Reversible Electrodes

Gas Electrode

(i) Standard Hydrogen Electrode (SHE) (**reference electrode**)

Metal-Metal Insoluble Salt Electrode

(i) Calomel Electrode (CE)

Calomel Electrode

Cl—Hg—Hg—Cl

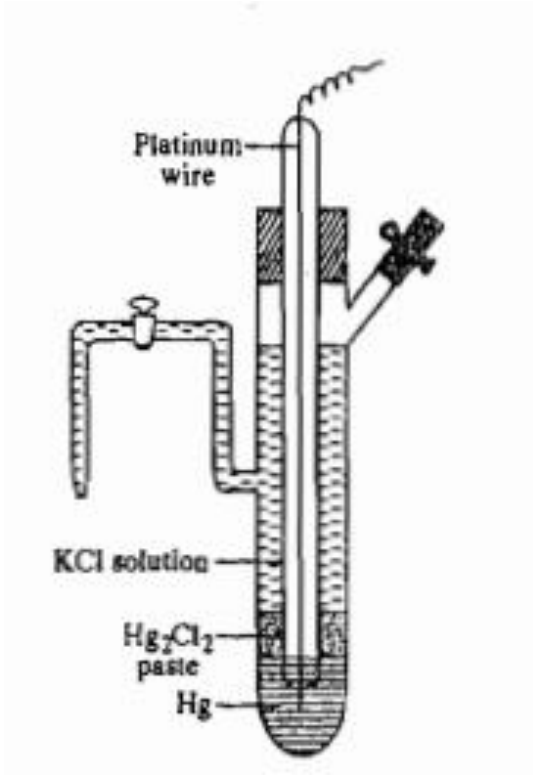
Also called secondary reference electrode.

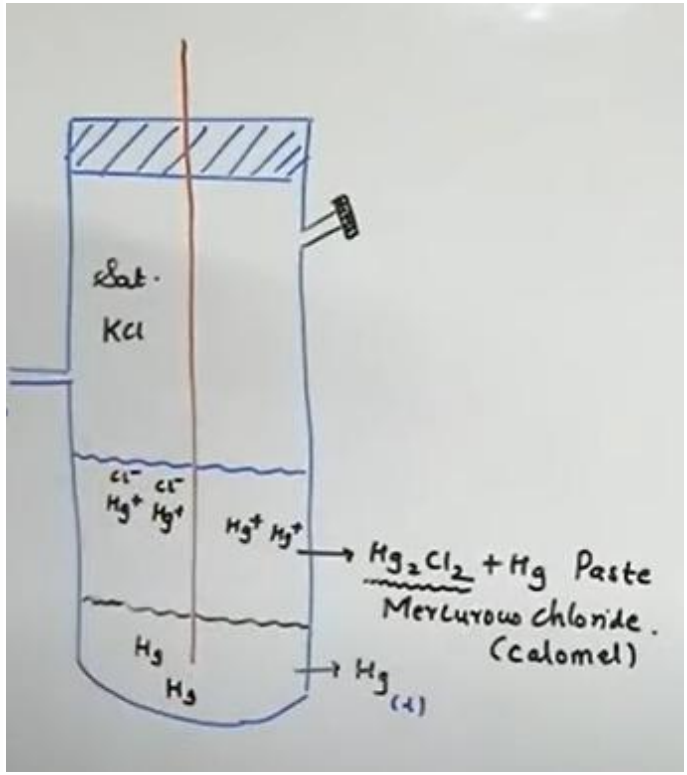
Calomel: Hg_2Cl_2 (mercurous chloride) + Hg paste

