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Electrochemistry

It is a branch of chemistry that deals with the relationship between chemical energy and electrical energy and their inter conversions.

ELECTROCHEMICAL CELLS

These are devices that convert chemical energy of some redox reactions to electrical energy. They are also called Galvanic cells or Voltaic cells. An example for Galvanic cell is Daniel cell.

It is constructed by dipping a Zn rod in $ZnSO_4$ solution and a Cu rod in $CuSO_4$ solution. The two solutions are connected externally by a metallic wire through a voltmeter and a switch and internally by a salt bridge.

A salt bridge is a U-tube containing an inert electrolyte like $NaNO_3$ or KNO_3 in a jelly like substance.

The functions of a salt bridge are:

1. *To complete the electrical circuit*
2. *To maintain the electrical neutrality in the two half cells.*

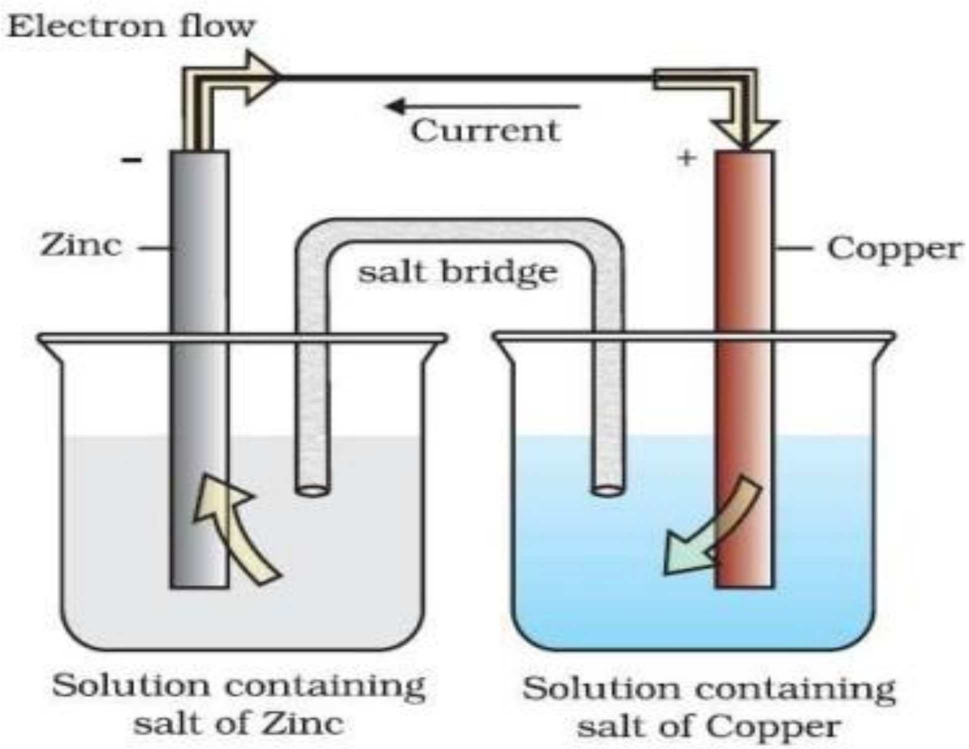
The reaction taking place in a Daniel cell is $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

This reaction is a combination of two half reactions:

(i) $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (reduction half reaction)

(ii) $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)

These reactions occur in two different portions of the Daniel cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.



Electrode Potential

The tendency of a metal to lose or gain electron when it is in contact with its own solution is called ***electrode potential***. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, *standard reduction potential is taken as the standard electrode potential*.

In a galvanic cell, the half-cell in which *oxidation* takes place is called **anode** and it has a negative potential. The other half-cell in which *reduction* takes place is called **cathode** and it has a positive potential.

In a cell, the electrons flow from negative electrode to positive electrode and the current flows in opposite direction.

The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. *The* ***cell potential*** *is the difference between the electrode potentials (reduction potentials) of the cathode and anode.*

The cell ***electromotive force (emf)*** *of the cell is the potential difference between the two electrodes, when no current is flow through the cell*.

By convention, while representing a galvanic cell, the anode is written on the left side and the cathode on the right side. Metal and electrolyte solution are separated by putting a vertical line and a salt bridge is denoted by putting a double vertical line.

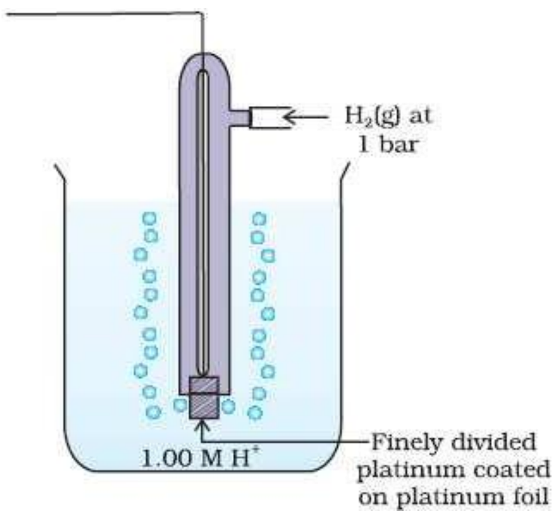
For Daniel cell, the cell representation is **$Zn(s)/Zn^{2+}(aq)//Cu^{2+}(aq)/Cu(s)$**

Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side

i.e. $E_{cell} = E_{right} - E_{left}$ Or, $E_{cell} = E_R - E_L$.

Measurement of Electrode Potential

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. For this purpose a half-cell called **Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE)** is used.



It consists of a platinum electrode coated with platinum black.

The electrode is dipped in an acidic solution of one molar concentration and pure hydrogen gas at 1 bar pressure and 298K is bubbled through it. It is represented as $Pt(s)/H_2(g)/H^+ (aq)$.

By convention, the electrode potential of SHE is taken as zero.

To determine the electrode potential of an electrode, it is connected In series with the standard hydrogen electrode and the emf of the resulting cell is determined by the equation, $E_{cell} = E_R - E_L$

Since the electrode potential of SHE is zero, the value of E_{cell} is equal to the electrode potential of the given electrode.

If the standard electrode potential of an electrode is greater than zero (i.e. +ve), then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species.

Electrochemical series

It is a series in which various electrodes are arranged in the decreasing order of their reduction potential. In this table, fluorine is at the top indicating that fluorine gas (F_2) has the maximum tendency to get reduced to fluoride ions (F^-). Therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent.

Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution.

For electrochemical series, see chapter electrochemistry (NCERT Book) which is present on Class -12th Science Whatsapp group

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