

Electrochemistry

1.1 Electrochemistry

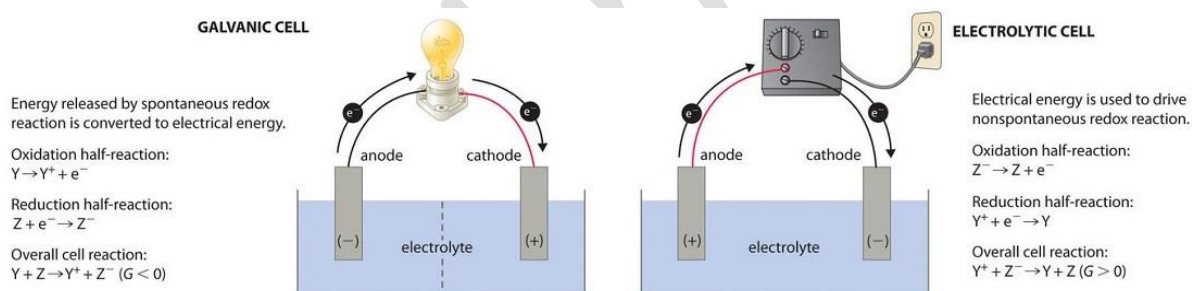
Definition

Electrochemistry is a branch of chemistry concerned with the relation between electricity and chemical change.

- Many spontaneously occurring chemical reactions liberate electrical energy, and some of these reactions are used in batteries and fuel cells to produce electric power.
- Conversely, electric current can be utilized to bring about many chemical reactions that do not occur spontaneously.

1.2 Electrochemical Cell

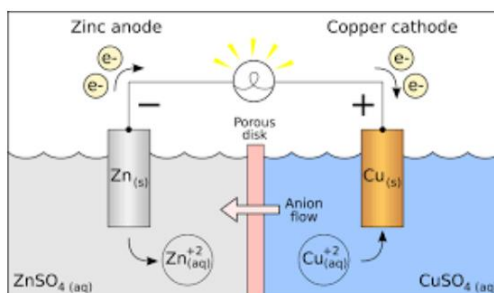
- An apparatus that is used to generate electricity from a spontaneous redox reaction or which uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.
- There are two types of electrochemical cells: galvanic cells and electrolytic cells.



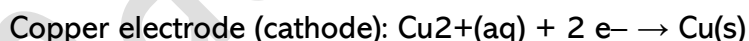
Galvanic Cell	Electrolytic Cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
The redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of molten electrolyte.
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.	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.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

1.3 Galvanic Cell or Voltaic Cell

- An electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy is known as a galvanic cell or a voltaic cell.



- A voltaic cell is an electrochemical cell that uses a chemical reaction to produce electrical energy.
- The cells are constructed in separate beakers. The metal electrodes are immersed in electrolyte solutions. Each half-cell is connected by a salt bridge, which allows for the free transport of ions between the two cells.
- When the circuit is complete, the current flows and the cell “produces” electrical energy.
- The anode is an electrode where oxidation occurs.
- The cathode is an electrode where reduction occurs.
- The operating principle of the voltaic cell is a simultaneous oxidation and reduction reaction, called a redox reaction. This redox reaction consists of two half-reactions. In a typical voltaic cell, the redox pair is copper and zinc, represented in the following half-cell reactions:

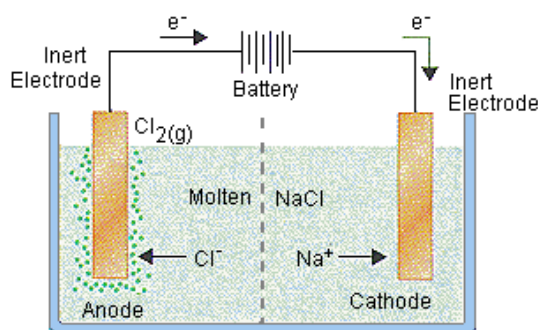


- When the switch is set on, due to the potential difference, electrons flow from the negative electrode to the positive electrode and electricity is generated.
- Voltaic cells are used in watches, clocks, toys, remote controllers, calculators, cell phones, cameras, laptops etc. They are also used as Fuel cells for engines to power up.