Hg_2Cl_2 is a dimeric molecule that ionises as

$$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^-$$

The oxidation state of mercury is **Hg^+**

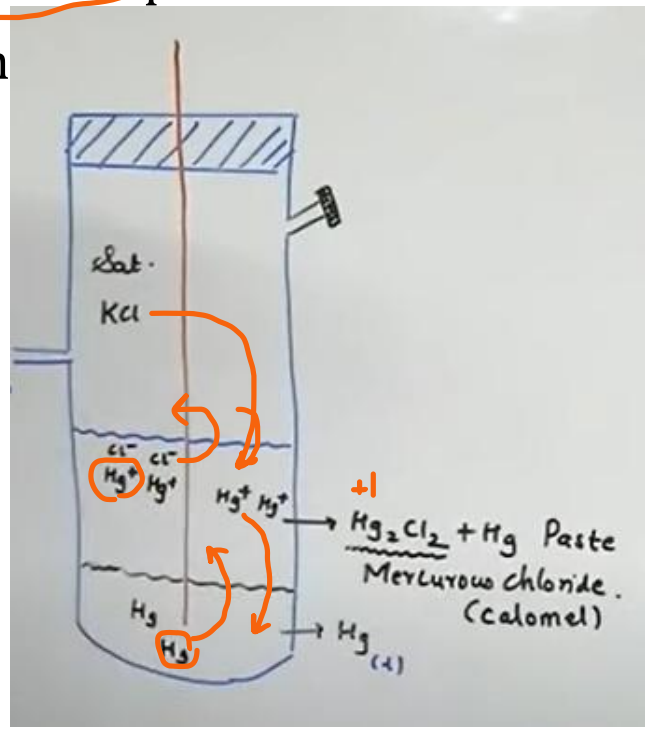




Components of the Electrode

The calomel electrode consists of mercury, mercurous chloride and a saturated solution of potassium chloride. Mercury of high grade is placed at the bottom of a glass tube having side tubes on each side. The layer of mercury at the bottom is covered by a paste of Hg_2Cl_2 and Hg (called Calomel). A saturated solution of KCl is introduced into the tube *via* a side tube and is placed in contact with the calomel layer. The KCl solution can be normal (1N or 1M), decinormal (0.1N or 0.1M) or saturated in terms of concentration. A platinum wire sealed into a glass tube is used to make contact between the electrode and the circuit.

- A calomel electrode can behave both as cathode or as anode under different conditions.
- If the calomel electrode behaves as the cathode i.e., the electrode where reduction takes place.
- In that case, Hg_2^{2+} species present in the calomel phase undergo reduction to form Hg which goes downward to the mercury layer leaving behind the Cl^- ions which move to the aqueous salt layer
- In other words, reduction at the calomel electrode leads to an increase in the number of Cl^- ions.



$$Hg_2Cl_{2\,(aq)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-_{(aq)};\ E^o_{KCl,\ Hg2Cl2/Hg}$$

If the calomel electrode behaves as the anode then, Hg from the Hg layer undergoes oxidation to form Hg_2^{2+} which combine with the Cl^- ions from saturated KCl solution to form sparingly soluble Hg_2Cl_2.

$$2Hg + 2Cl^-_{(l)} \rightarrow Hg_2Cl_{2\,(aq)} + 2e^-;\ E^o_{Hg/Hg2Cl2,\ KCl}$$

The Calomel electrode is reversible with respect to the Cl^- ion.

- The electrode potential (reduction) of the Calomel electrode depends upon the concentration of the KCl solution.

- 1N (or 1M), +0.242V
- 0.1 N (or 0.1M)KCl, +0.338V
- Saturated KCl, +0.242V

The Calomel electrode is robust and highly accurate.

Determination of ΔG, ΔH and ΔS for a cell reaction

For a chemical reaction, the Gibbs Free energy is related to the temperature and Enthalpy as given by the Gibbs-Helmholtz equation.

Enthalpy is the heat change at constant pressure:

$$+\Delta G = +\Delta H - T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P^*$$

=> $-nFE^o = \Delta H - T\{\delta(\Delta G)/dT)_p\}$

=> $E^o = -\{\Delta H/nF) + T/nF \times \{\delta(\Delta G)/\delta T)_p$

=> $E^o = -\{\Delta H/nF) + T/nF \times \{\delta(-nFE^o)/\delta T)_p$

=> $E^o = -\{\Delta H/nF) + T \times \{\delta E^o/\delta T)_p$

$-nFE^o$ is called the electrochemical energy of a cell and is either less than or equal to the enthalpy of the reaction.

The term $\{\delta E^o/\delta T)_p$ is called the temperature coefficient of the electrochemical cell.

For the Daniel cell, the value of $\{\delta E^o/\delta T)_p$ is negligible, so that $\Delta G = \Delta H$

Q. The EMF of a cell Cd, $CdCl_2.5H_2O||AgCl$, Ag in which the cell reaction is

$Cd_{(s)} + 2AgCl_{(aq)} \rightarrow CdCl_{2\,(aq)} + 2Ag_{(s)}$ is 0.6753V at 25 ^oC and 0.6915 V at 0 ^oC. Calculate ΔG, ΔH and ΔS for the reaction at 25 ^oC.

