell} = E_{right} - E_{left}$$

$$\boxed{E^o_{cell} = E^o_{cathode} - E^o_{anode}}$$

NOTE:

1. Electrode potential is the potential difference at the interface of metal (electrode) and solution.
2. Cell potential (Emf) is the potential difference between two electrodes.

Cell representation:

The electrochemical cell is represented as follows:

- Anode (negative electrode, where oxidation occurs) is written on the left
- Anode is represented by writing metal first and then metal ion, both are separated by vertical line [M_1/M_1^{n+}]
- Cathode (electrode where reduction occurs) is written on right hand side
- Cathode is represented by writing metal ion first and then metal, both are separated by vertical line [M_2^{n+}/M_2]
- Two half cells are separated by double vertical line, which represents salt bridge

$$M_1/M_1^{n+}// M_2^{n+}/M_2$$

- Concentration and state [solid (s), gas (g), etc] of chemical species are expressed within the brackets

Example: Cell reaction –

$$\mathrm{Fe_{(s)} + 2Ag^{+}_{(aq)} \rightleftharpoons Fe^{2+}_{(aq)} + 2Ag_{(s)}}$$

$$\text{At anode (oxidation): } \mathrm{Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2e^{-}}$$

$$\text{At cathode (reduction):} \mathrm{2Ag^{+}_{(aq)} + 2e^{-} \rightleftharpoons 2Ag_{(s)}}$$

The cell can be represented as,

$$\mathrm{Fe_{(s)}/Fe_{(aq)}{}^{2+}//\ Ag_{(aq)}{}^{+}/Ag_{(s)}}$$

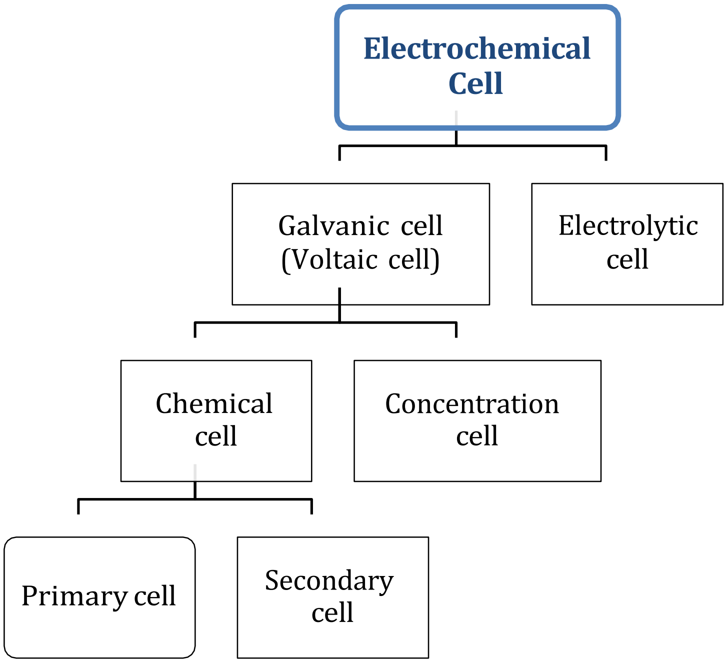
EMF of this cell can be determined by,

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

$$= E_{Ag+/Ag} - E_{Fe/Fe2+}$$

NOTE: The potential of individual half cell cannot be measured but only the difference between the two half cell potentials can be measured which is the emf of the cell.

Types of Electrochemical cells:



1. Electrolytic cell: These are the electrochemical cells which are used to convert electrical energy to chemical energy.

Eg: Electroplating, electrorefining

2. Galvanic cell:

- Also called as voltaic cell
- Convert chemical energy in to electrical energy

Galvanic cell is further divided in to two types:

I. Primary cells:

- These are the cells which serve as energy source only as long as the active species are present in the cell.
- The cell reactions are irreversible.
- These are designed for single use; once discharged cannot be charged again.
- Eg: Dry cell, Zn-HgO cell, Zn-Ag_2O cell, etc.