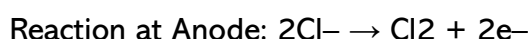
1.4 Electrolytic Cell

- An electrolytic cell can be defined as an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction.
- Electrolytic cells are electrochemical cells that can be used for the electrolysis of certain compounds.
- The three primary components of electrolytic cells are:

- Cathode (which is negatively charged for electrolytic cells)
- Anode (which is positively charged for electrolytic cells)
- Electrolyte
- Molten sodium chloride (NaCl) can be subjected to electrolysis with the help of an electrolytic cell
- Electrolytic Cell Diagram



- Two inert electrodes are dipped into molten sodium chloride (which contains dissociated Na⁺ cations and Cl⁻ anions).
- When an electric current is passed into the circuit, the cathode becomes rich in electrons and develops a negative charge.
- The positively charged sodium cations are now attracted towards the negatively charged cathode. This results in the formation of metallic sodium at the cathode.
- Simultaneously, the chlorine atoms are attracted to the positively charged anode.
- This results in the formation of chlorine gas (Cl₂) at the anode (which is accompanied by the liberation of 2 electrons, finishing the circuit).
- The associated chemical equations and the overall cell reaction are provided below.



- Applications of Electrolytic Cells

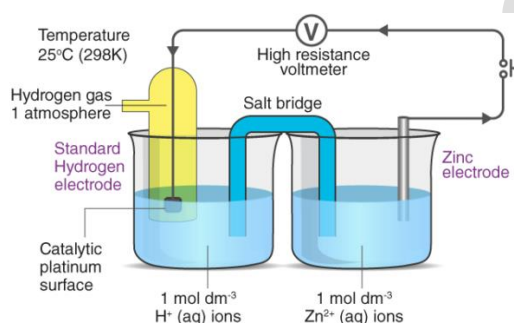
The primary application of electrolytic cells is for the production of oxygen gas and hydrogen gas from water, they are also used for the extraction of aluminium from bauxite. Another notable application of electrolytic cells is in electroplating, which is the process of forming a thin protective layer of a specific metal on the surface of another metal. The electrorefining of many non-ferrous metals is done with the help of electrolytic cells.

1.5 Electrode Potential

- The potential difference, which is measured in *volts* (v), depends upon the substances constituting the electrodes. For any electric cell, the total potential is the sum of those produced by the reactions at the two electrodes:

1.6 Standard Electrode Potential

- Definition:-** Under standard conditions, the standard electrode potential occurs in an electrochemical cell say the temperature = 298K, pressure = 1atm, concentration = 1M.
- The standard electrode potential of a zinc electrode with the help of the standard hydrogen electrode is calculated as follows; -



- If a redox reaction is spontaneous, the ΔG° (Gibbs free energy) must have a negative value. It is described by the following equation:

$$\Delta G^\circ_{\text{cell}} = -nFE^\circ_{\text{cell}}$$

- Where n refers to the total number of moles of electrons for every mole of product formed, F is Faraday's constant (approximately 96485 C.mol^{-1})
- The E°_{cell} can be obtained with the help of the following equation:

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

- Therefore, the E°_{cell} can be obtained by subtracting the standard electrode potential of the anode from that of the cathode.
- For a redox reaction to be spontaneous, the E°_{cell} must have a positive value and hence ΔG° value will be negative.
- This implies that in a spontaneous process,

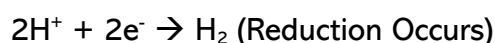
$$E^\circ_{\text{cell}} > 0$$

$$E^\circ_{\text{cathode}} > E^\circ_{\text{anode}}$$

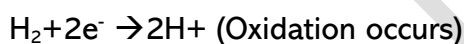
- Thus, the standard electrode potential of the cathode and the anode help in predicting the spontaneity of the cell reaction.
- ΔG° of the cell is **negative** in **galvanic cells** (Spontaneous reaction) and **positive** in **electrolytic cells** (Non-Spontaneous reaction).

