Daniell cell

* Among the galvanic cells when cell is designed is such a manner to make the use of spontaneous reaction between Zn and Cu ions to produce an electric current, the cell is called Daniell cell.

In Daniell cell, the anode is made up of Zn rod and dipped in a solution of $ZnSO_4$ (electrolyte). Similarly, the cathode is made up of Cu rod and dipped in the solution of $CuSO_4$.

When the Zn and Cu electrodes are joined by a wire the following observations are noted:

1. There is a flow of electric current in the external circuit from Cu electrode to Zn electrode i.e, (+)ve electrode to (−)ve electrode. (Saraswati)

2. The Zn rod loses its mass, while Cu rod gains its mass.

3. The concentration of $ZnSO_4$ solution increases while that of $CuSO_4$ solution decreases.

4. The solutions in both the compartments remain electrically neutral.

Actually Zn metal is oxidised at Zn electrode and the electrons released travel through the external circuit to Cu electrode where they are used in the reduction of Cu^{2+} ions into metallic Cu which is deposited on the electrode.

Thus, the overall redox reaction is,

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$
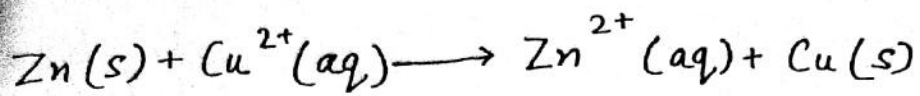
As you know that voltaic or galvanic cell consists of two halves as half-cells. The half-cell in which oxidation occurs is called oxidation half-cell, while in which reduction occurs is called reduction half-cell.
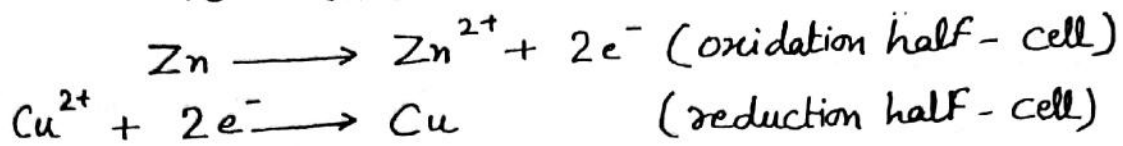
$$Zn \longrightarrow Zn^{2+} + 2e^- \quad (oxidation\ half-cell)$$
$$Cu^{2+} + 2e^- \longrightarrow Cu \quad (reduction\ half-cell)$$

Representation of a Galvanic Cell

The following conventions are used in representing an electro-chemical or Galvanic cell

1. The cell representation contains anodic half on the left hand side and cathodic half on the right hand side.

. The anodic side of the cell is represented by writing metal or solid phase first and then the electrolyte (infact cation of electrolyte).   Saraswati

. The cathodic side, on the other hand, is represented by writing the electrolyte first (anion) and then the metal or solid phase.

. Metal and cation are separated by a semicolon (;) or by a vertical line.(1).

. The concentration of electrolyte is also written within brackets after the cation.

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6. Salt bridge which separates two half-cells is represented by two vertical lines.   Saraswati

Thus, a complete cell can be represented as,

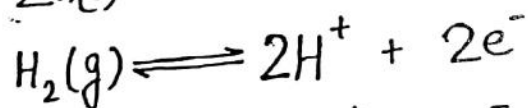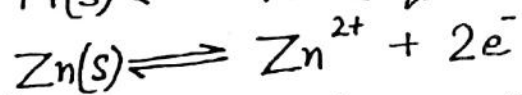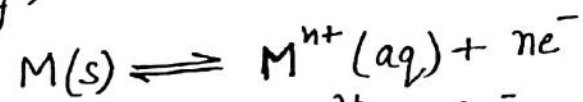$$Zn \mid Zn^{2+} (1M) \parallel Cu^{2+} (1M) \mid Cu.$$
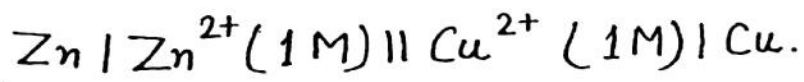
Electrode potential

← When a metallic electrode is dipped in its salt solution, a potential difference is developed between the electrode and its salt solution. The reason for the development of such a potential difference is exchange of electrons between the atoms of electrode and cations in its salt solution. Such a potential difference is called electrode potential. Thus, we can say that the electrode potential is the measure of the tendency of an electrolyte to gain or lose electrons in a half-cell. Saraswati

