SNS COLLEGE OF TECHNOLOGY

(AnAutonomousInstitution)

23CHT101-Engineering Chemistry

Unit- I Electrochemistry

Empathy:

- How might understanding electrode potential impact our ability to design more efficient batteries or fuel cells?
- What challenges could arise when trying to measure electrode potential in real-world applications?
- What is a Conductor?
- What are the different types of Conductors?
- Is it possible to carry AC current to everywhere?

Introduction to Electrochemistry:

Electrochemistry is a branch of chemistry deals with the chemical applications of electricity. It deals with the chemical reaction produced by passing electric current through an electrolyte or the production of electric current through chemical reactions.

Important Terms Involved in Electrochemistry:

1. CURRENT:
It is the flow of electrons through a conductor.

2. CONDUCTORS:

A substance that allows electric current to pass through it called a conductor.

The ability of a material to conduct electric current is called conductors.

Eg: All metals, graphite, aqueous solution of acids, bases etc..,

3. NON CONDUCTORS:

Materials which do not conduct electric current are called non-conductors.

Eg: Plastics, wood etc..,

TYPES OF CONDUCTORS
1.Metallic conductor 2.Electrolytic conductor

Metallic conductors:

Metallic conductors are solid substance which conducts electric current due to the movement of electrons from one end to another.

Eg: All metals, graphite.

Electrolytic conductors:

Electrolytic conductors conduct electric current due to the movement of ions in solution or in fused state .The conduction increases with increase of temperature.

Eg: Acids, bases, salts, etc..,

DIFFERCENCE BETWEEN METALLIC AND ELECTROLYTIC CONDUCTION

METALLIC CONDUCTION	ELECROLYTIC CONDUCTION
It involves the flow of electrons in a conductor.	It involves the movement of ions in a solution
Conduction decreases with increase in temperature.	Conduction increases with increase in temperature.
It does not involve any transfer of matter.	It involves the transfer of electrolyte in the form of ions
No change in the chemical properties of the conductor.	Chemical reactions occurs at the two electrodes

TYPES OF ELECTROLYTIC CONDUCTORS:

The electrolytic conductors are further classified into three types

a. Strong electrolytes:

Strong electrolytes are substance which ionise completely almost at all dilutions.

Eg: HCl, NaCl, NaOH etc..,

b. Weak electrolytes:

Weak electrolytes are substances which ionize to a small extent even at high dilutions.

Eg: CH_3COOH, $CaCO_3$, NH_4OH, etc..,

c. Non electrolytes:

Non electrolytes are substances which do not ionize at any solutions.

Eg: Glucose, Sugar, Alcohol, etc..,

IMPORTANT CELL TERMINOLOGY

- Oxidation: The tendency to lose electrons.
- Reduction: The tendency to gain electrons.
- Electrode: When a metal rod is dipped in its salt solution, it develops a positive or negative potential. This assembly is called electrode.
- Anode: Anode is an electrode at which oxidation occurs.
- Cathode: Cathode is an electrode at which reduction occurs.
- Electrolytes: Electrolyte is a water soluble substance forming ions in the solution and conduct an electric current.
- Half cell: Each half cell is an electrochemical cell where oxidation occurs and the half where the reduction occurs is called half cell.

Cell: Cell is a device consisting of two half cell. The two half cells are connected through the wire

TYPES OF CELLS

Based on the type of reaction occurring in a cell, cells are classified into two types

1. Electrolytic cells

Electrolytic cells are the cells in which electrical energy is used to bring about a chemical reaction. Eg: Electroplating etc..,

2. Electrochemical cells

Electrochemical cells are the cells in which chemical energy is converted into electrical energy. Eg: Daniel cell.

REPRESENTATION OF A CELL

We will consider that a cell consists of two half cells .Each half cell is again made of a metal electrode in contact with metal ion in the solution.

1. A single vertical line (|) represents a phase boundary between metal electrode and ion solution (electrolyte).Thus the two half cell in voltaic cell are indicated as

$Zn|Zn^{2+}$ $Cu^{2+}|Cu$ (|-phase boundary)

Anode half cell Cathode half cell

The metal electrode in anode half-cell is on the left, while in cathode half -cell is on the right of the metal ion.

2.In the complete cell diagram ,the two half cells are separated by a double vertical line in between zinc -copper cell can be written as

$Zn|Zn^{2+} || Cu^{2+}|Cu$ (||-Salt bridge)

The symbol for an inert electrode like the platinum electrode is often enclosed in a bracket.

$Mg|Mg^{2+}||H^{+}|H_2(Pt)$-inert electrode

Anode electrode cathode electrode

EMF OF A CELL

Electromotive force is defined as the difference of potential which cause flow of current from one electrode of higher potential to the other electrode of lower potential.

Thus the EMF of a galvanic cell can be calculated using the following relationship.

EMF = {standard reduction potential of right hand side electrode} - {standard reduction potential of left hand side electrode}

FACTORS AFFECTING EMF OF A CELL:

1. Nature of the electrolyte and electrodes.
2. Concentration and composition of the electrolytes.
3. PH and temperature of the solution.

Electrode potential

Empathy question:

1. How chemical reactions occur in electrochemical cells, such as batteries, fuel cells, and corrosion processes.

A metal (M) consists of metal ions (M^{n+}) with valence electrons when the metal (M) is placed in a solution of its own salt, any one of the following reactions will occur.

