

Module:3 **CONCEPT OF ELECTROCHEMISTRY**

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Q1. Define Electrochemistry. State its significance.

Electrochemistry is the branch of physical chemistry which deals with the study of relationship between electricity and chemical changes. These reactions involve electric charges moving between electrodes and an electrolyte (or ionic species in a solution). Thus electrochemistry deals with the interaction between electrical energy and chemical change.

Significance of electrochemistry

- 1) Electrochemistry is used for the production of metals like Na, Mg, Ca, Al, Cu, Ag, Au, etc
- 2) Electrochemistry is used in the storage batteries and cells used in various instruments.
- 3) Electrochemistry is used in the fabrication of electronic devices, doping etc.
- 4) For electroplating, galvanizing, tinning, drawing metal wires etc.

Q2. Explain the concept of half reactions with suitable examples. Explain Redox reaction.

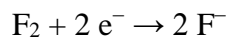
Chemical reactions where electrons are transferred directly between molecules and/or atoms are called oxidation-reduction or redox reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte. The processes of oxidation and reduction occur simultaneously and cannot happen independently of one another. The oxidation alone and the reduction alone are each called a *half-reaction*, because two half-reactions always occur together to form a whole reaction. When writing half-reactions, the gained or lost electrons are typically included explicitly in order that the half-reaction be balanced with respect to electric charge.

Eg: Reaction between hydrogen and fluorine in which hydrogen is being oxidized and fluorine is being reduced:

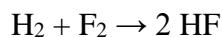
Oxidation reaction:



Reduction reaction:



We can write this overall reaction as two half-reactions:



Q3. Define and explain a typical electrochemical cell with a neat labeled diagram.

An electrochemical cell is a device capable of either generating electrical energy from chemical reactions or using electrical energy to cause chemical reactions. In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. A redox reaction can be described as two half-reactions, one representing the oxidation process and the other reduction process.

Example of electrochemical cell is Daniel cell

Daniel Cell: It consists of two half-cells. The left hand half-cell contains a zinc metal electrode dipped in ZnSO_4 solution. The half-cell on the right hand side consists of Cu metal electrode in a solution of CuSO_4 . A salt bridge that prevents the mechanical mixing of the solution joins the half-cells.

When the zinc and copper electrodes are joined by a wire the following observation are made.

- (a) There is flow of electric current through the external circuit.
- (b) The Zn rod loses its mass while copper rod gains in the mass.
- (c) The concentration of ZnSO_4 solution increases while the concentration of CuSO_4 solution decreases.
- (d) The solutions in both the compartments remain electrically neutral.

During the passages of electric current through external circuit, electrons flow from zinc electrode to the copper electrode. At the zinc electrode, zinc metal is oxidized to zinc ions, which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu^{2+} ions to metallic copper which is deposited on the electrode.