1.7 Standard Hydrogen Electrode (SHE)

- Standard hydrogen electrode is the reference electrode that is used to calculate electrode potential of any electrode. It is also called as SHE or NHE
- This setup consists of a beaker having 1 molar HCL solution. In it, a sealed tube having platinum wire is dipped. This platinum wire is further attached to platinum foil. This complete cell is connected to the cell. Then continuously hydrogen gas maintained at 1 atm is bubbled. Platinum foil here acts as a site of reaction.
- The Standard electrode potential of SHE is zero volt. This SHE can act as anode or cathode, depending upon the half cell that is attached to it.
- If it acts as cathode, then following reaction occurs:



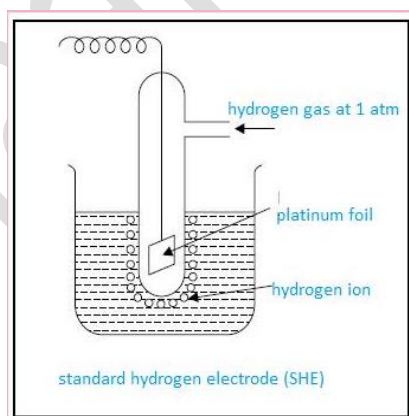
- If it acts as anode, then following reaction occur:



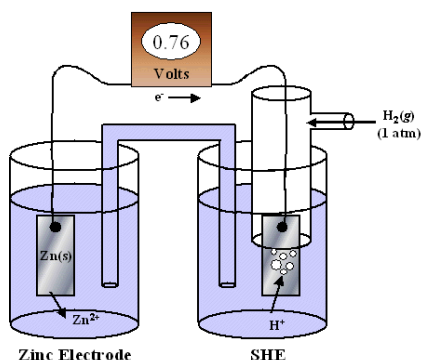
- Applications:

This is used to calculate the electrode potentials of various half cells.

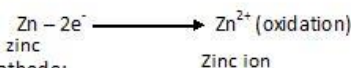
Let us calculate the electrode potential of Zn half-cell. The apparatus is set as shown:



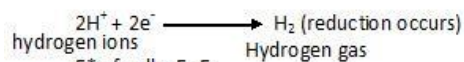
- Zinc is more reactive than hydrogen, and has more tendency to lose electrons. Therefore, the following reactions occur:



At Anode:



At Cathode:



$$E^* \text{ of cell} = E_c - E_a$$

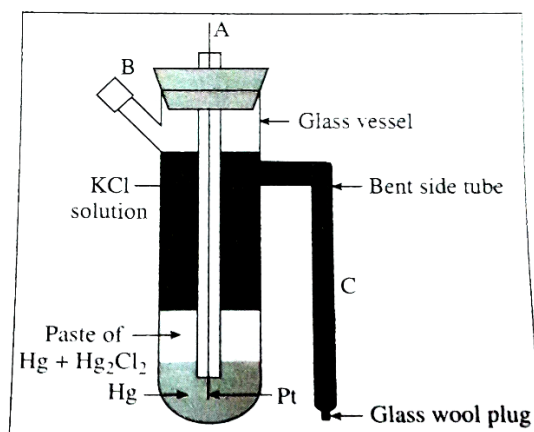
$$0.76 = 0 - E_s$$

Or $E_s = -0.76$ volt

- **Advantages of Standard Hydrogen Electrode (S.H.E.):**
 - Small potential is developed on the hydrogen electrode; hence it can be taken as zero.
 - In determining the single electrode potential, using S.H.E. as a reference, the potential of the unknown potential will be equal to the e.m.f. of the cell.
- **Disadvantages of Standard Hydrogen Electrode (S.H.E.):**
 - It is not convenient to assemble the apparatus.
 - It is difficult to maintain the pressure of hydrogen gas and concentration of HCl.
 - It is difficult to get pure, dry hydrogen gas and prepare ideal platinised platinum plate.
 - The impurities present in H_2 and HCl poison the Pt and affect the equilibrium at the electrode.

