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Electrochemistry

Over voltage or over potential

overvoltage may 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 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 overvoltage for hydrogen is independent of pH but sometimes decreases to a little extent in alkaline solution. It also decreases with rise in temperature. The bubble overvoltage of metals in dilute H_2SO_4 are as follows
platinised platinum 0.005 V, smooth pt 0.21 V
Ag 0.15 V, pb 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 overvoltages

(2) Hydrogen overvoltage:-

At a platinised platinum electrode H_2 is liberated practically at the reversibly hydrogen potential of the solution with other electrode a more negative

potential is required to secure its liberation.

The hydrogen overvoltage may be defined as "The difference between the potential of an electrode at which hydrogen gas is actually evolved and 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.

Tafel (1905) made measurements with solution freed from oxygen and found that hydrogen overvoltage at mercury electrode was a function of current and is given by.

$$i = k e^{-\beta v} \qquad (1)$$

where i = current

v = potential of the cathode.

k = a ~~const~~ constant.

$\beta = F/2RT$

This was confirmed by Lewis and Jakson taking logarithm of Tafel's equation and replacing β by $\frac{F}{2} \times \frac{1}{2.303\,RT}$ we have

$$\log i = \log k - \frac{VF}{RT \times 2.303 \times 2}$$

$$\text{or} - \frac{dv}{d\log i} = \frac{4.606}{F} RT$$

$$\text{or} \quad - \frac{dv}{d\log i} = 0.116 \text{ volt at } 18^\circ C.$$

It is thus clear that the cathode potential becomes 0.116 volt more negative each ten fold increase in the current.

(ii) oxygen overvoltage :—

similarly, effects had been observed in the libration of oxygen at the anode by Caehn and Osaka. It is found that the anode potential at most metals must considerably more pasilive than the calculated value. It will be observed that metals which have a high hydrogen overvoltage usually have a low oxgen overvoltage. and vice versa.

(3) Metal overvoltage :—

common metals, except Fe, Co, Ni, start to be deposited from solution of their reversible potential. For first triad of group VIII there is, however, a definite overvoltage for their deposition of the order of 0.2 - 0.3 volts at 18°C. on heating there is a marked reduction in overvoltage.