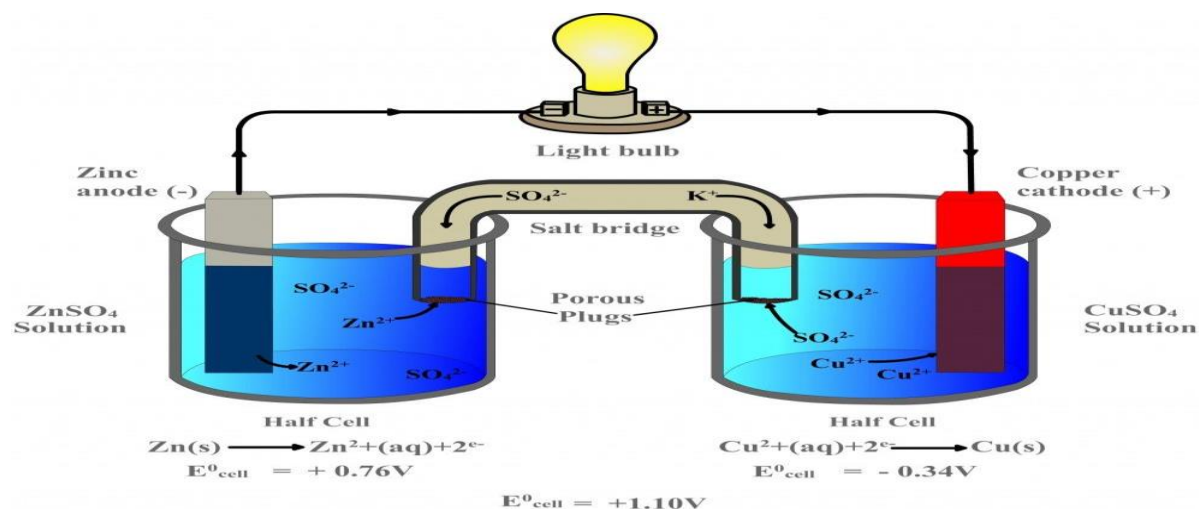
Cell Reaction

$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ (Oxidation so anode)

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

Net reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

At the zinc rod, oxidation occurs. So it is the anode of the cell and negatively charged.



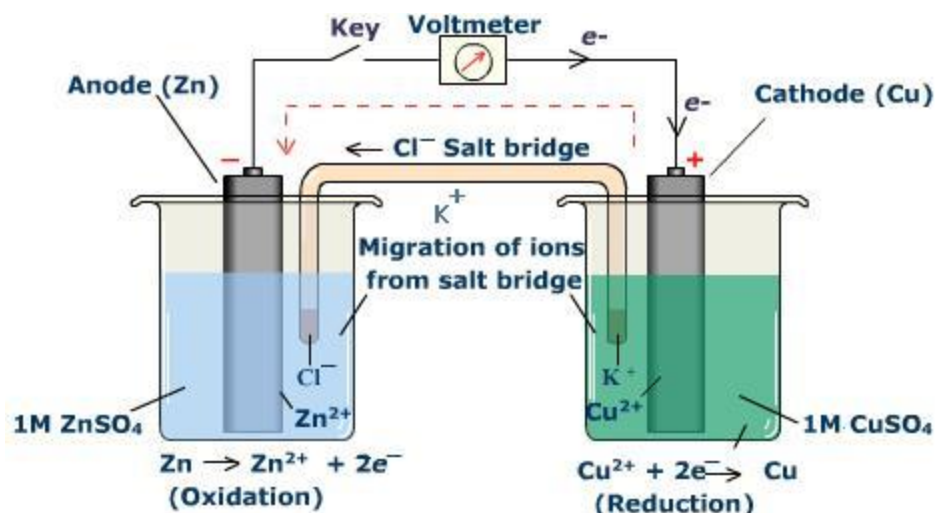
Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and Cu is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction. A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

Q4.What are the types of electrochemical cells?

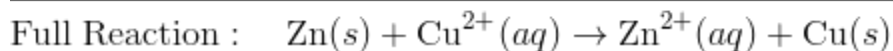
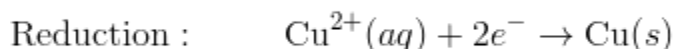
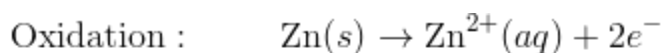
The four types of electrochemical cells are

1. Galvanic cells (also known as Voltaic cells)
2. Electrolytic cells
- 3) Concentration cell
- 4) Fuel cell

1) A **galvanic cell or voltaic cell**, is an [electrochemical cell](#) that derives electrical energy from spontaneous [redox](#) reactions taking place within the cell. It generally consists of two different metals immersed in an electrolyte, or of individual half-cells with different metals and their ions in solution connected by a [salt bridge](#) or separated by a porous membrane.



The process that occurs in this redox reaction is shown below as two separate half-reactions, which can then be combined into the full redox reaction.