Ans; ΔG (at 25 ^oC) = -nFE = -2 x 96500 x 0.6753 J = -130332.9 J = -130.3329 kJ

We have, $\mathbf{E = -\{\Delta H/nF) + Tx\ \{\delta E^o/\delta T)_p}$

We can re-write this equation as:

$$\mathbf{E_{25^o} = -\{\Delta H_{25^o}/nF) + T_{25^o}\ x\ \{\delta E/\delta T)_p}$$

The temperature coefficient of the cell can be calculated as:

$$\mathbf{\{\delta E/\delta T)_p}$$

$$=(E_2-E_1)/(T_2-T_1)$$

$$=(E_{25^o}-E_{0^o})/(T_{25^o}-T_{0^o})$$

$$=(0.6753-0.6915)/(298 - 273)\ VK^{-1}$$

$$= -\ 6.48 \times 10^{-4}\ VK^{-1}$$

Now,

$0.6753 = \mathbf{-\{\Delta H_{25^o}/2 \times 96500) + 298 \times (-6.48 \times 10^{-4})}$

$\mathbf{\Delta H_{25^o} = -167717\ J = -167.717\ kJ}$

Therefore,

$\Delta G_{25} = \Delta H_{25} - T\Delta S_{25} \Rightarrow \Delta S = (\Delta H - \Delta G)/T = (-167.717-(-130.3329))/298\ kJ/K = -0.1238\ kJ/K$

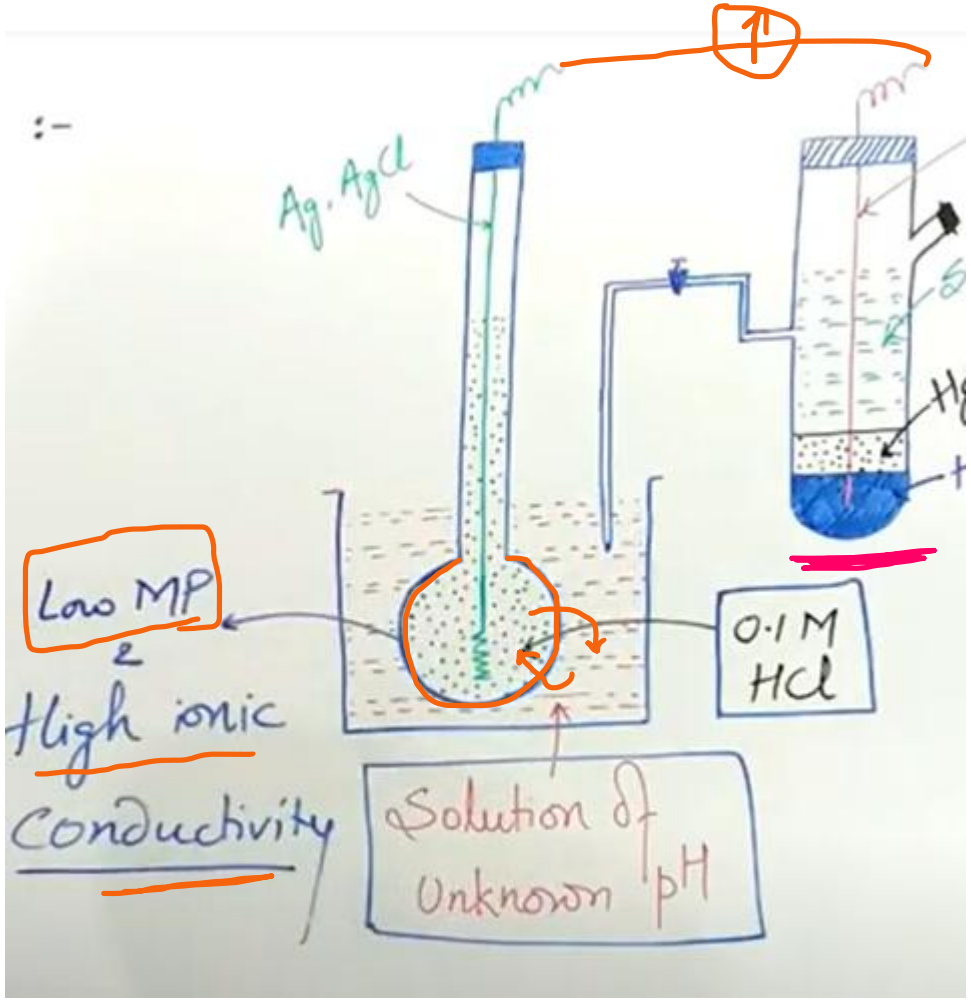
$= -123.8\ J/K$

Glass Electrode

(Ion Selective Electrode)

It is mainly used for the determination of the pH of a solution. The glass electrode is selective for H^+ ions. An indicator electrode is normally used in conjugation with a reference electrode.

