

UNIT I

ELECTRO-CHEMICAL ENERGY SYSTEMS.SINGLE ELECTRODE CONCEPT.

5.13 ELECTRODE POTENTIAL

A metal (M) consists of metal ions (M^{n+}), with the valency electrons that bind them together. Now, if a metal is in contact with a solution of its own salt, the positive

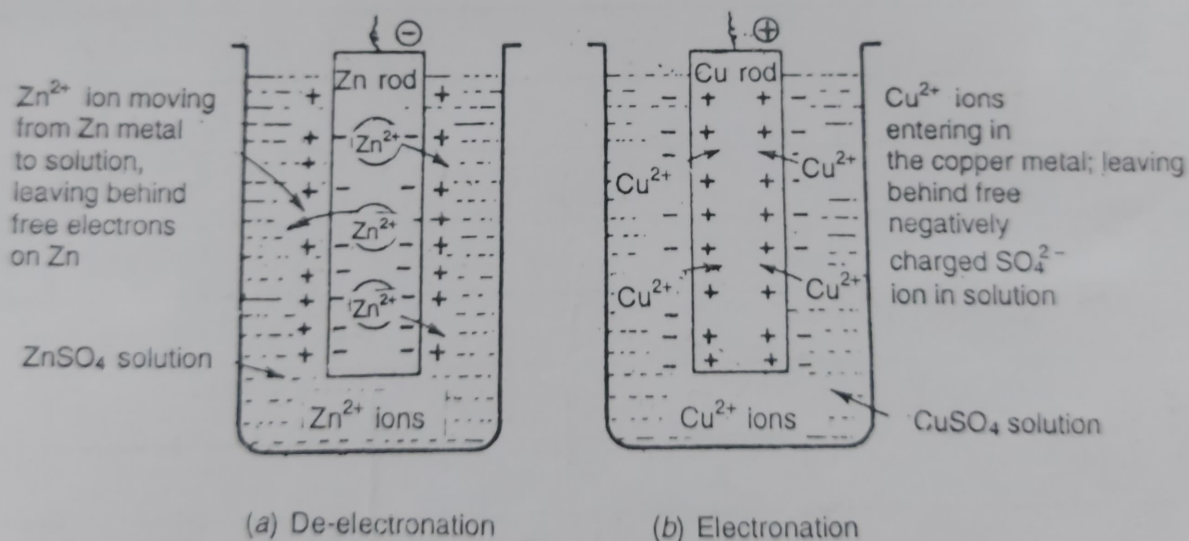
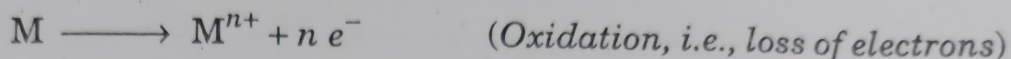


Fig. 6. Electrode potential.

ions in the metal come into equilibrium with those in the solution ; leaving behind an equivalent number of electrons on the metal. Thus, the metal acquires a *negative*

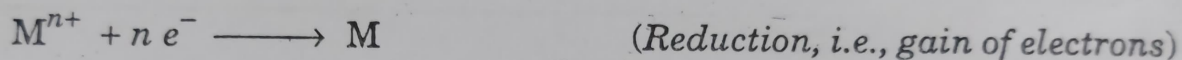
charge, since it is now left with excess number of electrons and a number of positive metallic ions are formed in solution [see Fig. 6 (a)], e.g., in case of Zn in ZnSO_4 solution. Conversely, if the positive metallic ions, from the solution, enters the metallic lattices, then metal acquires a positive charge, e.g., in case of Cu in CuSO_4 solution [see Fig. 6 (b)]. Thus, following *two* chemical reactions take place, when a metal is in contact with its salt solution :

(1) *Positive metallic ions passing into solution.*



when n electrons are left behind on the metal; and it acquires a *negative charge*. The rate of this reaction depends on : (i) the nature of the metal ; (ii) the temperature, and (iii) the concentration of metal ions in solution.

(2) *Positive ions depositing on the metal electrode.*

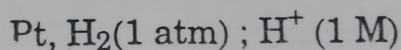


when metal acquires a *positive charge*. The rate of this reaction depends on the above three factors.

When a metal is placed in the solution of its own salt, the chemical reaction (1) or (2), as the case may be, takes place and ultimately a dynamic equilibrium is established, because negative or positive charge developed on the metal attracts the positively or negatively charged free ions in the solution. Due to this attraction, the positive or negative ions remain quite close to the metal. Thus, a *short of layer of positive ions* [see Fig. 6 (a)] or *negative ions* [see Fig. 6 (b)] is formed all around the metal. This layer, is called **Helmholtz electrical double layer**. A difference of potential is, consequently, set up between the metal and the solution. This potential difference will persist as long as the charge is allowed to remain on the metal; and this will prevent any further passing of the positive ions from or to the metal. At equilibrium, the potential difference between the metal and solution becomes a constant value. The equilibrium potential difference so-established, is called the "*electrode potential*" of the metal. Thus, **electrode potential of a metal** is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25°C . Consequently, the tendency of an electrode to **lose electrons** is a direct measure of its tendency to get oxidised ; and this tendency, is called **oxidation potential**. Similarly, the tendency of an electrode to **gain electrons** is a direct measure of its tendency to get reduced; and this tendency, is known as **reduction potential**. It is quite obvious that the value of reduction potential is *negative* of its oxidation potential and *vice versa*. Thus, if the oxidation potential of an electrode is $+X$ volt, then its reduction potential will have a value of $-X$ volt.