2) An electrolytic cell is an [electrochemical cell](#) that drives a non-spontaneous [redox](#) reaction through the application of electrical energy. In an electrolytic cell a current is passed through the cell by an external voltage, causing an otherwise non-spontaneous chemical reaction to proceed.

When Na⁺ ions collide with the negative electrode, the battery carries a large enough potential to force these ions to pick up electrons to form sodium metal.

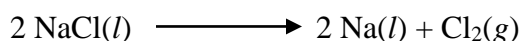


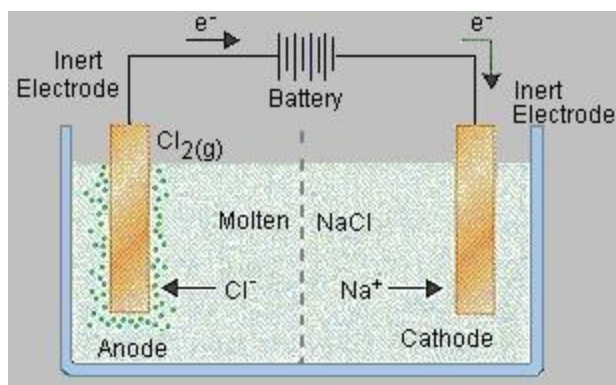
Cl⁻ ions that collide with the positive electrode are oxidized to Cl₂ gas, which bubbles off at this electrode



The net effect of passing an electric current through the molten salt in this cell is to decompose sodium chloride into its elements, sodium metal and chlorine gas.

This is an example of electrolysis process. The suffix *-lysis* comes from the Greek stem meaning to loosen or split up. Electrolysis literally uses an electric current to split a compound into its elements.





Q5. Distinguish between Galvanic cell and Electrolytic cell.

Electrochemical cell (Galvanic Cell)

- 1) A Galvanic cell converts chemical energy into electrical energy.
- 2) Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.
- 3) The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.
- 4) Here the anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
- 5) The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.

Electrolytic cell

- 1) An electrolytic cell converts electrical energy into chemical energy.
- 2) The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
- 3) Both the electrodes are placed in a same container in the solution of molten electrolyte.
- 4) Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
- 5) The external battery supplies the electrons. They enter through the cathode and come out through the anode.

Q6. Explain a concentration cell with a suitable example and proper reactions.

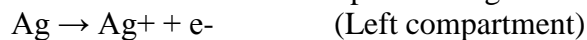
A **concentration cell** can be defined as cell in which emf arises as a result of different concentrations of the same electrolyte in the component half cells.

Construction:

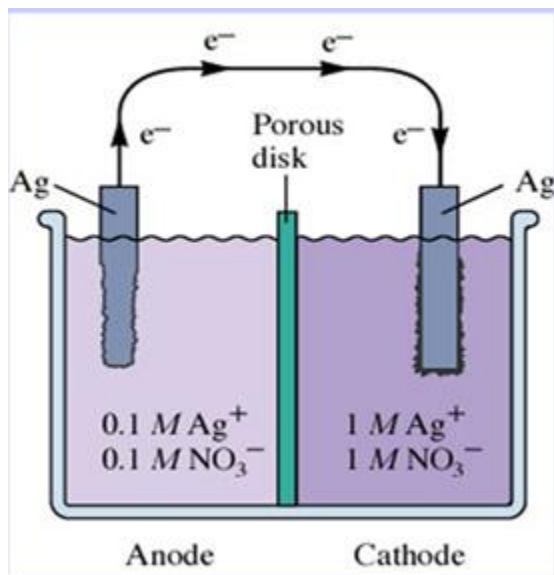
- a) It is constructed by pairing two half cells in which identical electrodes are dipped in a solution of different concentrations of the same electrolyte.
- b) It consists of two silver electrodes one immersed in 0.1 M silver nitrate solution and the other in 1M solution of the same electrolyte.
- c) The two solutions are in contact through a membrane (or a salt bridge)
- d) When the electrodes are connected by a wire, it is found that electron flow from the electrode in more dilute (0.1M) solution to that in the more concentrated (1M) solution.

e) There is a natural tendency to equalize the concentration of Ag^+ ions in the two compartments. This can be done if the electrons are transferred from the left compartment to the right compartment.