It consists of a glass tube with a glass bulb at the end, the glass bulb is made of a thin glass membrane of high ionic conductivity and low melting point. The glass bulb is filled with a solution of 0.1 M HCl. A glass packed silver wire coated with AgCl is inserted to the tube and is used to make contact between the solution and the electric circuit. The glass bulb is dipped into a solution of a unknown pH. The half cell obtained as such is paired with a reference electrode such as calomel electrode to form a Galvanic cell.



- The glass bulb membrane, being conducting in nature can allow the movement of H^+ ions through it. The difference in the concentration of H^+ ions in and out of the glass bulb, generates a potential difference across the glass membrane as such it is a membrane electrode. The presence of Na_2O in the glass membrane helps it in the conduction of H^+ ions. The thickness of the glass membrane is 0.01 – 0.03 mm.
- The glass electrode can be represented **as Ag, AgCl (s)/ HCl (0.1 M), Glass/Unknown solution.**
- The migration of H+ ions in and out of the glass depends upon the concentration difference in and out of the glass membrane.
  - $H^+ + e^- \rightarrow \frac{1}{2} H_2$
- The electrode potential of a glass electrode E_g is given by (at 298K)

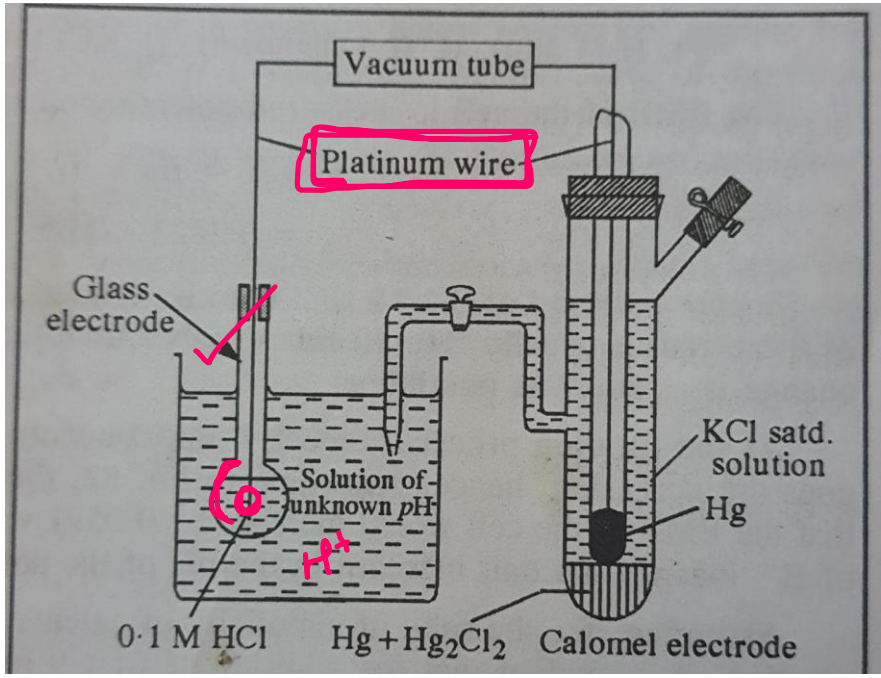
$$E_g = E^o_g - RT/nF \, Ln \{1/[H^+]\}$$

$$E_g = E^o_g - 2.303RT/F \log \{1/[H^+]\}$$

$$E_g = E^o_g - 0.0591 \{ \log 1 - \log[H^+]\}$$

$$E_g = E^o_g - 0.0591 \{0 + (-\log[H^+]\} = E^o_g - 0.0591 \, pH$$

$$E_g = E_g^o - 0.0591 \, pH \Rightarrow E_g = E_g^o + 0.0591 \log [H^+]$$



Upon forming a cell by connecting glass electrode with calomel electrode

A potential of E is observed. In general, the glass electrode behaves as the

cathode.

