

Dr. Yogendra Prasad Singh

M.Sc. Sem-I  
CC-2. Unit II

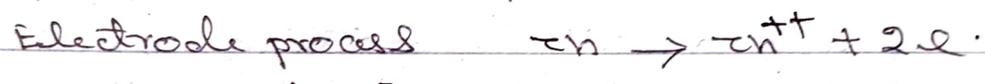
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Electrode potential in terms of chemical potential and activity

The electrode potential and cell potential depends on (i) The nature of the metal (ii) concentration (iii) of the solution (iii) temperature.

Nernst equation gives a relationship between the electrode potential or cell potential with temperature and concentration of solutions.

Let us take the zinc electrode dipped in a solution of  $Zn^{++}$  ions.



If  $E_{Zn}$  and  $E^{\circ}_{Zn}$  denote the electrode potential of zinc in solution of  $Zn^{++}$  ions of activity  $a_{Zn^{++}}$  and in a solution of  $Zn^{++}$  ions of unit activity respectively.

Then applying Nernst equation.

$$E_{Zn} = E^{\circ}_{Zn} - \frac{RT}{2F} \ln \frac{a_{Zn^{++}}}{a_{Zn}}$$

$$E_{Zn} = E^{\circ}_{Zn} - \frac{RT}{2F} \ln a_{Zn^{++}}$$

[  $\because$  activity of pure  $Zn$  metal i.e.  $a_{Zn} = 1$  ]

$E^{\circ}_{Zn}$  is electrode potential of  $Zn$  in a standard solution of  $Zn^{++}$  ions of unit activity.

$E^{\circ}_{Zn}$  = standard electrode potential of  $Zn$ .

$\therefore$  oxidation takes place so, it is also:

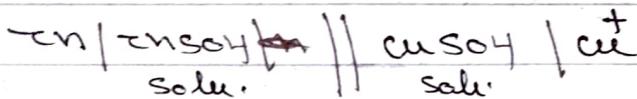
known as oxidation potential or standard oxidation potential.

If instead of oxidation reduction takes place, then it is called reduction potential. For a given electrode, the oxidation and reduction potential are exactly equal in magnitude but opposite in sign.

The oxidation potential of  $\text{Zn}$  electrode in a solution of  $\text{Zn}^{2+} = 0.1$  is  $0.799$  volts. The reduction potential in same solution would be  $-0.799$  volts.

### EMF of cells and Electrode potential

Every cell has a (+ve) and (-ve) terminal called positive and negative electrode. To express a cell in writing +ve electrode placed on right and negative at the left. e.g. in Daniell cell.

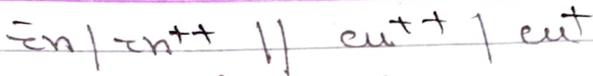


At positive terminal on the right, the current enters the external circuit and flow towards negative terminal.

At +ve terminal electrons are used up, hence reduction occurs. At (-ve) terminal the current enters the cell, electrons are produced and so oxidation occurs.

The emf of the cell is  ~~$E = E_{\text{cathode}} - E_{\text{anode}}$~~  algebraic sum of the actual potential of the two electrodes.

for Daniell cell.



The cell reaction is



The e.m.f of cell

$$= E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}} \cdot a_{\text{Cu}}}{a_{\text{Cu}^{2+}} \cdot a_{\text{Zn}}}$$

$$= E^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \quad \text{--- (A)}$$

The oxidation potential of the negative Zn electrode is

$$E_{\text{Zn}} = E^{\circ}_{\text{Zn}} - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$

$$= E^{\circ}_{\text{Zn}} - \frac{RT}{nF} \ln a_{\text{Zn}^{2+}} \quad [; a_{\text{Zn}} = 1]$$

The oxidation potential of the +ve copper electrode is

$$E_{\text{Cu}} = E^{\circ}_{\text{Cu}} - \frac{RT}{nF} \ln \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}}}$$

$$= E^{\circ}_{\text{Cu}} - \frac{RT}{nF} \ln a_{\text{Cu}^{2+}} \quad [; a_{\text{Cu}} = 1]$$

$$\therefore \text{cell e.m.f} = E_{\text{Zn}} - E_{\text{Cu}}$$

$$= E^{\circ}_{\text{Zn}} - \frac{RT}{nF} \ln a_{\text{Zn}^{2+}} - E^{\circ}_{\text{Cu}} + \frac{RT}{nF} \ln a_{\text{Cu}^{2+}}$$

$$= (E^{\circ}_{\text{Zn}} - E^{\circ}_{\text{Cu}}) - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

$$= E^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \quad \text{--- (B)}$$

Eqn. (A) and (B) are same.

The normal standard of the cell is the difference of the normal electrode potential

$$E^{\circ} = E^{\circ}_{\text{Zn}} - E^{\circ}_{\text{Cu}}$$