This electron transfer will produce Ag^+ ions in the right compartment by the half cell reactions:



Thus to equalize concentration of Ag

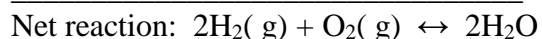
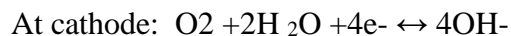
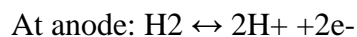


Q7. Explain a fuel cell with a suitable example and proper reactions.

Fuel Cell: The cell in which electric energy is produced without combustion of oxygen and a gas that can be oxidized. It converts chemical energy of fuel directly into electrical energy.

Construction: It consists of two electrodes made of graphite impregnated with a catalyst (Pt, Ag or a metal oxide). The electrodes are placed in an aqueous solution of KOH or NaOH. O_2 and H_2 are constantly bubbled through cathode and anode respectively.

Reactions:



Application:

- (a) Auxiliary engine source in space vehicle. Submarines
- (b) The weight of fuel battery for 15 days in space is about 250 kg.
- (c) It produces H_2O , which proved to be a valuable source of fresh water.

Characteristic of fuel cell

- (a) They don't store chemical energy
- (b) Reactants are to supply constantly, while products are removed constantly.

Q8. Explain the concept of Electrode potential.

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential.

Following two changes occur when a metal rod is dipped in its salt solution.

- (a) Oxidation: Metal ions pass from the electrode into the solution leaving an excess of electrons and thus forming a negative charge on the electrode.



- (b) Reduction: Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode. Metal ions start depositing on the metal surface leading to a positive charge on the metal.



In the beginning, both these changes occur with different speeds but soon an equilibrium is established.



In practice, one effect is greater than the other,

If first effect (Oxidation) is greater than the second (Reduction), the metal acquires a negative charge with respect to solution and if the second (Reduction) is greater than the first (Oxidation), it acquires positive charge with respect to solution, thus in both the cases a potential difference is set up.

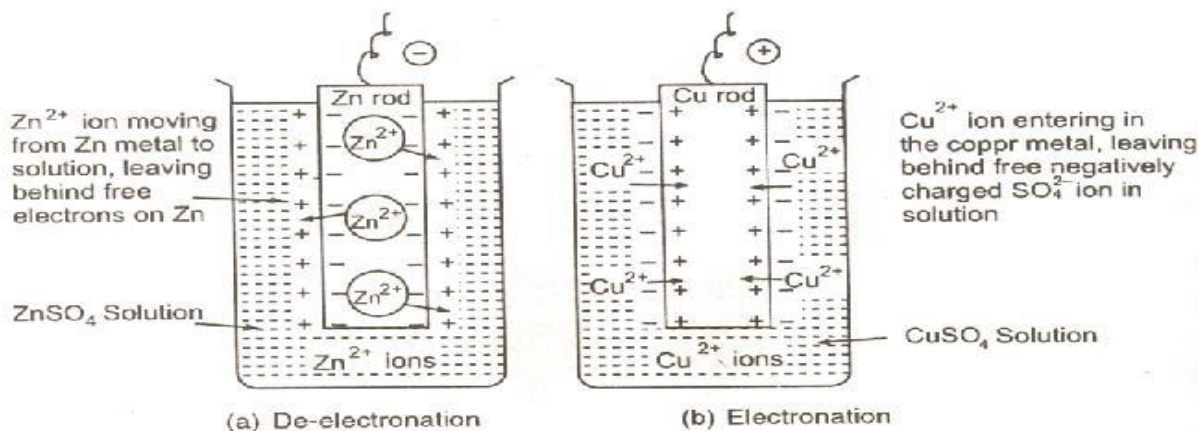


Fig. 6.3 Electrode potential.