1. Positive metal ions may pass into the solutions.

$M \longrightarrow M^{n+} + ne^{-}$ (oxidation)

2. Positive metal ions from the solution may deposit over the metal

$M^{n+} + ne^{-} \longrightarrow M$ (reduction)

Example 1) Zn electrode dipped in $ZnSO_4$ solution.

When Zn electrode dipped in $ZnSO_4$ solution, Zn goes into the solution as Zn^{2+} ions due to oxidation.

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

Now the Zn electrode attains a negative charge, due to the accumulation of valence electrons on the metal. The negative changes developed on the electrode attract the positive ions solution. Due to this attraction the positive ions remain close to the metal.

➞Cu electrode dipped in $CuSO_4$ Solution

When Cu electrode is dipped in $CuSO_4$ solution, Cu^{2+} ions from the solution deposit over the metal due to reduction

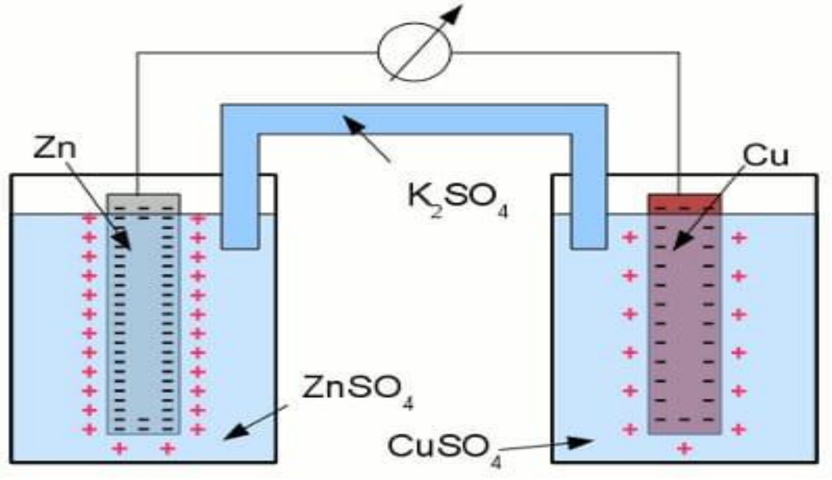
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

Now, the Cu electrode attains a positive charge, due to the accumulation of Cu^{2+} ions the metal. The positive charge charges developed on the electrode attract the negative ions from the solution due to this attraction the negative ions remain close to the metal.

➞Zn electrode in $ZnSO_4$ solution

Thus, a sort of layer (+) or (-) ions is formed all around the metal. This layer is called Helmholtz electrical double layer. This layer prevents passing of the positive ions form or to the metal. A difference of potential is consequently set up between the metal and the solution.

At equilibrium, the potential difference between constant value, which is known as the electrode potential of a metal



OXIDATION POTENTIAL

If oxidation occurs at the electrode, at equilibrium, the potential of the electrode is oxidation potential. The tendency of an electrode to lose electrons is oxidation potential.

REDUCTION POTENTIAL

The tendency of an electrode to gain electrons is called reduction potential.

SINGLE ELECTRODE POTENTIAL (E)

It is a measure of tendency of metallic electrodes to lose or gain electrons, when it is in contact with a solution of its own salt.

STANDARD ELECTRODE POTENTIAL (E)

The tendency of metallic electrodes to lose or gain electrons when it is in contact with a solution of its own salt of 1 molar concentration at 298K

NERNST EQUATION FOR ELECTRODE POTENTIAL

Empathy Question:

1. Studying the Nernst equation is important because it provides crucial insights into the behavior of ions in electrochemical systems and biological membranes.
2. Here’s why it’s essential and where it’s applied?
3. To understand how neurons communicate and generate electrical signals.
4. To predict how different ion concentrations in the electrolytes affect the voltage and efficiency of these devices.

5. Corrosion: To assess and mitigate the effects of ion concentration on the corrosion of metals and materials.

Nernst equation for electrode potential

Consider the following redox reaction

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

For such a redox reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter related as

$$\Delta G = -RT \ln K + RT \ln \frac{[Product]}{[Reactant]}$$

$$= \Delta G^\circ + RT \ln \frac{[Product]}{[Reactant]} \qquad \text{........ (1)}$$

where,

ΔG° = Standard free energy change

The above equation (1) is known as ***Van't Hoff isotherm.*** The decrease in free energy (− ΔG) in the above reaction involves transfer of 'n' number of electrons, then '*n*' faraday of electricity will flow. If E is the emf of the cell, then the total electrical energy (nEF) produced in the cell is

$$-\Delta G = nEF$$

(or)

$$-\Delta G^\circ = nE^\circ F \qquad \text{........ (2)}$$

where,

− ΔG = decrease in free energy change.

(or) − ΔG° = decrease in standard free energy change. Comparing equation 1 and 2, it becomes

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]} \qquad \text{....... (3)}$$

Dividing the above equation (3) by − nF

[Activity of solid metal [M] = 1]

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

In general, $E = E° - \frac{RT}{nF} \ln \frac{[Product]}{[Reactant]}$

(or)

$$E = E° + \frac{2.303RT}{nF} \log [M^{n+}] \text{-----------------}(4)$$

When, R = 8.314 J/K/mole; F = 96500 coulombs; T = 298 K (25°C), the above equation becomes

$$E = E^{o}_{red} + \frac{0.0591}{n}\log[M^{n+}] \qquad \text{---------}(5)$$

$$E = E^{o}_{oxi} - \frac{0.0591}{n}\log C$$

$$E = E^{o}_{oxi} - \frac{0.0591}{n}\log[M^{n+}] \qquad \text{----------------}(6)$$

The above equation 5&6 are known as “Nernst equation for single electrode potential”.

