Overpotential or overvoltage

The overvoltage of an electrochemical reaction may be defined as the difference between the potential of an electrode, (a) at which the reaction is actively taking place and another electrode, (b) which is at the equilibrium potential for the same reaction. With platinum and lead electrodes we require a current of 1·7 and 2·2 volt, respectively for the electrolysis of dilute H_2SO_4 against a theoretical value of 2·3 volt. This is explained by the fact that the passage of a small current is accompanied by a relative large polarisation which depends upon the nature of the electrode. So, overvoltage may also be defined as the difference between the potential of an electrode when gas evolution is actually observed and the theoritical reversible value for the same solution.

The concept of overvoltage was extended by Tafel (1905). He measured the excess potential over the reversible values at a cathode at which hydrogen was being evolved at a definite current density (defined as "current per unit area of electrode surface", and is expressed as ampere or milliampere per sq. cm). So, the point at which the gas bubble formation commences is termed as bubble overvoltage. The bubble overvoltages of metals in dilute H_2SO_4 areas follows: Platinised platinum 0·005 v., smooth platinum 0·201 v., silver 0·15 v. lead 0·64 v.

The effect of surface on overvoltage is that a roughened surface has an invariably low overvoltage than a smooth electrode of the same metal.

Types of Overpotentials or Overvoltages

(1) Hydrogen Overvoltage :- The hydrogen overvoltage may be defined as, "the difference between the potential of an electrode at which hydrogen gas is actually evolved and the potential of the reversible hydrogen electrode with reference to the same solution". At platinised platinum and at zero current density, the hydrogen overvoltage is zero.

(2) Oxygen Overvoltage - Similarly, effects had been observed in the liberation of oxygen at the anode by Coehn and Osaka. It is found that the anode potential at most metals, must be considerably more positive than the calculated value, in order to cause the liberation of oxygen at any appreciable rate. It will be observed that metals which have a high hydrogen overvoltage, usually have a low oxygen overvoltage and vice-versa.

metal overvoltage - Common metals, except Fe, Co and Ni, start to be deposited from solution at their reversible potentials. For first triad of group VIII there is, however, a definite over-voltage for their deposition of the order of 0.2-0.3 volt at 18°. On heating, there is a marked reduction in overvoltage. It is supposed that these metals are first deposited from solution in a metastable state, which is then followed by the deposition of a solid solution of metastable and stable forms, which are considered

to be deposited at more negative potential than the reversible value for the stable metal. The reverse of overvoltage occurs when the deposited metal is capable of dissolving in the cathode. For example, sodium will deposit from normal solutions of its salts on a mercury cathode at a potential of 1·2 volt instead of at about −2·7 volt, owing to the formation of sodium amalgam.

Factors Affecting Overvoltage

(i) **Current density** - Provided hydrogen is not removed by reaction with oxygen or other oxidising agents, the overvoltage, w increases with increasing current density, I according to the equation

$$w = a + b \log I$$

where a and b are constants.

(ii) **pH** - In the absence of strongly adsorbed ions, the overvoltages at most cathodes are independent of hydrogen ion concentration over a large range of pH values in strongly acidic or alkaline solutions, deviations sometimes occur, which may be due to a large concentration of hydrogen or hydroxyl ions, respectively.

(iii) **Temperature** - Overvoltage decreases generally with increasing temperature. The change is approximately 2 millivolt per degree.

(iv) **Impurity** - Overvoltage is susceptible to the presence of impurities in the cathode material.

(v) **Pressure** - At higher pressure, the overvoltage is slightly affected, while at lower pressure, it increases rapidly on cathodes of copper and nickel etc.

(vi) **Surface Area** - On smooth, even and polished surface, the overvoltage is greater than ona rough, uneven surface.