DETERMINATION OF STANDARD ELECTRODE POTENTIAL

Measurement of electrode potential : It is impossible to know the absolute value of a single electrode potential (e.g., potential difference between an electrode and the surrounding solution of its own salt). We can only measure the difference in potential between two electrodes potentiometrically, by combining them to form a complete cell. In other words, we can only determine the *relative value* of electrode potential, if we can *fix arbitrarily* the potential of any one electrode. For this purpose, the potential of a **standard hydrogen electrode (SHE)** or **normal hydrogen electrode (NHE)** [i.e., a platinum electrode in contact with 1 M H^+ ion concentration and hydrogen gas at atmospheric pressure is constantly bubbled over it] (see Fig. 7) has been arbitrarily fixed at **zero**; and all other electrode potentials are expressed in comparison with this value. This electrode is represented as :



and either of the following reactions may take place at this electrode :

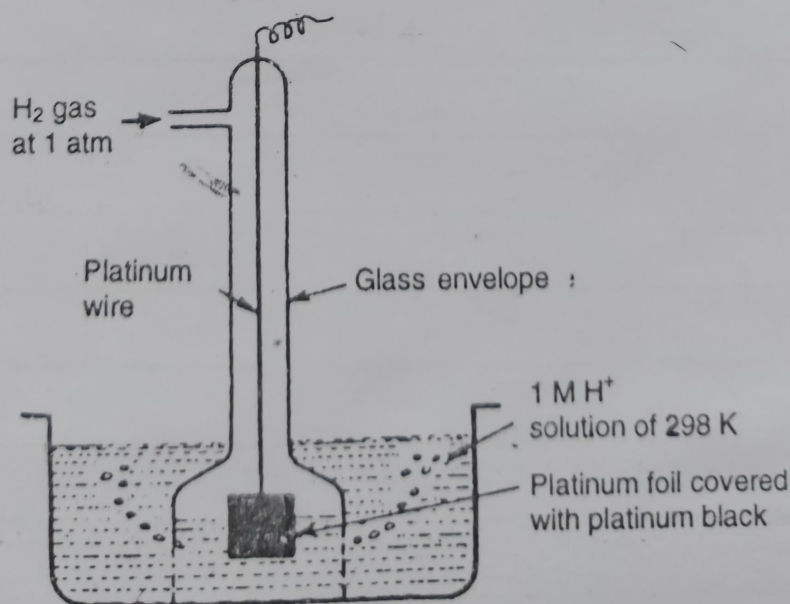


Fig. 7. Normal hydrogen electrode.

Thus, in order to measure the electrode potential (say of Zn electrode dipping in 1M ZnSO_4), we couple this electrode with SHE through a salt bridge [see Fig. 8]. The voltmeter reading directly gives the electrode potential, since the potential of SHE is zero. As zinc electrode acts as **anode** (or electron-releasing) in this case, so the electrode potential, 0.76 volt, is *oxidation potential*. Consequently, *reduction potential of zinc electrode is -0.76 volt*. According to **modern conventions**, if on

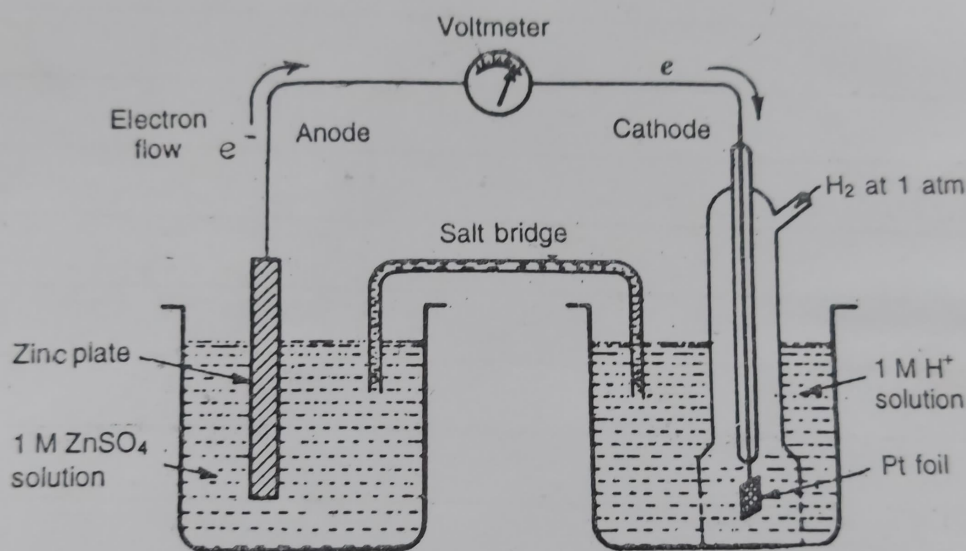
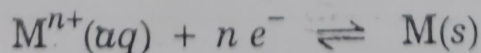


Fig. 8. Measurement of electrode potential of zinc electrode (Zn^{2+}/Zn). Here Zn electrode acts as *anode* w.r.t. SHE, so electrode potential of Zn is given a negative sign (viz., - 0.76 volt).

coupling of an electrode with SHE, reduction occurs at the given electrode, the electrode potential (reduction) is given a positive sign; and if oxidation occurs at the given electrode, the electrode potential (reduction) is given a negative sign. It is clear from Fig. 9 that electrode potential of copper electrode is positive (i.e. + 0.34 volt).

Expression for electrode potential : Consider a general redox reaction :



Now for a *reversible reaction*, the free energy change (ΔG) and its equilibrium constant (K) are inter-related as ;