Applications of Nernst equations

1. Nernst equation is used to calculate electrode potential of unknown metal.
2. Corrosion tendency of metals can be predicted.
3. It is used to calculate the EMF of a cell.
4. pH of a solution can be calculated by measuring emf.

PROBLEM BASED ON NERNST EQUATION

Calculate the reduction potential of lead electrode in contact with a solution of 0.015M Pb^{2+} ions.

(E^0 = -0.13 volt)

GIVEN

Standard Oxidation potential is given as $Pb^{2+} + 2e^- \rightarrow Pb$; $E^0 = -0.13v$

Concentration of Pb^{2+} = 0.015M

Solution

The Nernst equation for reduction potential is

$$E = E^0_{red} + 0.0591/n \log(Pb^{2+})$$

$$E = -0.13 + .02955(-1.824)$$

$$E = -0.1839V$$

Oxidation potential of Pb = -0.1839V

Reference Electrodes

Standard Hydrogen Electrode:

The potential of unknown electrode can be measured by coupling it with another electrode, called reference electrode whose potential is already known or arbitrarily fixed as zero. The important reference electrode is standard hydrogen electrode, whose standard electrode potential is taken as zero at all temperature. So, it is called primary reference electrode. It is very difficult to set up a hydrogen electrode. So, other electrode called secondary reference electrode (like calomel electrode) is used.

Standard Hydrogen electrode is called a primary reference electrode because 1) The emf developed by the standard hydrogen electrode is arbitrarily fixed as zero at 1 atm pressure and the value of which is treated as constant at all temperature. 2) It is an only electrode with which the potential of all other electrodes are compared.

The typical standard hydrogen electrode is shown in the figure

Construction of Standard Hydrogen Electrode.

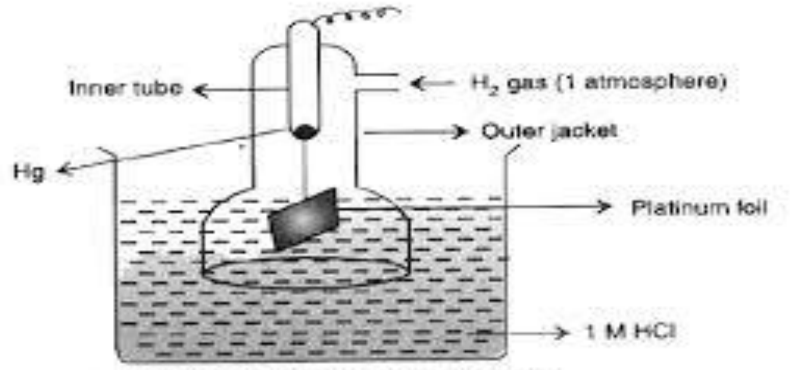


Fig. Standard hydrogen electrode

It consists of rectangular platinum foil which is connected to a platinum wire and sealed in a glass tube. A glass jacket surrounds the tube carrying the platinum foil. The jacket is closed at the top and opened at the bottom. A side tube attached to the outer jacket is used for the injection of hydrogen gas into the cell. This electrode, when dipped in a 1 M HCl solution at 25 ^{0}C and hydrogen gas at 1 atm is passed, forms a standard hydrogen electrode.

When this electrode acts as anode, the electrode reaction is as follows:

$$H_2(g) \longrightarrow 2H^+ + 2e^- \text{(oxidation)}$$

When this electrode acts as cathode, the electrode reaction is as follows:

$$2H^+ + 2e^- \longrightarrow H_2(g) \text{ (reduction)`}$$

The standard hydrogen electrode is represented as,

Pt, H_2(1atm)/H^+(1M);E^o= 0V

Development of EMF of SHE

When hydrogen gas is bubbled through the solution, it is adsorbed by the platinum foil. Due to the adsorption ofhydrogen gas, the equilibrium is established between hydrogen molecules and H^+ ions. The electrode potential developed during this equilibrium is taken as zero and treated as constant at all temperature.

Limitation

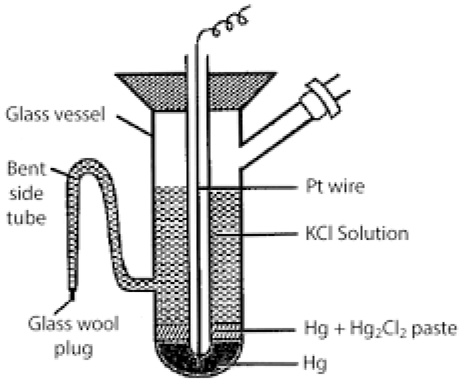
- It requires H_2 gas and is difficult to setup and transport.
- It requires considerable volume of test solution.
- The solution may affect the surface of the platinum electrode.
- The potential of the electrode is altered by changing the pressure of H_2 gas.

Need for Secondary Reference Electrode

1. It is very difficult to maintain the H^+ ion concentration at 1 M and hydrogen gas pressure at1 atm.

2. Platinum electrode is poisoned by the presence of impurities in the solution or gas.

Calomel Electrode or Secondary Reference Electrode



Calomel Electrode

To overcome the limitations of hydrogen electrode, the calomel electrode is developed. This is called the secondary reference electrode. It consists of a glass tube. Pure mercury is placed at the bottom of the tube and is covered with a paste of mercurous chloride. The remaining portion of the tube is filled with a saturated solution of KCl. The bottom of the tube is sealed with a platinum wire.