$E_{cell} = E_{cathode} - E_{anode}$

$E_{cell} = E_g - E_{cal}$

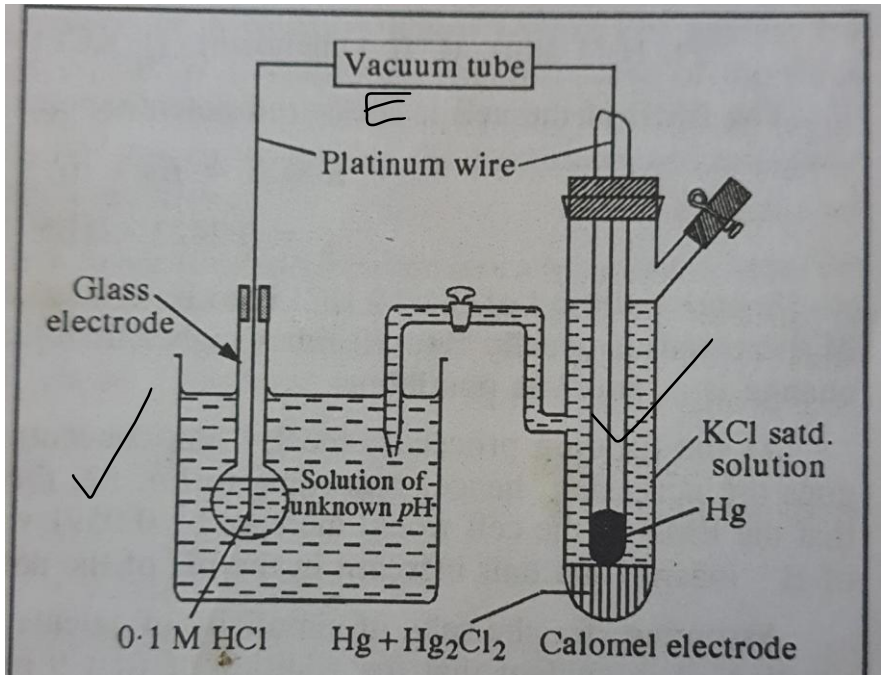
$\Rightarrow E_{cell} = E_g^o - 0.0591\ pH - E_{cal}$

$\Rightarrow pH = (E_g^o - E_{cal} - E_{cell})/0.0591$ at 25 ^oC.

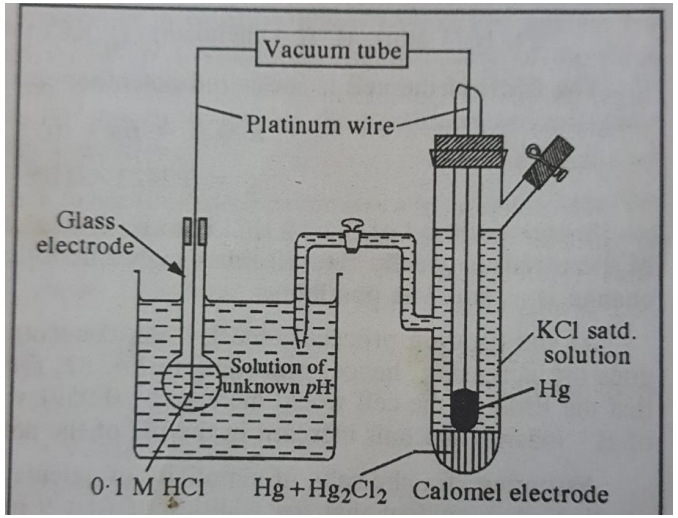
For standard calomel electrode

$E_{cal} = +0.242$ V

$pH = (E_g^o - 0.242 - E)/0.0591$



Q. Upon connecting a glass electrode with a standard calomel electrode (+0.2422 V) at 25 °C and dipping the glass electrode into a solution of pH 4.02, a voltage of +0.814V is measured. What will be the voltage generated when the solution of pH 4.02 is replaced by an acid of pH 3.88.