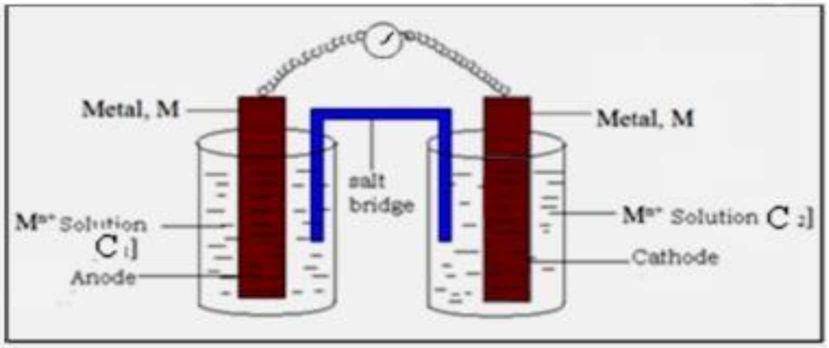
II. Secondary cells:

- These are the electrochemical cells which can be charged and used.
- The cell reactions are reversible and hence called as reversible cells.
- During discharging, these cells act as voltaic cells by converting chemical energy in to electrical energy.
- During charging, these cells act as electrolytic cell by converting electrical energy in to chemical energy.
- Eg: Ni-MH cell (Nickel-metal hydride cell), Lithium-ion cells

Concentration Cell:

It is a type of galvanic cell in which electrode and electrolyte present in both half cells are same but only the concentration of metal (electrode) or electrolyte is different.

- A concentration cell is made up of two half cells having identical electrodes except that the concentration of ions at the electrodes are different.
- The half-cell may be joined by salt bridge.
- There is no net cell reaction in concentration cell.
- In galvanic cell, emf arises due to the change in the free energy of the chemical reaction taking place in the cell. But in concentration cell, emf arises due to the change in the concentration of either electrolytes or electrodes.
- Eg: Copper concentration cell, Zinc concentration cell, etc.



"The electrode which is dipped in less concentrated solution (C_1) act as anode with lower potential and undergoes oxidation. The electrode which is dipped in higher concentration (C_2) acts as cathode with higher potential and undergoes reduction".

Concentration cell is represented as,

$$M/M^{n+}{}_{(C1)}//M^{n+}{}_{(C2)}/M$$

$$\text{At anode (oxidation): } M \longrightarrow M^{n+}{}_{(C1)} + ne^-$$

$$\text{At cathode (reduction): } M^{n+}{}_{(C2)} + ne^- \longrightarrow M$$

$$\text{Overall reaction: } M^{n+}{}_{(C2)} \longrightarrow M^{n+}{}_{(C1)}$$

Because both the half-cells are made of same electrode, E^o_{cell} (standard emf) for concentration cell is zero. Nernst equation for electrolyte concentration cell is,

$$Ecell = E^0_{cell} + \frac{2.303RT}{nF} \log \frac{[M^{n+} \text{ at cathode}]}{[M^{n+} \text{ at anode}]}$$

But, $E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0$

Therefore,

$$Ecell = 0 + \frac{2.303RT}{nF} \log \frac{[M^{n+} \text{ at cathode}]}{[M^{n+} \text{ at anode}]}$$

$$\boxed{Ecell = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}}$$

OR

$$\boxed{Ecell = \frac{0.0591}{n} \log \frac{[\text{cathode}]}{[\text{anode}]}} \qquad \text{at 298K}$$

Types of electrodes:

1. Metal-Metal ion electrode

- These electrodes consist of a metal dipped in a solution of its own ions.
- Eg: Zn/Zn^{2+}, Zinc rod dipped in zinc sulphate solution.
  Cu/Cu^{2+}, Copper rod dipped in copper sulphate solution.
- These electrodes are reversible with respect to cations.

2. Metal-insoluble salt electrode

- Also called as metal-metal salt ion electrode.

- In this electrode, a metal is in contact with its insoluble salt, which is dipped in a solution of soluble salt having an ion common with insoluble salt.
- Potential arises due to oxidation of metal to its insoluble salt or reduction of insoluble salt of metal.
- These electrodes are used as secondary reference electrode.
- Eg: a) Calomel electrode: $Hg/Hg_2Cl_2/Cl^-$

  b) Silver-silver chloride electrode: $Ag/AgCl/ Cl^-$

  c) Lead-lead sulphate electrode: $Pb/PbSO_4/SO_4^{2-}$

3. Gas electrode

- In these electrodes, gas (H_2 or O_2 or Cl_2) is continuously bubbled through a solution of its corresponding ions (OH^- or H^+ or Cl^-) using an inert metal like Pt or Au.
- Metal provides an electrical contact
- Eg: a) H_2 electrode: $Pt/H_2/H^+$

  b) Chlorine electrode: $Pt/Cl_2/Cl^-$

4. Oxidation-Reduction electrode (Redox electrode)

- It is an electrode in which the electrode potential arises due to the presence of oxidized and reduced forms of the same substance in solution.
- Eg: a) $Pt/Fe^{2+}, Fe^{3+}$

  b) $Pt/Ce^{3+}, Ce^{4+}$

  c) $Pt/Sn^{2+}, Sn^{4+}$
- Potential arises from the tendency of an ion to change its oxidation state to more stable one.
- Potential developed is picked up by an inert electrode like platinum.