If the electrode acts as anode, the reaction is

$$2Hg\ (l) \longrightarrow Hg^{2+} + 2e^{-}$$

$$Hg^{2+} + 2Cl^{-} \longrightarrow Hg_2Cl_2\ (s)$$

$$\underline{\overline{2Hg\ (l) + 2Cl^{-} \longrightarrow Hg_2Cl_2(s) + 2e^{-}}}$$

Mercury undergoes oxidation to produce mercurous ion (Hg^{2+}) and combines with chloride ion to give mercurous chloride (Hg_2Cl2). Hence, the concentration of chloride ions is decreased. Calomel electrode the electrode acts as cathode, the reaction is

$$Hg_2\ Cl_2\ (s) \longrightarrow 2Hg^{2+} + 2Cl^{-}$$

$$Hg^{2+} + 2e^{-} \longrightarrow 2\ Hg\ (l)$$

$$Hg_2Cl_2(s) + 2e^{-} \longrightarrow 2\ Hg\ (l) + 2Cl^{-}$$

The mercurous ion present in the mercurous chloride undergoes reduction to give mercury. Hence the concentration of chloride ions is increased.

Calomel electrode is represented by Hg | Hg_2Cl_2(s), KCl (sat.solution).

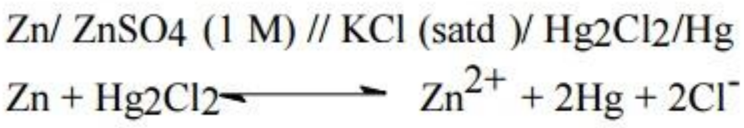
Characteristics of calomel electrode:

1) The electrode potential of calomel electrode depends on the activity of the chloride ions. When the concentration of chloride ion decreases, the electrode potential of calomel Electrode increases. The single electrode potential of calomel electrode with various concentration of KCl on the hydrogen scale at 298 K are given below
2) 0.1 N KCl = 0.3338 V
3) 1 N KCl = 0.2800 V
4) Saturated KCl = 0.2422 V

Measurement of single electrode potential using a reference electrode (saturated calomel electrode):

The given electrode, say zinc electrode, is coupled with saturated calomel electrode as in the figure. Since the reduction potential of zinc electrode less than that of calomel electrode, zinc acts as anode and calomel as cathode. The cell reaction will be

Zn/ $ZnSO_4$ (1 M) // KCl (satd)/ Hg_2Cl_2/Hg



Zn/ ZnSO4 (1 M) // KCl (satd)/ Hg2Cl2/Hg

$$Zn + Hg_2Cl_2 \longrightarrow Zn^{2+} + 2Hg + 2Cl^-$$

The emf of the cell is measured using a potentiometer. The value of E_{cell} = 1.002 volt.

Now, $E_{cell} = E^O_{right} - E^0_{left}$

$= E^O cal - E^O_{Zn}$

$1.002 = 0.242 - E^0_{Zn}$

$E_{Zn} = 0.242-1.002$

$E_{Zn} = - 0.76$ volt.

Advantages of Reference Electrode (Calomel Electrode):

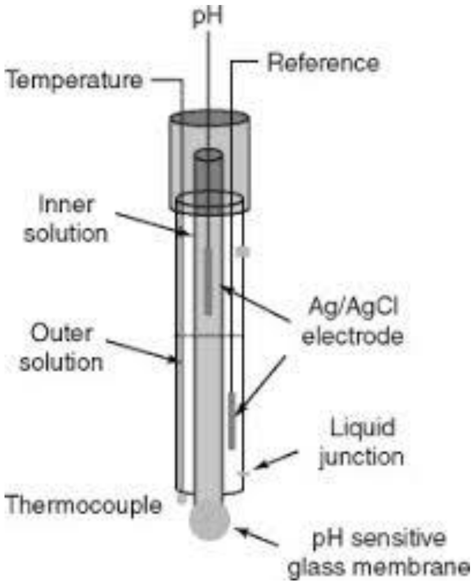
- Easy to set up.
- Easily transportable
- Long shelf life
- Reproducibility of emf
- Low temperature coefficient
- Electrode can be used in a variety of solutions.
- E^o value is accurately known.

ION-SELECTIVE ELECTRODE

These are the electrodes having the ability to respond only to a particular ions and develop potential, ignoring the other ions in a mixture. The potential developed by an ion selective electrode depends only on the concentration of particular ions.

GLASS ELECTRODE

The glass electrode is the most widely used hydrogen ion responsive electrode. When a glass membrane is immersed in a solution, a potential is developed between the two surface of the membrane which is a linear function of the hydrogen ion concentration of the solution i.e. pH value.



CONSTRUCTION

- A glass electrode consists of thin walled glass bulb (the glass is a special type having low melting point and high electrical conductivity) containing a Pt wire in 0.1 M HCl. The glass electrode is represented as

- Pt = 0.1 M HCl / Glass

HCl in the bulb furnishes a constant H^+ ion concentration. Glass electrode is used as the internal reference electrode. The pH of the solution especially coloured solution containing oxidizing or reducing agent can be determined. The thin walled glass bulb called Glass membrane functions as an ion exchange resin and equilibrium is set up between the Na^+ ions of glass and H^+ ions in solution.

