Application of EMF Measurements

The EMF measurement find a number of applications of these are given below –

1 Determination of PH.

1 By using hydrogen electrode.

The potential of a hydrogen electrode in contact with a solution of H^+ ions involving the reaction

$$H^+ + e \longrightarrow \frac{1}{2} H_2 \ (1 atm)$$

is given by Nernst equation is

$$E_{el} = E^0_{el} + 2.303 \frac{RT}{F} \log [H^+] \quad \text{—— (1)}$$

By conversion E^0_{el} i.e the standard potential of hydrogen electrode is zero

So,

$$E_{el} = 0 + 2.303 \frac{RT}{F} \log [H^+]$$

$$E_{el} = -2.303 \frac{RT}{F} \, pH$$

$$E_{el} = -0.059 \, pH \quad \text{at } 25^\circ C$$

Thus potential of hydrogen electrode depends on the PH of solution with which it is contact. This can be determined by combining the hydrogen electrode with a reference electrode Calomel electrode

$$Pt, H_2 (1 atm) \mid H^+ (c = \text{unknown}) \parallel KCl (\text{sat. soln}) \mid Hg_2Cl_2, Hg$$

The EMF of the cell = $E_R - E_L$

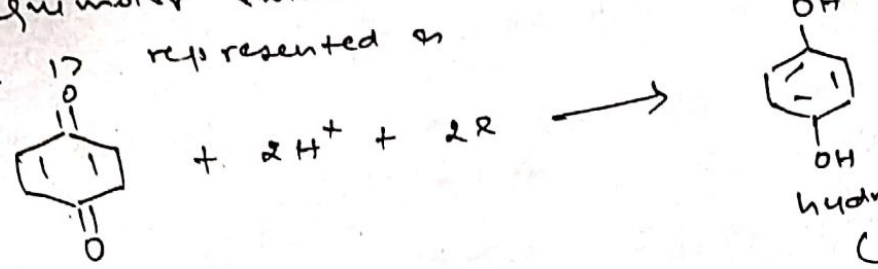
$$E = 0.2422 - (-0.059) \, pH$$

$$E = 0.2422 + 0.059 \, pH$$

$$\boxed{pH = \frac{E - 0.2422}{0.059}}$$

(ii) By using Quinhydrone Electrode.

Quinhydrone consists of a platinum wire placed in a solution containing hydroquinone (QH_2) and Quinone (Q) in equimolar amount. The electrode reaction in this case is represented as



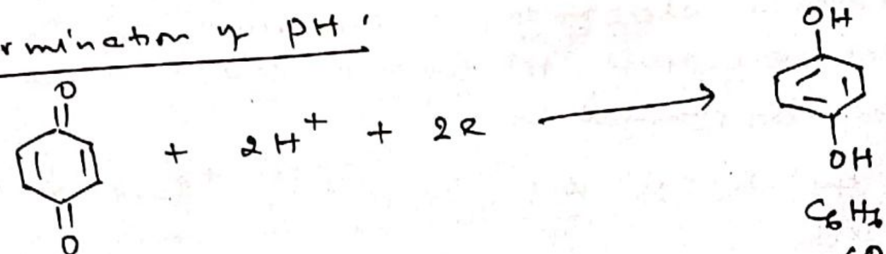
Quinone
(Q)

hydroquinone
(QH_2)

The electrode is represented as $Pt, Q, QH_2 \mid H^+(aq)$,

It is reversible electrode with H^+ ions.

Determination of pH:



$C_6H_4O_2$
(Q)

$C_6H_6O_2$
(QH_2).

Applying Nernst equation

$$E = E^0 - \frac{2.303\,RT}{2F} \log \frac{[QH_2]}{[Q]\,[H^+]^2}$$

$$E = E^0 + \frac{2.303\,RT}{2F} \log \frac{[Q]\,[H^+]^2}{[QH_2]}$$

$$E = E^0 + \frac{2.303\,RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303\,RT}{2F} \log [H^+]^2$$

$$E = E^0 + \frac{2.303\,RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303\,RT}{\cancel{2}F} \times \cancel{2} \log [H^+]$$

$$E = E^0 + \frac{2.303\,RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303\,RT}{F} \log [H^+]$$

Since QH_2 and Q are taken in equimolar amount.

so, $\frac{[Q]}{[QH_2]} = 1$ and $\log \frac{[Q]}{[QH_2]} = 0$

$$E = E^0 + 0 + \frac{2.303\,RT}{F} \log [H^+]$$

$$E = E^0 - \frac{2.303\,RT}{F}\, pH$$

$$E = E^0 - 0.059\, pH \quad \text{at } 25^\circ C$$

The standard electrode potential of quinhydrone electrode $(E^0) = +0.6996$ V

$$E = 0.6996 - 0.059\, pH$$

Thus, potential of quinhydrone electrode depends upon the pH of solution with which it is in contact.

Quinhydrone electrode is combined with a saturated calomel electrode to form a cell. The combination may be represented as:

$$Hg,\ Hg_2Cl_2(s),\ KCl\ (\text{sat. soln})\ ||\ H^+(\text{unknown conc}^n)\ Q, QH_2;\ Pt$$

The EMF of the cell $= E_R - E_L$

$$E = (0.6996 - 0.0591\, pH) - 0.2422 \quad \text{at } 25^\circ C$$

$$0.0591\, pH = 0.6996 - 0.2422 - E$$

$$\boxed{pH = \frac{0.6996 - 0.2422 - E}{0.059}}$$

Limitation of quinhydrone electrode.

The quinhydrone electrode can not be used for solution of pH more then 8. It is more alkaline solutions, hydroquinone ionises appreciably as an acid and also gets oxidised partly by atmospheric oxygen. This alters the normal equilibrium between quinone and hydroquinone which forms the basis of above equation.