{Extra Info: The electrolyte solution contains ions of both forms (Fe^{2+} and Fe^{3+}). Fe^{3+} is more stable than Fe^{2+}. Hence, Fe^{2+} tends to convert to Fe^{3+} in the solution. This change leads to develop potential at the electrode}

5. Amalgam electrode

- Amalgam is the alloy of mercury (Hg).
- Amalgam electrodes are the electrodes in which metal-amalgam (like Pg-Hg) is in contact with a solution containing its own metal ions.
- Eg: Lead amalgam electrode (Pg-Hg/Pb^{2+})
  Zinc amalgam electrode (Zn-Hg/Zn^{2+})

6 Ion-selective electrodes (Membrane electrode)

This is a type of electrode in which membrane is in contact with a solution with which it can exchange specific ions.
Eg: Glass pH electrode (selective towards H^+ ions)

REFERENCE ELECTRODE

Definition: Reference electrodes are the electrodes with reference to those the electrode potential of any other electrode can be measured.

Criteria for an electrode to act as reference electrode:

i. Its electrode potential should be known under the conditions of utility.

ii. The potential of such electrode should show minimum variation with respect to temperature.

Types of reference electrode:

I. Primary reference electrode

- Standard hydrogen electrode (SHE) is the only primary reference electrode (gas electrode).
- Represented as $Pt/H_{2(g)(1\ atm)}/HCl_{(1M)}$
- The potential of SHE is taken as zero by convention. Therefore, potential values of all other electrodes are expressed w.r.t. this electrode.

Limitations of SHE:

a) Construction and maintenance is difficult since it's a gas electrode.

b) Pt metal used in the electrode is easily poisoned by any impurity present in the system.

c) Cannot be used in the presence of oxidizing agents like nitrates, H_2S, chlorides, etc. as they poison Pt.

d) Difficulty in maintaining pressure at 1 atm.

<u>II. Secondary reference electrode</u>

<u>Definition:</u> These are the electrodes whose potential is measured w.r.t. SHE and then can be used as reference electrode for measuring potentials of other electrodes.

Eg: Calomel electrode, silver-silver chloride electrode

Advantages:

a) Easy to set up and operate.

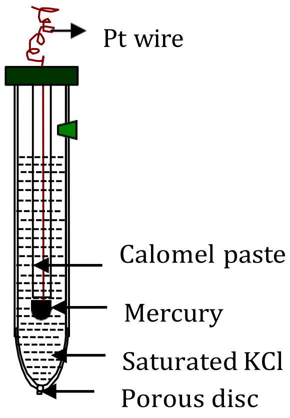
b) Potential values do not vary much with variation in temperature.

c) Not poisoned by oxidizing impurities.

<u>Construction and Working of Calomel Electrode</u>

- Calomel electrode is a secondary reference electrode.
- It belongs to the category of Metal-insoluble salt electrode.
- It is also called as Mercury (Hg)-Mercurous chloride (Hg_2Cl_2).

<u>Construction:</u>



- It consists of a glass tube in which pure mercury (Hg) is placed at the bottom.

- It is covered by a paste of Hg and mercurous chloride (Hg_2Cl_2) which is further in contact with KCl solution.
- Hg_2Cl_2 is commonly called as calomel and it is sparingly soluble in water.
- A platinum wire is dipped in the mercury layer, which is used to make electrical contact with other electrode and to measure potential at the electrode.
- KCl solution used in calomel electrode is of known concentration.
- Electrode potential of the cell depends upon the concentration of KCl used.

Cell representation: Pt, $Hg_{(l)}$, $Hg_2Cl_{2(s)}/Cl^-$ **OR** $Hg_{(l)}$, $Hg_2Cl_{2(s)}/KCl$

Working: Calomel electrode can be used as cathode or anode depending upon the nature of the other electrode of the cell.