Q9. What is Cell Potential or EMF of a cell (E)?

Every galvanic or voltaic cell is made up of two half-cells, the oxidation half-cell (anode) and the reduction half-cell (cathode). One of the electrodes must have a higher electrode potential (higher tendency to lose electrons) than the other electrode. As a result of this potential difference, the electrons flow from an electrode at a higher potential to the electrode at a lower potential. The difference between the electrode potentials of the two half-cells is known as electromotive force (EMF) of the cell or cell potential or cell voltage. The EMF of the cell or cell potential can be calculated from the values of electrode potential of the two half cells constituting the cell.

$$E_{\text{cell}} = E_{\text{anode}} + E_{\text{cathode}}$$

Q10. What is Standard Potential (E°)?

The standard cell potential or standard emf of a galvanic cell is the potential of a cell when all the substances involved in the cell reaction are in their standard states. The solutions are at 1M concentrations, gases are at 1 atm pressures, solids and liquids are in pure forms and all at 25°C.

According to IUPAC convention, the standard reduction potential of an electrode is simply called standard potential of the electrode. Therefore, the standard cell potential is written in terms of the standard(reduction) potentials of both the electrodes.

Thus the standard emf of the cell is the difference between the standard potential of cathode (right hand electrode) and the standard potential of anode (left hand electrode).

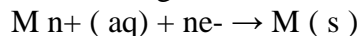
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode (RHE)}} - E^{\circ}_{\text{anode (LHE)}}$$

Q11. Derive and explain Nernst equation.

The electrode potential and the EMF of the cell depend upon the nature of the

electrode, temperature and the activities (concentrations) of the ions in solution. The variation of electrode and cell potential with concentration of ions in solution can be obtained from thermodynamic considerations.

Consider a general reaction



According to Law of Mass Action and Vant Hoff's reaction isotherm,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\text{Since } Q = \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\therefore \Delta G = \Delta G^\circ + RT \ln \frac{[M(s)]}{[M^{n+}(aq)]}$$

$$\text{As } [M(s)] = 1$$

$$\text{So, } \Delta G = \Delta G^\circ + RT \ln \frac{1}{[M^{n+}(aq)]}$$

Since in a reversible reaction, the electrical energy produced at the expense of the free energy change i.e. $-\Delta G = nFE$, $\Delta G^\circ = -nFE^\circ$,

where E and E^o are standard electrode potential.

F – Faraday's of electricity = 96500 coulombs

n – number of electrons involved in the cell reaction

$$\text{So, } -nFE = -nFE^\circ + RT \ln \frac{1}{[M^{n+}(aq)]}$$

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

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

At 250C, T = 298K, F = 96500 coulomb, R = 8.314 JK⁻¹mole⁻¹

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$$\text{or } E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\text{or } E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Oxidn}]}{[\text{Redn}]}$$

Q12. What are the applications of Nernst equation?

Applications of Nernst Equation:

- 1) The potential of an electrode and EMF of a cell can be calculated at any temperature and concentration.
- 2) The concentration of reactants can be calculated by knowing the potential of an electrode.
- 3) The pH of a solution can be calculated by measuring the EMF.
- 4) The concentration of a solution in the galvanic cell can be determined.

Q13. What are reference electrodes?

For the measurement of a potential of a single electrode, it must be combined with another electrode whose potential is either zero or known. This second electrode whose potential is arbitrarily considered as zero is known as the standard electrode or reference electrode. The potentials of the other electrodes are then expressed relative to the reference electrode.

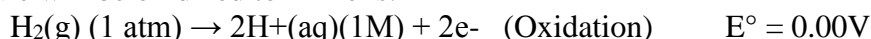
Q14. Write a short note on Standard Hydrogen Electrode (SHE).

The reference electrode used is the standard or normal hydrogen electrode (SHE or NHE). So the electrode potential of a given electrode is measured by connecting a standard hydrogen electrode through a salt bridge. The e.m.f of the cell is measured either by a calibrated potentiometer or by a high resistance voltmeter.