Ans: For glass electrode combined with a SCE, the pH of the unknown solution is given by:

$$pH = \frac{E_g^{o} - E_{cal} - E}{0.0591}$$

For the first solution, $4.02 = \frac{E_g^{o} - (+0.2422) - 0.814}{0.0591} \Rightarrow E_g^{o} = (4.02 \times 0.0591) + 0.2422 + 0.814 = +1.293\ V$

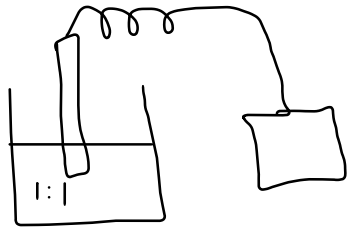
For the second solution (pH = 3.88), $3.88 = \frac{E_g^{o} - E_{cal} - E'}{0.0591} = \frac{1.293 - 0.2422 - E'}{0.0591}$

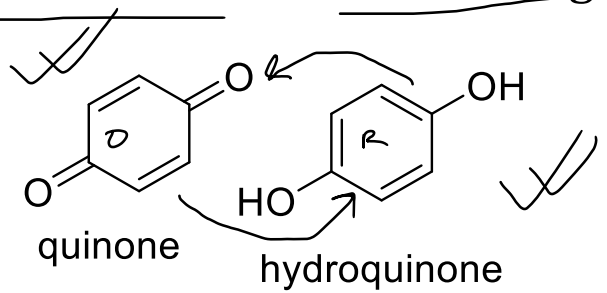
$$\Rightarrow E' = 1.293 - (3.88 \times 0.0591) - 0.2422 = +0.82\ V$$

Oxidation-Reduction Electrode

The term oxidation reduction electrode is used for those electrodes in which the potential is developed due to the presence of ions of the same substance in two different oxidation states. Such an electrode is formed when a non reactive electrode (such as platinum) is dipped into a suitable solution For example, if a platinum electrode is dipped into a solution containing both Fe^{3+} and Fe^{2+} ions, a potential is seen to develop.

The potential at such an electrode arises due to the tendency of the ions in one oxidation state to change into the other more stable oxidation state.



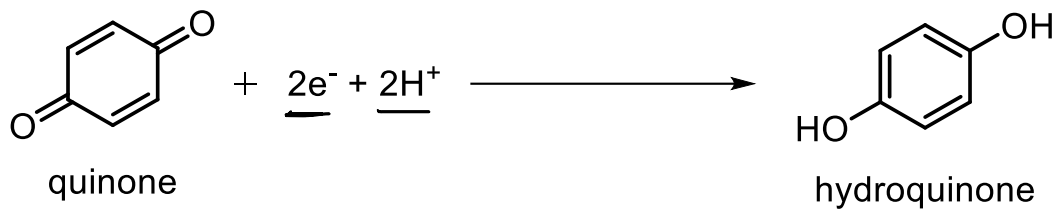


Quinhydrone Electrode

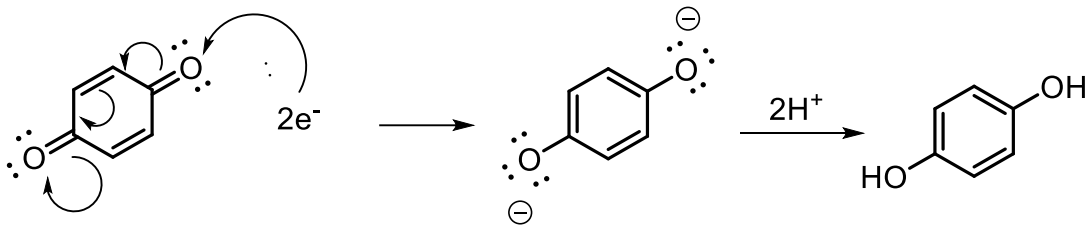
A quinhydrone electrode is an important indicator electrode. It is a type of oxidation reduction electrode. The oxidized form is quinone and the reduced form is hydroquinone.

A quinhydrone electrode consists of a platinum wire placed in a solution containing hydroquinone (QH_2) and quinone (Q) in equimolar amounts.