- The potential difference varies with H+ ions concentration and its emf is given by the expression

$$E_G = E^o_G + 0.0591\ pH$$

Determination of pH of a solution using Glass Electrode

The Glass electrode is placed in the solution under test and is coupled with saturated calomel electrode.

The emf of the cell is measured from the emf, the pH of the solution is calculated as follows:

$$E\ cell = E\ right - E\ left$$

$$E\ cell = 0.2422\ V - [E^o\ _{Glass} + 0.0591\ V\ pH]$$

$$E\ cell = 0.2422\ V - E^o\ _{Glass} - 0.0591\ V\ pH$$

$$pH = \underline{0.2422\ V - E^o\ _G - E\ cell}$$

ADVANTAGES

- The results are accurate.
- It is not easily poisoned.
- Equilibrium is rapidly achieved.
- It can be easily constructed and readily used.

DISADVANTAGES

Since the resistance is quote high, special electronics potentiometers are employed for measurement.
The Glass electrode can be used in solutions only with pH range of 0 to 10. However above the pH 12 (high alkalinity) cations of the solution affect the Glass and make the electrode useless.

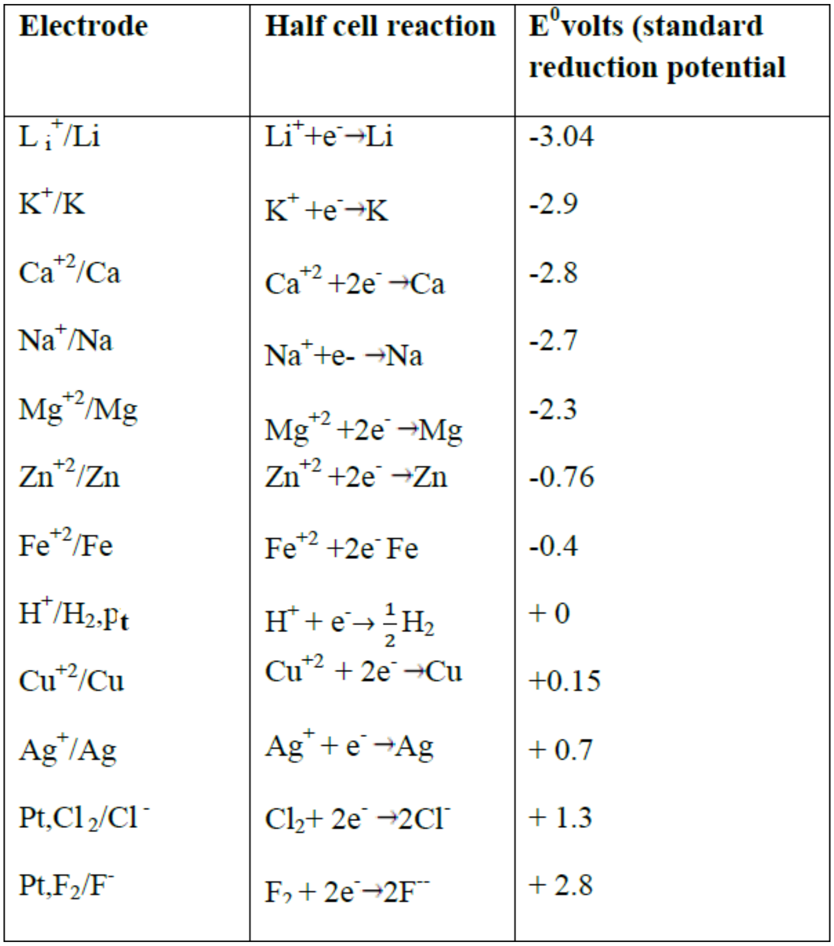
APPLICATIONS OF ISEs

ISEs are used in determining the concentrations of cations like H^+, Na^+, K^+, Ag^+, Li^+.

- ISEs are used for the determination of hardness (Ca^{2+} and Mg^{2+} ions)
- pH of the solution can be measured by using gas sensing electrode.
- Concentrations of anions like NO_3-, CN-, S^{2-}, halides (X^-) can be determined.

ELECTROCHEMICAL SERIES OR EMF SERIES

- The increasing value of standard reduction potentials are called as electrochemical series.
- The standard electrode potential of a number of electrodes is given in table. The values are determined potentiometrically by combining the electrode with another standard electrode, whose electrode potential is zero.



Electrode	Half cell reaction	E^0volts (standard reduction potential
L_i^+/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	$Fe^{+2} + 2e^- Fe$	-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

1. CALCULATION OF STANDARD EMF OF THE CELL:

The standard emf of the cell (E°) can be calculated if the standard electrode potential values are known using the following reaction.

$$E^\circ \text{ cell} = E^\circ_{RHE} - E^\circ_{LHE}$$

2. RELATIVE CASE OF OXIDATION OR REDUCTION

Higher the value of standard reduction potential (+ve value) greater is the tendency to get reduced. (i.e metals on the top (- ve value) are more easily ionized).

a. The fluorine has higher positive value of standard reduction potential (+ 2.87 V) and shows higher tendency towards reduction.

b. The lithium has higher negative value (- 3.01 V) and shows higher tendency towards oxidation

3. DISPLACEMENT OF ONE ELEMENT BY THE OTHER

Metals which lie higher in the emf series can displace those elements which lie below them in the series.