The electrode potential can be of two types

a) **Oxidation potential** :- The tendency of an electrode to lose electrons or to get oxidised is called its oxidation potential (E_{oxi}) e.g.,
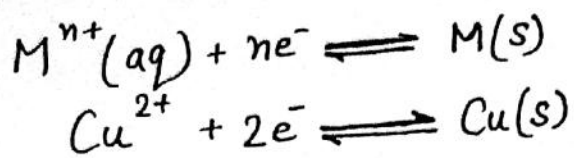
$$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$$
$$Zn(s) \rightleftharpoons Zn^{2+} + 2e^-$$
$$H_2(g) \rightleftharpoons 2H^+ + 2e^-$$
$$Na(s) \rightleftharpoons Na^+ + e^-$$

(Saraswati chemistry)

Such an electrode is negatively charged with respect to its salt solution. Saraswati.

b) **Reduction potential** :- The tendency of an electrode to gain electrons. i.e, to get reduced is called reduction potential (E_{red}), e.g.,

$$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$$

Such an electrode is positively charged with respect to its salt solution.

$$E_{oxi} = -E_{red}$$

The half-cell reactions are always written as reduction half reactions and their potential are represented as reduction potential. Saraswati
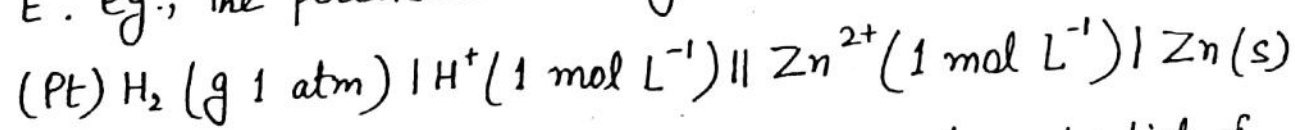
The electrode potential depends upon

(i) Nature of metal and its ions,

(ii) Concentration of ions in the solution,

(iii) Temperature.

Standard Electrode Potential

The potential difference developed between metal electrode and solution of its ions of unit molarity (1M) at 1 atm pressure and 25°C (298 K) is called standard electrode potential. The standard electrode potential is denoted by E^o. eg., The potential of the galvanic cell, Sasaswati

$$(Pt) \, H_2 \, (g \, 1 \, atm) \, | \, H^+ (1 \, mol \, L^{-1}) \, || \, Zn^{2+} (1 \, mol \, L^{-1}) \, | \, Zn(s)$$

at 298 K, is called the standard electrode potential of Zinc electrode. This is denoted by $E^o_{Zn^{2+}/Zn}$

(Saraswati chemistry)

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$$E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

Thus, the standard electrode potential of an electrode describes the electrons accepting tendency of the electrode relative to that of a standard hydrogen electrode, under standard conditions, viz 298 K, 1 atm pressure and 1 mol L^{-1} concentration. Saraswati

Measurement of Electrode Potential

The measurement of absolute value of electrode potential is not possible for a single electrode. Only the difference of potentials between two electrodes can be measured experimentally. It is due to the reason that oxidation or reduction cannot occur alone (i.e, oxidation and reduction occur simultaneously). For indirect measurement of potential of an electrode. we couple the electrode with another electrode whose potential is known. This electrode is called reference electrode. The emf of resulting cell is measured experimentally. Now, as we know the emf as well as the potential of reference electrode, the potential of other electrode is determined. Some important reference electrode are as follows.

Normal Hydrogen Electrode (NHE)

Hydrogen electrode is the primary reference electrode as it is used normally to know the electrode potential of a half-cell of galvanic cell. The reason for such a usage is that it can act as a cathode as well as an anode with respect to other electrode, due to following reactions   Sarraswati

$$H_2(g) \longrightarrow 2H^+ + 2e^-$$

$$2H^+ \xrightarrow{+2e^-} H_2$$
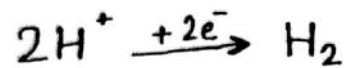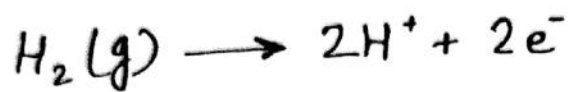
The electrode potenial of NHE is taken as zero. It is represented as

$$Pt \mid H_2 \,(atm) \mid H^+ \,(1M)$$
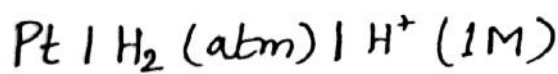
The hydrogen electrode is constructed by bubbling H_2 gas at a certain pressure over platinised platinum sheet immersed in 1 M HCl Solution. Saraswati

Standard Hydrogen Electrode (SHE)

A hydrogen electrode in which the pressure of H_2 gas is maintained at 1 atm and the concentration of H^+ ions in the solution is 1 M, is called Standard hydrogen electrode. The emf of SHE is taken as 0.00V at all temperatures.

Saraswati

$\leftarrow H_2(g)$ at 1 bar

1.00 M HCl

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