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Topic :- Electrochemistry

Determination of pH using Quinhydrone electrode

The quinone – hydroquinone system involves the following equilibrium

$$C_6H_6O_2 \rightleftarrows C_6H_4O_2 + 2H^+ + 2e$$

Hydroquinone (H_2Q) Quinone (Q)

The Potential (E) developed on a platinum electrode immersed in this system is given by the equation,

$$E = E^0 - \frac{2.303RT}{2F} \log \frac{[Q][H^+]^2}{[H_2Q]}$$

$$= E^0 - \frac{2.303RT}{2F} \log \frac{Q}{[H_2Q]} - \frac{2.303RT}{F} \log H^+ \quad \text{---(1)}$$

Instead of taking quinone and hydroquinone a small amount of quinhydrone which is an equimolecular compound of quinone (Q) and hydroquinone (H_2Q) is taken. since hydroquinone (H_2Q) is a weak acid, its ionisation is very small. Particularly if the pH value of the solution is less than 7. Therefore, the concentration of the hydroquinone (H_2Q) is the same

as that of the quinone (Q), i.e the quantity $\frac{[Q]}{[H_2Q]}$ is unity. The middle term in the equation (1) reduces to zero.

Hence $E = E_Q^\circ - \frac{2.303RT}{F} \log[H^+]$

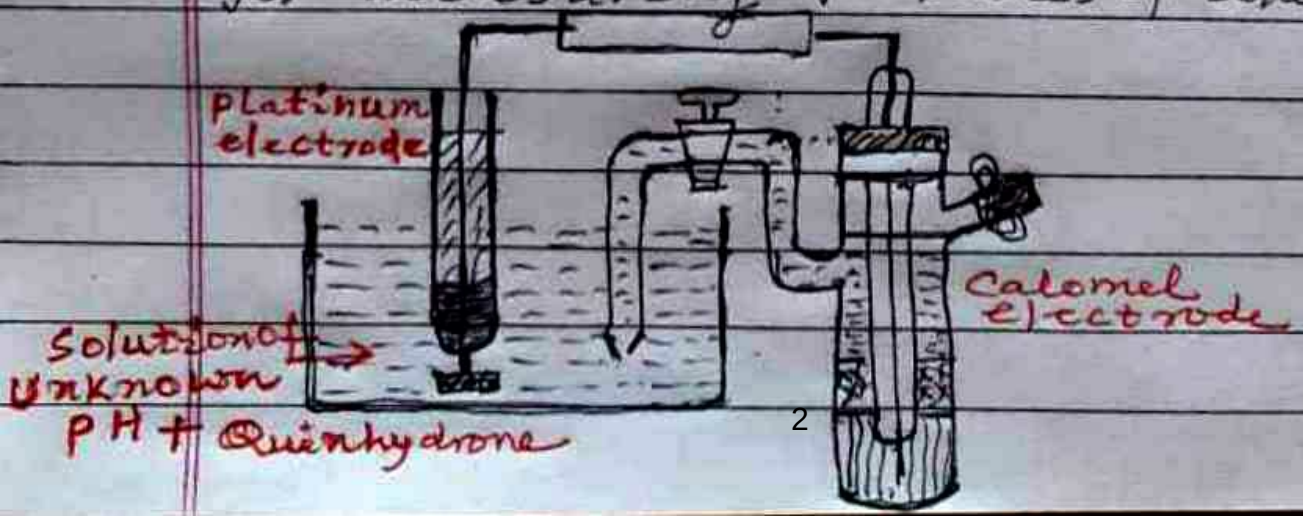
$= E_Q^\circ - 0.0591 \log[H^+]$ at 25°c

$= E_Q^\circ + 0.0591\ pH$ ——— (2)

But E°_Q, the standard oxidation Potential of quinhydrone (when the H^+ ion concentration is unity) is equal to -0.6994. Hence,

$E = -0.6994 + 0.0591\ pH$ ——— (3)

Thus, the potential of the quinhydrone electrode, just as that of the hydrogen electrode, depends upon the pH value of the solution with which it is in contact, i.e the quinhydrone electrode behaves as a reversible hydrogen electrode. Consequently, this electrode can be used for measuring pH values of solution.



This electrode is Preferred to the hydrogen electrode as it can be set up easily by merely adding a pinch of quinhydrone to the solution under examination and inserting a clean Platinum electrode for making electrical connections. The electrode gives accurate results even in the Presence of oxidising ions which usually interfere with the working of the hydrogen electrode

The Potential of the quinhydrone electrode is determined by Connecting it with a Calomel electrode (Reference) The combination may be represented as

$Hg, Hg_2Cl_2(s), KCl(sat\ soln) \| H^+(Unknown\ Concentration)$
$Q \cdot QH_2, Pt$

The EMF of the cell is determined Potentiometrically.

$$EMF = E_{Calomel} - E_{quinhydrone}$$
$$= -0.2422 - (-0.6994 + 0.0591\ PH)$$
$$= 0.6994 - 0.2422 - 0.0591\ PH$$
$$\therefore pH = \frac{0.6994 - 0.2422 - E.M.F}{0.0591}$$

Limitation:-

The quinhydrone electrode Cannot be used for solution of pH value more than 8.