Construction: In the standard hydrogen gas electrode, hydrogen gas at atmospheric pressure is passed into 1M HCl at 298K in which a foil of platinum coated with platinum black (finely divided platinum) remains immersed. The electrode is usually represented as

$$\text{Pt}, \text{H}_2(\text{g}) | \text{H}^+(\text{aq}) (1\text{m})$$

If the electrode serves as anode, the half reaction taking place will be oxidation. Hydrogen molecule will be oxidized to H^+ ions.



When the electrode serves as cathode, the half reaction taking place will be reduction. H^+ ions will be reduced to hydrogen molecule.



So the half-reaction responsible for the potential that develops at this electrode is



By convention, the potential of the standard hydrogen electrode is assigned a value of 0.000 V at all temperatures.

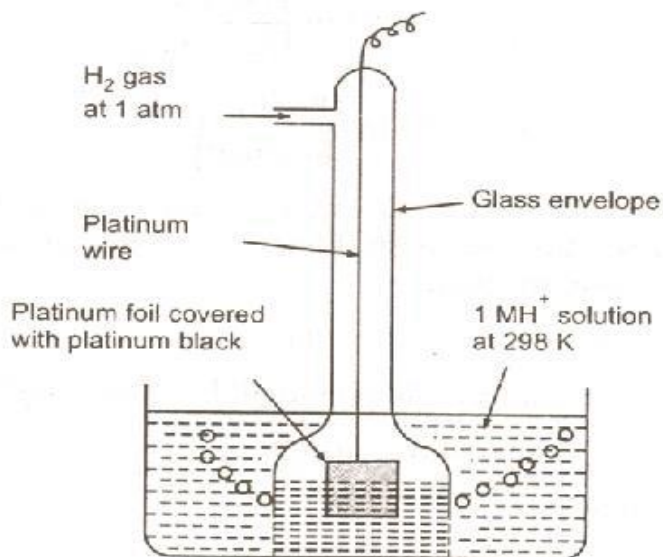
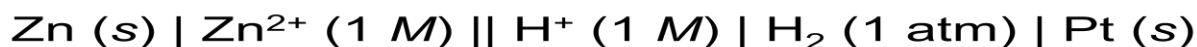
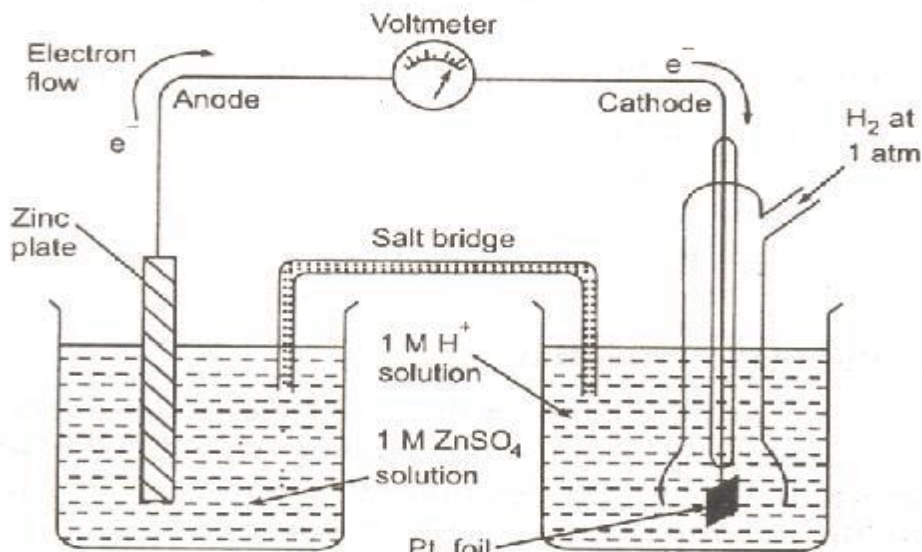


Fig. 6.4 Normal hydrogen electrode.