For example: We may know whether Cu will displace Zn from the solution or vice versa. We know that standard reduction potential of Cu and Zn i.e

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

So, Cu^{2+} has a great tendency to acquire Cu form than Zn 2+ has acquiring Zn form

4. DETERMINATION OF EQULIBRIUM CONSTANT FOR THE REACTION.

Standard electrode potential can also be used to determine the standard free energy charge (G) and equilibrium constant (K) for the reaction. We know that

$$G^o = RT \ln k = 2.303\ RT \log K$$

$$\log K = \ - G^o / 2.303\ RT$$

$$\log K = nF\ E^o / 2.303\ RT \quad \text{i.e} - \ G^o = nF\ E^o$$

From the value of E°, the equilibrium constant for the cell reaction can be calculated.

5. DISPLACEMENT BEHAVIOR OF HYDROGEN

Metals with negative reduction potential will displace the hydrogen form an acid solution.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$E^o_{Zn} = -0.76V$$

From the value of E°, the equilibrium constant for the cell reaction can be calculated.

The metal with positive reduction potential will not displace the hydrogen from an acid solution.

$$Ag + H_2SO_4 \longrightarrow \text{no reaction}$$

$$E^o_{Ag} = +0.80\ V$$

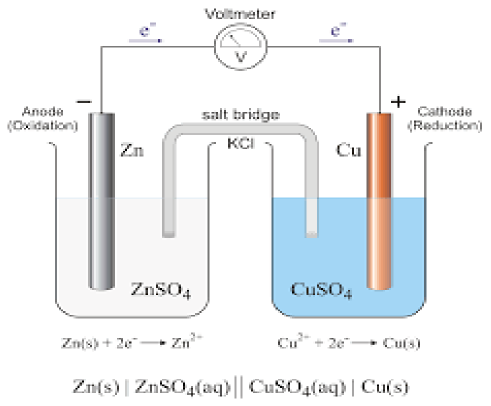
Electrochemical Cells:

An electrochemical cell is a device that generates electrical energy from chemical reactions or uses electrical energy to cause chemical reactions.

Galvanic (Voltaic) Cells:

Galvanic cell is an electrochemical cell in which the electrons transferred due to redox reaction are connected into electrical energy.

Example: Daniel cell



Galvanic cell consists of a zinc electrode dipped in 1M $ZnSO_4$ solution and a copper electrode dipped in 1M $CuSO_4$ solution. Each electrode is known as a half cell. The two solutions are interconnected by a salt bridge and the electrodes are connected by a wire through a voltmeter.

AT ANODE:

Oxidation takes place in zinc electrode by the liberation of electrons, so this electrode is called negative electrode or Anode.

AT CATHODE:

Reduction takes place in the copper electrode by the acceptance of electrons. So this electrode is called Positive electrode or Cathode.

- At cathode: $Cu^{2+} + 2e^- \rightarrow Cu$
- At anode: $Zn \rightarrow Zn^{2+} + 2e^-$

SALT BRIDGE

It consists of U tube containing saturated solution of KCl or NH_4NO_3 in agar- agar gel. It connects the two half cells of the galvanic cells.

FUNCTIONS OF SALT BRIDGE:

- It eliminates liquid junction potential.
- It provides the electrical continuity between the two half cells.

Representation of Electrochemical Cell (Galvanic Cell)

(a) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

(b) The anode of the cell is represented by writing metal or solid phase and then the metal ion present in the electrolytic cell. Both are separated by a vertical line or a semicolon. For example

e.g.(i)$Zn|Zn^{2+} or Zn;Zn^{2+}$

$Zn|ZnSO_4 or Zn_{(s)}|ZnSO_4$(0.1m)

(c) The cathode of the cell is represented by writing the cat-ion of theelectrolyte first and then the metal. Both are separated by a vertical line or semicolon.

Cu^{2+}|Cu or Cu^{2+}; Cu or Cu^{2+}(1M)|Cu.

For gaseous electrode e.g.Cl^{-}(1m)|Cl_2(1atm), P_{2}|

(d) The salt bridge which separates the two half-cell is indicated by two parallel vertical line. For example the Daniel cell can be represented as

$$Zn_{(s)}|ZnSO_{4(aq)}||CuSO_{4(aq)}|Cu_{(s)}$$

Anobe Salt bridge Cathode

DIFFERENCE BETWEEN ELECTROLYTIC CELL AND ELECTROCHEMICAL CELL

ELECTROLYTIC CELL	ELECTROCHEMICAL CELL
Electrical energy is converted into chemical energy.	Chemical energy is converted into chemical energy
The anode carries (+) charges	The anode carries (-) charges
The cathode carries (-) charges	The cathode carries (+) charges
The electrons are supplied to the cell from the external battery (i.e) electron move in through cathode and comes out from anode	But electrons are drawn from the cell (i.e) electrons move from anode to cathode through external circuit.
Ex. Electroplating	Ex. Battery

Measurement of EMF-Electrolytic cell

EMFOFACELL

Definition

Electro motive force is defined as, "the difference of potential which causes flow of current from one electrode of higher potential to the other electrode of lower potential.

Thus, the emf of a galvanic cell can be calculated using the following relationship.