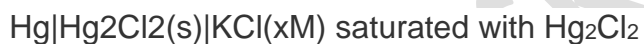
1.8 Calomel Electrode

- Calomel electrode is a type of reference electrode that is based on reactions between mercury (I) chloride (calomel) and elemental mercury.
- These electrodes are commonly used in used in voltmeters and pH meters.
- It used by many two-electrode systems where the supporting electrolyte is a non-reactive chloride salt.
- The calomel electrode's structure consists of an outer glass tube that is fitted with a ceramic frit at the bottom. This permits electrical contact with a solution outside the electrode. An inner tube is placed inside an outer tube. The bottom of the inner tube has glass wool at the bottom to provide for electrical contact between the contents of both tubes.
- Mercury paste is packed on the innermost tube, with mercurous chloride being dispersed in a saturated potassium chloride solution.

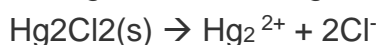


Calomel electrode

- The calomel electrode is a type of half-cell in which the electrode is mercury coated with calomel (Hg₂Cl₂) and the electrolyte is a solution of potassium chloride and saturated calomel. This can be represented as:



- The electrode reaction is:



Overall reaction:



- Advantages of Standard Calomel Electrode:**

- It is very handy, compact, and easy to transport.
- Its potential can remain constant, and it can easily be reproduced.
- It is easy to construct and maintain.
- No separate salt bridge is required
- Potential does not change drastically with change in time and temperature

- Disadvantages of Standard Calomel Electrode:**

- It can not be used in the measurement of cells where K⁺ and Cl⁻ interfere with electrochemical reactions of the cell.
- The oxidation potential depends upon the concentration of KCl. If concentration of KCl changes then oxidation potential changes too.

1.9 Nernst Equation

- Nernst equation is an equation relating the capacity of an atom/ion to take up one or more electrons (reduction potential) measured at any conditions to that measured at standard conditions (standard reduction potentials) of 298K and one molar and one atmospheric pressure.

- Consider a metal in contact with its own salt aqueous solution. Reactions of metal losing an electron to become an ion and the ion gaining electron to return to the atomic state are equally feasible and are in an equilibrium state.



$$K_{eq} = [M/M^{n+}]$$

The Nernst Equation is derived from the Gibbs free energy under standard conditions.

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

$$\text{Therefore } \Delta G = -nFE$$

Under standard conditions,

$$\Delta G^{\circ} = -nFE^{\circ}$$

From thermodynamics, the Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard Equations via

$$\Delta G = \Delta G^{\circ} + RT \ln Q \text{-----(1)}$$

Substituting $\Delta G = -nFE$ and $\Delta G^{\circ} = -nFE^{\circ}$ in equation (1)

$$-nFE = -nFE^{\circ} + RT \ln Q$$

Divide both sides of the Equation above by $-nF$, we get

$$E = E^{\circ} - (RT/nF) \ln Q \text{-----(2)}$$

Converting in the form of \log_{10} .

$$E = E^{\circ} - 2.303(RT/nF) \log_{10} Q \text{-----(3)}$$

At standard temperature $T = 298 \text{ K}$, $F = 96500 \text{ C}$ and $n = 8.314 \text{ J K}^{-1} \text{ M}^{-1}$

Substituting the same we get,

$$E = E^{\circ} - (0.0592/n) \log_{10} Q$$

As $Q = K$ at equilibrium,

$$E = E^{\circ} - (0.0592/n) \log_{10} K_{eq}$$

$$E = E^{\circ} - (0.0592/n) \log_{10} [M/M^{n+}] \text{---(4)}$$

Important Questions:-

1. Define Electrochemistry.
2. Describe galvanic cell. Give applications.
3. Explain electrolytic cell and give applications.
4. Distinguish between Galvanic and Electrolytic cell.
5. Describe standard hydrogen electrode with suitable diagram and reactions.
6. Define standard electrode potential. How is it calculated?
7. Distinguish between electrochemical series and Galvanic series.
8. Describe calomel electrode with suitable diagram and reactions.
9. Derive Nernst equation.
10. Solve numerical problems. (refer one note)