The reversible reactions are:

$$\begin{array}{lcl} Hg_2^{2+} + 2e^- & \rightleftharpoons & 2Hg \\ Hg_2Cl_2 & \rightleftharpoons & Hg_2^{2+} + 2Cl^- \\ \hline Hg_2Cl_2 + 2e^- & \rightleftharpoons & 2Hg + 2Cl^- \\ \hline \end{array}$$

- The electrode reactions are reversible w.r.t. Cl^- ions. In other words the potential of calomel electrode depends on the concentration of chloride ions.
- Nernst equation for calomel electrode is given as:

$$E_{calomel} = E^0_{calomel} - \frac{2.303RT}{nF} \log [Cl^-]^2$$

At 298K and n=2, it can be simplified to

$$E = E^0 - 0.0591 \log [Cl^-]$$

Potential value of calomel electrode decreases with increase in KCl concentration

0.1 N KCl	E = 0.33 V
1 N KCl	E = 0.28 V
Saturated KCl	E = 0.24 V

Advantages of Calomel electrode are:

a) Simple to construct
b) Stable
c) Electrode potential value is reproducible

Applications:

a) It is used as secondary reference electrode in the measurement of single electrode potential.
b) It is the most commonly used reference electrode in all potentiometric determinations.

ION SELECTIVE ELECTRODE (ISE)

- These are the electrodes which selectively respond to specific ion in a mixture, while ignoring other ions.
- ISEs are membrane based electrodes and hence are also called as membrane electrodes.
- These electrodes are used to measure the concentration of a particular cation or anion in a mixture.
- The potential developed at the electrode is a function of the concentration of specific ion in the solution.
- The membrane in the electrode is capable of exchanging specific ions with the solution with which it is in contact.
- ISEs are highly sensitive, selective and suitable for rapid, low cost and accurate analysis.

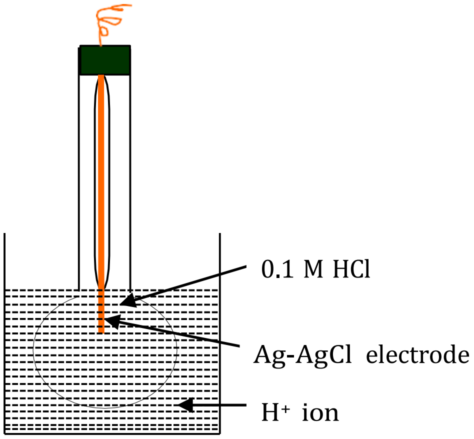
Applications:

a) Determination of hardness of water
b) Determination of calcium concentration in milk
c) Nitrate monitoring in waste water
d) Estimation of salinity in sea water
e) Determination of H^+ ion concentration

Glass pH Electrode

- Glass electrode or pH electrode is the electrode which is selective towards H^+ ions in the solution containing a mixture of ions.
- It is used in the measurement of concentration of H^+ ions (pH) in the solution.
- When two solutions of different pH values are separated by a thin glass membrane, there develops a potential difference between the two surfaces of the membrane.

Construction:



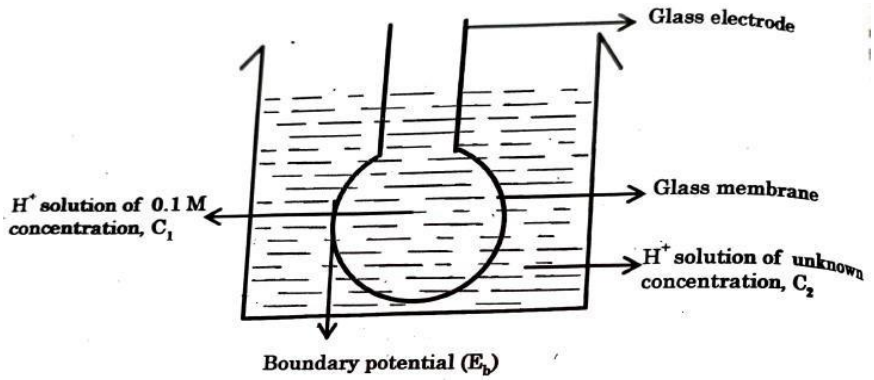
Glass electrode

- Glass electrode is a long glass tube with a glass membrane bulb at the bottom.
- Glass membrane is made up of silicate with composition: SiO_2 (72%), Na_2O (22%) and CaO (6%).
- The thickness of glass membrane varies from 0.03-0.1 mm.
- Ag/AgCl electrode is immersed in 0.1 M HCl, is used as internal reference electrode to measure the boundary potential.
- The metal is also used for making electrical contact with other electrodes.