Q15. How standard electrode potential of $\text{Zn} / \text{Zn}^{2+}$ electrode is determined experimentally with reference to standard hydrogen electrode?

A cell comprising of a Zn electrode immersed in 1m ZnSO_4 solutions and standard hydrogen is setup and connected to it through a salt bridge. Both the electrodes are connected with a voltmeter as shown in figure,



Reactions

Anode (oxidation): $\text{Zn (s)} \rightarrow \text{Zn}^{2+} (1 \text{ M}) + 2\text{e}^{-}$

Cathode (reduction): $2\text{H}^{+} (1 \text{ M}) + 2\text{e}^{-} \rightarrow \text{H}_2 (1 \text{ atm})$

Over all Reaction : $\text{Zn (s)} + 2\text{H}^{+} (1 \text{ M}) \rightarrow \text{Zn}^{2+} + \text{H}_2 (1 \text{ atm})$

Here the Zn electrode potential is unknown. It is measured experimentally. The cell potential is found to be 0.763 V.

$$E^{\circ} \text{ cell} = E^{\circ} \text{ SHE} - E^{\circ} \text{Zn}$$

$$E^{\circ} \text{ cell} = 0 - E^{\circ} \text{Zn} = 0.763$$

$$E^{\circ} \text{Zn} = - 0.763 \text{ V}$$

Disadvantages of SHE

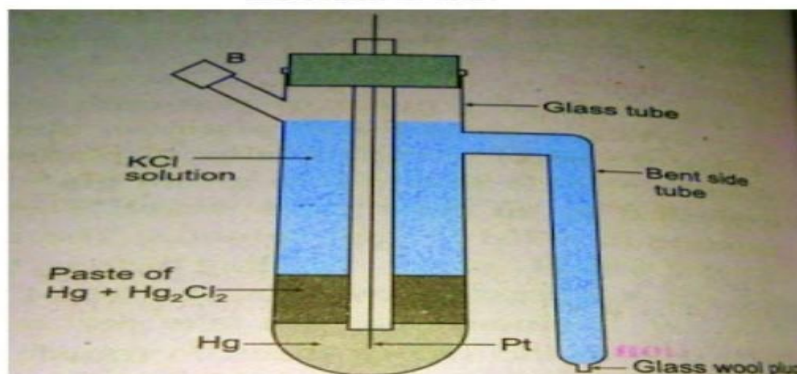
- 1) It is difficult to get pure and dry hydrogen gas.
- 2) It is difficult to maintain the pressure of hydrogen gas at exactly 1 atm throughout the measurement.
- 3) It is difficult to maintain the concentration of H^{+} ions as exactly 1M throughout the measurement.

4) It is not handy.

Q16. Write a short note on Calomel Half Cell or calomel electrode.

Because of the experimental difficulty involved in the preparation and use of standard hydrogen electrode (SHE), secondary reference electrodes have been composed with the former and widely used. Amongst these, there are calomel electrode which is extensively used as reference electrode.

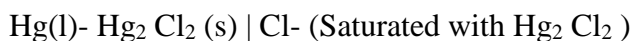
Secondary electrode or calomel electrode



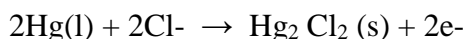
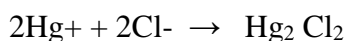
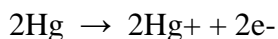
Construction

The electrode consists of a glass vessel A to which one side arm B is attached for making electrical contact and another arm C for insertion of any desired solution into the bottom of A. A Pt-wire is sealed into the bottom of A over which are placed in turn a layer of specially purified mercury and paste of mercury and calomel and then the appropriate KCl solution saturated with calomel was filled into the cell.