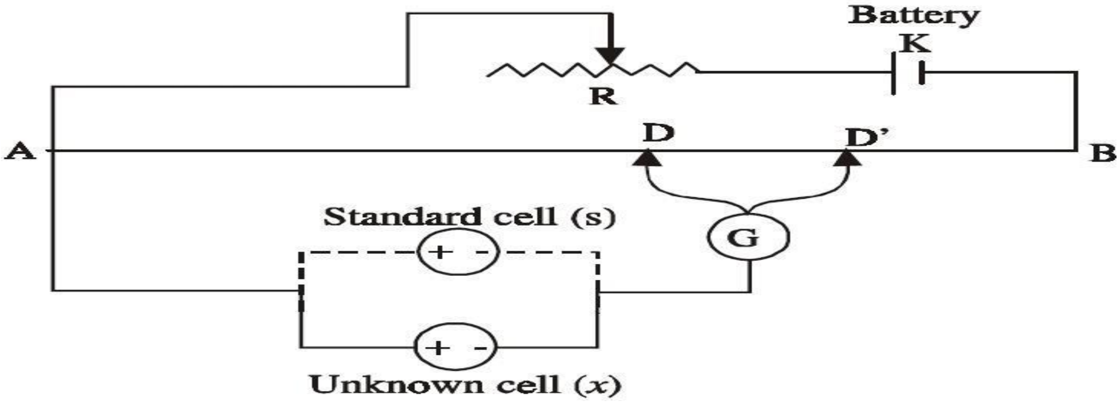
Standard EMF of the cell = [standard reduction potential of R.H.S.electrode]–

[Standard reduction potential of L.H.S.electrode]

$$E^{\circ}_{cell} = E^{\circ}_{right} - E^{\circ}_{left}$$

Measurement of emf of a cell

The potential difference or emf of a cell can be measured on the basis of poggendorff's compensation principle. Here the emf of the cell is just opposed or balanced by an emf of standard cell (external emf), so that no current flows in the circuit.



The potentiometer consists of a uniform wire AB

A storage battery (K) is connected to the ends A and B of the wire through a rheostat (R).The cell of unknown emf (x) is connected in the circuit by connecting its positivepole to A and the negative pole is connected to a sliding contact (D) through agalvanometer G. The sliding contact is freely moved along the wire AB till no current flows through the galvanometer. Then the distance AD is measured. The emf of unknown cell is directly proportional to the distance AD.

$$E_x \propto AD$$

Then the unknown cell (x) is replaced by a standard cell (s) in the circuit.The sliding contact is again moved till there is null deflection in the galvanometer. Then the distance AD′ is measured. The emf of standard cell Es is directly proportional to the distance AD′.

$$E_s \propto AD'$$

Then, the emf of the unknown cell can be calculated from the following equation.

$$\frac{\text{Emf of the unknown cell x}}{\text{Emf of the standard cell s}} = \frac{\text{Length AD}}{\text{Length AD'}}$$

$$\frac{E_x}{E_s} = \frac{AD}{AD'}$$

$$\therefore \text{Emf of the unknown cell} = E_x = \frac{AD}{AD'} \text{ X } E_s$$

Electrolytic cell

Conversion of electrical energy is into chemical energy. The anode is positive plate and cathode is negative plate. Electrons are supplied to the cell from the external power supply. The extent of chemical reaction occurring at the electrode is governed by Faraday's law of electrolysis. The amount of electricity passed during electrolysis is measured by Coulometer.

e.g: Electroplating, Electrolysis

ELECTROPLATING OR ELECTRODEPOSITION

Definition: Electroplating is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.

- The base metal to be plated is made cathode whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity (like graphite).

Objectives:

Electroplating is carried out for 1) Decoration or better appearance 2) Increasing the resistance to corrosion of the coated metal. 3) Improving the hardness of the metal 4) Increasing the resistance to chemical attack 5) Electro refining.

Theory:

E.g. if $AuCl_3$ solution is used as an electrolyte it

ionses as $\rightleftharpoons$ Au^{3+} and $3Cl^{-}$

On passing current Au^{3+} ions go to the cathode and get deposited their

$$Au^{3+} + 3e^{-} \rightarrow Au \text{ (at cathode)}$$

The free chloride ions migrate to the Au anode and dissolve an equivalent amount of Au to form $AuCl_3$

$$Au + 3Cl^{-} \rightarrow AuCl_3 + 3e^{-} \text{(at anode)}$$

The $AuCl_3$ formed to get dissolved in the electrolyte. Thus there is a continuous replenishment of electrolyte during electrolysis.

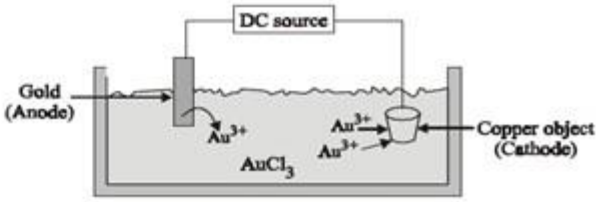


Fig. 3.1 Electroplating

PROCESS:

- The article is to be plated first treated with organic solvent like carbon tetrachloride, acetone, tetrachloro ethylene to remove oils, greases etc.
- Then it is made free from surface scale, oxides, etc. by treating with dil. HCl or H_2SO_4(pickling acid).
- The cleaned article is then made as the cathode of the electrolytic cell.
- The anode is either the coating metal itself or an inert material of good electrical conductivity.
- The electrolyte is a solution of soluble salt of the coating metal.
- When direct current is passed, coating metal ions migrate to the cathode and get deposited there.
- Thus, a thin layer of coating metal is obtained on the article made as the cathode.
- In order to get strong, adherent and smooth deposit, certain types of additives (glue, gelatin, boric acid) are added to the electrolytic bath.
- In order to improve the brightness of the deposit, brightening agents are added in the electrolyticbath.