Cell representation:

$$Ag_{(s)}/AgCl_{(s)}/HCl_{(0.1M)}/\text{glass membrane}$$

Working:



- The boundary potential ($E_b = E_2 - E_1$) arises due to the difference in concentration of H^+ ions inside and outside the glass bulb.
- Boundary potential is given by the equation:

$$E_b = E_2 - E_1 = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

where C_1 and C_2 are the concentration of inner and outer acid solutions.

Potential of glass electrode (E_G) is sum of three potentials

1) Boundary potential (E_b)
2) Potential of Ag/AgCl electrode ($E_{Ag/AgCl}$)
3) Asymmetry potential (E_{asym})

[Asymmetry potential is a small potential that exist due to the unevenness in the membrane and strain on the surface of the membrane]

Electrode potential of glass electrode is given as,

$E_G = E_b + E_{Ag/AgCl} + E_{asym}$

Applying the value of E_b in the above equation,

$$E_G = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]} + E_{Ag/AgCl} + E_{Asym}$$

$$E_G = \frac{0.0591}{n} \log [C_2] + \frac{0.0591}{n} \log \frac{1}{[C_1]} + E_{Ag/AgCl} + E_{Asym}$$

$$E_G = \frac{0.0591}{n}\log[C_2] + E_G^0$$

Where, $E_G^0 = \frac{0.0591}{n}\log\frac{1}{[C_1]} + E_{Ag/AgCl} + E_{Asym}$ and n=1

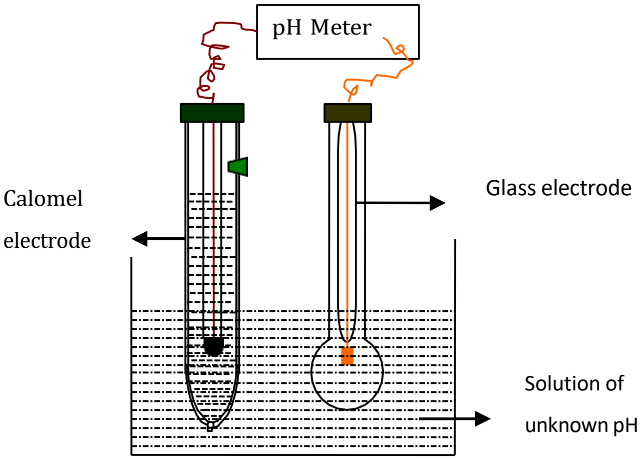
$$E_G = 0.0591\log[H^+] + E_G^0$$

We know that pH = -log [H⁺], Substituting this in the above equation

$$\boxed{E_G = E_G^0 - 0.0591\,pH}$$

Determination of pH of a solution using Glass electrode

- The pH of any given solution is measured by a galvanic cell, constructed by combining glass electrode with standard saturated calomel electrode as reference electrode.



EMF of the above cell i.e. E_{cell} when immersed in a solution of unknown pH is,

$E_{Cell} = E_{Cathode} - E_{Anode}$

$E_{Cell} = E_G - E_{SCE}$

Where E_G = potential of glass electrode

E_{SCE} = potential of saturated calomel electrode

$E_{Cell} = E^{o}_{G} - 0.0591\ pH - E_{SCE}$

Rearranging the equation for pH,

$$\boxed{pH = \frac{E^{0}_{G} - E_{SCE} - E_{cell}}{0.0591}}\quad at\ 298K$$

E_{G}° is determined by constructing a similar cell with solution of known pH.

<u>Advantages of Glass electrode:</u>

1. This electrode can be used to determine p^{H} in the range 0-9, with special type of glass even up to 12 can be calculated.
2. It can be used even in the case of strong oxidizing agents and biological fluids.
3. The equilibrium is reached quickly.
4. It is simple to operate, gives accurate values of pH.

<u>Limitations of Glass electrode:</u>

1. The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used; hence it is necessary to use electronic potentiometers.
2. This electrode cannot be used to determine the pH above 9 accuratelydue to alkaline error.
3. This cannot be used in case of fluoride ions.

Numerical problems on concentration cells

1. A galvanic cell is obtained by combining two Zn electrodes immersed in zinc sulphate solutions of concentrations 0.05 and 0.25 M at 30 °C. Give the cell representation, cell reaction and calculate the EMF of the cell.