Representation



Reaction



Advantages of Calomel electrode

- 1) It is easy to construct and convenient to handle.
- 2) The potential of the electrode is reproducible and remains constant.
- 3) No separate salt bridge is required for constructing a galvanic cell by combining it with other electrode.

Q17. How standard electrode potential of Zn / Zn^{2+} electrode is determined experimentally with reference to calomel electrode?

It is a secondary reference electrode to determine the standard potential of other electrodes.

Cell representation

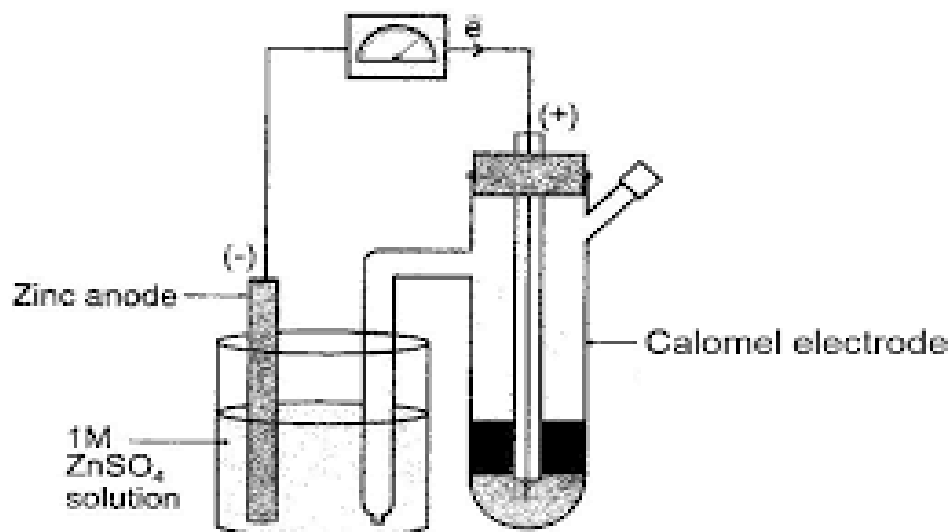


The Emf of cell can be measured experimentally. From the measured cell potential, the standard potential of the given electrode can be calculated as follows:

$$E_{cell} = E_{cal} - E^{\circ}Zn$$

$$E^{\circ}Zn = E_{cell} - E_{cal}$$

Here E_{cal} is the emf of calomel electrode which depends on the concentration of KCl solution.



Determination of standard electrode potential by calomel electrode

Q18. Explain the term electrochemical series or emf series.

When the electrodes are arranged in the order of their increasing standard reduction potentials on a hydrogen scale, it is called electrochemical series.

The reason for using the hydrogen scale is that the values of the standard reduction potentials are measured with the standard hydrogen electrode (SHE) as the reference electrode whose potential is considered as zero.

Characteristics of electrochemical series

- The metals at the top of the series, such as the alkali metals and the alkaline earth metals, are more reactive or are most easily oxidized than the metals found at the bottom of the series.
- These metals at the top of the activity series are called active metals.
- The metals at the bottom of the series, such as the transition metals, are very stable and form compounds less readily.
- These metals, such as copper and gold, are used to make coins and jewellery and are called noble metals because of their low reactivity.
- Reduction always takes place at the cathode and oxidation at the anode.
- Higher the reduction potential , greater is the tendency of the element to get reduced.

	Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E° , volt
(More Reactive Elements) Acts as Anode Easily Oxidized Stronger Reducing Agent Weaker Oxidising Agent	Li	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
	K	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.925
	Ca	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
	Na	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714
	Mg	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
	Al	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
	Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.7628
	Cr	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
	Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
	Cd	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.403
	Ni	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.25
	Sn	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
	H_2	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
	Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.337
(Less Reactive Elements) Acts as Cathode Easily Reduced Stronger Oxidising Agent Weaker Reducing Agent	I_2	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.535
	Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.799
	Hg	$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.885
	Br_2	$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.08
	Cl_2	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36
	Au	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.50
	F_2	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87



All The Best