The favorable conditions for a good electrodeposits are

i) Optimum temperature ii) Optimum current density

iii) Low metal ion concentrations.

Gold Electroplating:

Anode: Gold

Cathode: Metal article

Electrolyte: Gold + KCN

Temperature: 60°C

Current density (mA/cm^2): 1-10

Use:

i) This is used for electrical and electronic applications.

ii) It is used for high quality decorations and high oxidation resistant coatings iii)Usually for ornamental jewellery, a very thin gold coating (about 1x10^{-4} cm) is given

Question Bank

PART A

01. Define an Electrochemical cell. Give one example
02. What do you mean by redox reaction?
03. State single electrode potential
04. State standard electrode potential
05. Define an origin of electrode potential.
06. Write the limitations of hydrogen electrode
07. Define oxidation potential and reduction potential.
08. How an electrochemical is measured? Define EMF of an electrochemical cell.
09. What are the applications of electrochemical cell?
10. Define electrochemical series.
11. Write the significance of electrochemical series.
12. Write the mathematical form of Nernst equation and give one application.
13. Define Electro plating and Electroless plating
14. What are the types of electrolytes? Give an example for each type.
15. How will you predict the spontaneity of a reaction using emf series?
16. Zinc displaces H_2 from HCl but Cu does not. Why?
17. What is galvanic series? What are the significance of it?
18. Discuss the rules to be followed while representing a cell.
19. What are single and Std. Electrode potentials?
20. Calculate the electrode potential of Zinc electrode dipped in 0.1M zinc sulphate solution at 25^0 C
21. Bring out the symbolic representation of SHE. What are its limitations?

PART B

1. What is electrochemical cell? Explain with example of Daniel cell.

2. How electrochemical cell is measured by potentiometrically? Or What is emf?

3. What are electrochemical series? Give its applications.

4. Derive Nernst equation

5. Explain the electroplating of Gold

6. How will you measure pH of a solution using ion selective glass electrodes?

7. With a neat sketch explain the principle, working of SHE.

8. Explain the concept of secondary reference electrode, taking calomel electrode as example. Calculate the emf of the cell Zn/Zn^{2+} (0.1M) $//Ag^{+}$ (0.1M)/Ag ;$E°_{cell}=1.56$ v

9.Consider the cell reaction $Zn(s)+Fe^{2+}(0.005M)\leftrightarrow Zn^{2+}(0.01M)+Fe(s)$

PUZZLES QUESTION:

1. Which term refers to the device used to convert chemical energy into electrical energy?

Choices:
A) Electrode
B) Battery
C) Electrolyte
D) Voltmeter

Answer:
B) Battery

2. What is the process called when a substance gains electrons?

Choices:
A) Oxidation
B) Reduction
C) Electrolysis
D) Ionization

Answer:
B) Reduction

3. What is the negatively charged electrode in an electrochemical cell?

Choices:
A) Anode
B) Cathode
C) Electrolyte
D) Salt Bridge

Answer:
B) Cathode

4. What is the name of the electrolyte used in a lead-acid battery?

Choices:

A) Hydrochloric Acid
B) Sulfuric Acid
C) Nitric Acid
D) Acetic Acid

Answer:
B) Sulfuric Acid

What is the movement of ions through a solution called?

Choices:
A) Conductivity
B) Diffusion
C) Migration
D) Electrolysis

Answer:
C) Migration

Which law relates the amount of substance deposited during electrolysis to the quantity of electricity passed?

Choices:
A) Boyle's Law
B) Faraday's Law
C) Ohm's Law
D) Kirchhoff's Law

Answer:
B) Faraday's Law

Missing letters:

1._ _ D _ C _ _ _ Y
(Hint: The flow of electric charge)

Answer:
CONDUCTIVITY

2. R _ D _ _ _ T _ O _
(Hint: Gain of electrons in a chemical reaction)

Answer:
REDUCTION

3.A _ _ D E
(Hint: The electrode where oxidation occurs)

Answer:
ANODE

4._ L _ C _ _ _ L Y _ _ S
(Hint: The process of using electrical energy to drive a chemical reaction)

Answer:
ELECTROLYSIS

5._ A _ T _ _ B _ _ D _ E
(Hint: A device that connects two half-cells in a galvanic cell)

Answer:
SALT BRIDGE

Across

1. A positively charged ion (7 letters):
    - Answer: CATION
2. The electrode where reduction occurs (7 letters):
    - Answer: CATHODE
3. An apparatus that produces electricity through a chemical reaction (7 letters):
    - Answer: BATTERY
4. The process of gaining electrons (9 letters):
    - Answer: REDUCTION
5. A substance that conducts electricity when dissolved in water (11 letters):
    - Answer: ELECTROLYTE

Down

1. The electrode where oxidation occurs (5 letters):
    - Answer: ANODE
2. The study of the relationship between electricity and chemical reactions (15 letters):
    - Answer: ELECTROCHEMISTRY
3. A bridge that maintains electrical neutrality in a cell (10 letters):
    - Answer: SALTBRIDGE
4. The measure of a solution’s ability to conduct electricity (12 letters):
    - Answer: CONDUCTIVITY
5. A device used to measure electrical potential difference (9 letters):
    - Answer: VOLTMETER