Solution: Both electrodes in the cell are made of same metal immersed in same electrolyte solution but of different concentrations. Hence it is an electrolyte concentration cell. Cell representation is

$$Zn/ZnSO_{4\ (0.05M)}/ZnSO_{4\ (0.25M)}/Zn$$

Cell reaction:

$$\begin{array}{ll} \text{At anode:} & Zn \longrightarrow Zn^{2+} + 2e^- \\ \text{At cathode:} & Zn^{+2}_{(0.25)} + 2e^- \longrightarrow Zn \\ \hline \text{Cell reaction:} & Zn^{+2}_{(0.25)} \longrightarrow Zn^{2+}_{(0.05)} \\ \hline \end{array}$$

EMF of the cell:

$$Ecell = \frac{2.303RT}{nF} \log \frac{[\mathrm{M}^{n+} \text{ at cathode}]}{[\mathrm{M}^{n+} \text{ at anode}]}$$

$$= \frac{2.303 \ X \ 8.314 \ X \ 303}{2 \ X \ 96500} \log \frac{[0.25]}{[0.05]}$$

$$\boldsymbol{Ecell = 0.02 \ V}$$

2. EMF of the cell $Cu/CuSO_{4\ (0.01)}//CuSO_{4\ (X)}/Cu$ at 300 K is 0.015 V. Find the concentration of copper sulphate at cathode.

Solution: EMF of a concentration cell is given by

$$Ecell = \frac{2.303RT}{nF} \log \frac{[\mathrm{M}^{n+} \text{ at cathode}]}{[\mathrm{M}^{n+} \text{ at anode}]}$$

$$Ecell = \frac{2.303RT}{nF} \log \frac{[\mathrm{Cu}^{2+} \text{ at cathode}]}{[\mathrm{Cu}^{2+} \text{ at anode}]}$$

$$[\text{Cu}^{2+}\text{ at cathode}] = [\text{Cu}^{2+}\text{ at anode}] \text{ x Antilog } \frac{\text{E}_{\text{cell}} \text{ x n x F}}{2.303 \text{ x R x T}}$$

$$[\text{Cu}^{2+}\text{ at cathode}] = 0.01 \text{ x Antilog } \frac{0.015 \text{ x } 2 \text{ x } 96500}{2.303 \text{ x } 8.314 \text{ x } 300}$$

$$[\mathbf{Cu^{2+}\ at\ cathode}] = \mathbf{0.0319}\ \boldsymbol{M}$$

3. EMF of the cell $Cd/CdSO_{4\ (X)}//CdSO_{4\ (0.02M)}/Cd$ at 29 °C is 0.025 V. Find the concentration of cadmium sulphate at anode.

Solution: EMF of a concentration cell is given by

$$Ecell = \frac{2.303RT}{nF} \log \frac{[\text{M}^{n+}\text{ at cathode}]}{[\text{M}^{n+}\text{ at anode}]}$$

$$Ecell = \frac{2.303RT}{nF} \log \frac{[\text{Cd}^{2+}\text{ at cathode}]}{[\text{Cd}^{2+}\text{ at anode}]}$$

$$[\text{Cd}^{2+}\text{ at anode}] = [\text{Cd}^{2+}\text{ at cathode}] \text{ x Antilog } \frac{2.303 \text{ x R x T}}{\text{E}_{\text{cell}} \text{ x n x F}}$$

$$[\text{Cd}^{2+}\text{ at anode}] = 0.02 \text{ x Antilog } \frac{2.303 \text{ x } 8.314 \text{ x } 302}{0.03 \text{ x } 2 \text{ x } 96500}$$

$$[\mathbf{Cd^{2+}\ at\ anode}] = \mathbf{0.29}\ \boldsymbol{M}$$

4. In a spontaneous galvanic cell, $M/M^{n+}_{(0.03\ N)}$ // $M^{n+}_{(0.064\ N)}/M$ develops an EMF of 0.013V at 25 °C. Calculate the valency of metal.

Solution: EMF of a concentration cell is given by

$$Ecell = \frac{0.0591}{n} \log \frac{[\text{cathode}]}{[\text{anode}]}$$

$$0.013 = \frac{0.0591}{n} \log \frac{[0.064]}{[0.03]}$$

$$n = \frac{0.0591}{0.013} \log \frac{[0.064]}{[0.03]}$$

$$\boldsymbol{n = 1.5}$$

Problems from previous year question papers

1. Find the value of X in the concentration cell Cd/CdSO$_4$ $_{(0.0093M)}$// CdSO$_4$ $_{(XM)}$/Cd, EMF = 0.086V at 25 ^{o}C and write the cell reactions.

References

1. Basuchandra's Engineering Chemistry
2. Engineering Chemistry by Jain & Jain
3. Engineering Chemistry: Fundamentals and Applications by Shikha Agarwal