The electrode reaction (reduction) in this case can be represented as follows:

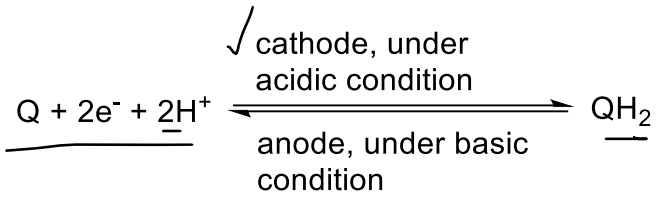


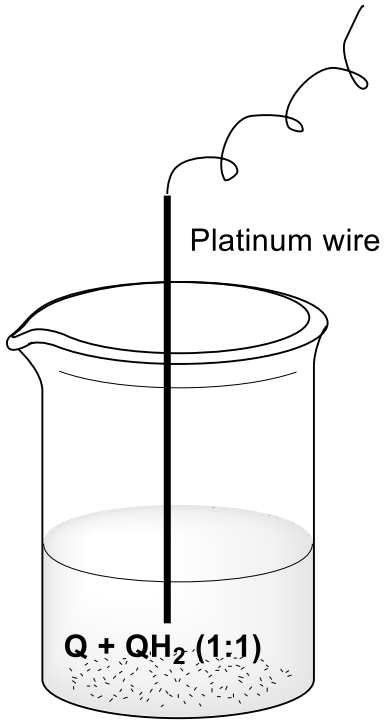
quinone hydroquinone



The quinhydrone electrode is reversible with respect to the hydrogen ions.

In acidic condition, the electrode acts as the cathode while under basic condition it acts as the anode





The Nernst equation can be applied to the reduction half reaction of the quinhydrone electrode as:

$$E_{el} = E^{o}_{el} - \frac{RT}{nF} \ln \frac{[QH_2]}{[Q][H+]^2} = E^{o}_{el} - \frac{RT}{nF} \ln \left\{ \frac{[QH_2]}{[Q]} \times \frac{1}{[H+]^2} \right\} = E^{o}_{el} - \frac{RT}{nF} \ln \left\{ \frac{[QH_2]}{[Q]} \times \frac{1}{[H+]^2} \right\}$$

For electrochemical calculations, instead of concentration, activity term (a) is more preferred. Activity usually refers to effective concentration and is used for concentrated solutions.

The above Nernst equation can be written as:

$$E_{el} = E^{o}_{el} - \frac{RT}{nF} \ln \frac{a_{QH_2}}{a_Q \{a_{H+}\}^2}$$

$$= E^{o}_{el} - \frac{RT}{nF} \ln \left\{ \frac{a_{QH_2}}{a_Q} \times \frac{1}{\{a_{H+}\}^2} \right\}$$

$$= E^{o}_{el} - \frac{RT}{nF} \left[\ln \left\{ \frac{a_{QH_2}}{a_Q} \right\} + \ln \left\{ \frac{1}{(a_{H+})^2} \right\} \right]$$

$$= E^{o}_{el} - \frac{RT}{nF} \left[\ln \left\{ \frac{a_{QH_2}}{a_Q} \right\} + \ln \left\{ \frac{1}{(a_{H+})^2} \right\} \right]$$

$$= E^{o}_{el} - \frac{2.303RT}{nF} \left[\log \left\{ \frac{a_{QH_2}}{a_Q} \right\} + \log \left\{ \frac{1}{(a_{H+})^2} \right\} \right]$$

$$= E^{o}_{el} - \frac{2.303RT}{nF} \left[\log \left\{ \frac{a_{QH_2}}{a_Q} \right\} - 2 \log a_{H+} \right] \quad \text{(I)}$$

$\log \left(\frac{1}{x^2}\right) = -\log x^2$

$\log a^b = b \log a$

For equimolar solution of Q and QH_2 , $a_Q = a_{QH2}$

$$E_{el} = E^o_{el} - \frac{2.303RT}{nF} \left[\log \left\{\frac{a_{QH_2}}{a_Q}\right\} - 2\log a_{H+}\right]$$

$-\log a_{H^+} = pH$

$$E_{el} = E^o_{el} - \frac{2.303RT}{nF} [\log 1 + 2pH]$$

$$E_{el} = E^o_{el} - \frac{2.303RT}{\cancel{2}F} \times \cancel{2}pH \quad \text{(Since n = 2)}$$

$$E_{el} = E^o_{el} - \frac{2.303RT}{F} \times pH$$

The Standard reduction potential for quinhydrone electrode is $E^o_{Q/QH2,\,Pt} = +0.699V$

$$E_{el} = 0.699 - \frac{2.303RT}{F} \times pH ,$$

At 25 ^oC, E_{el} or $E_{QH} = 0.699 - 0.0591$ pH (under acidic conditions, cathode)

- If the quinhydrone electrode is in an acidic medium, then it acts as the Cathode.

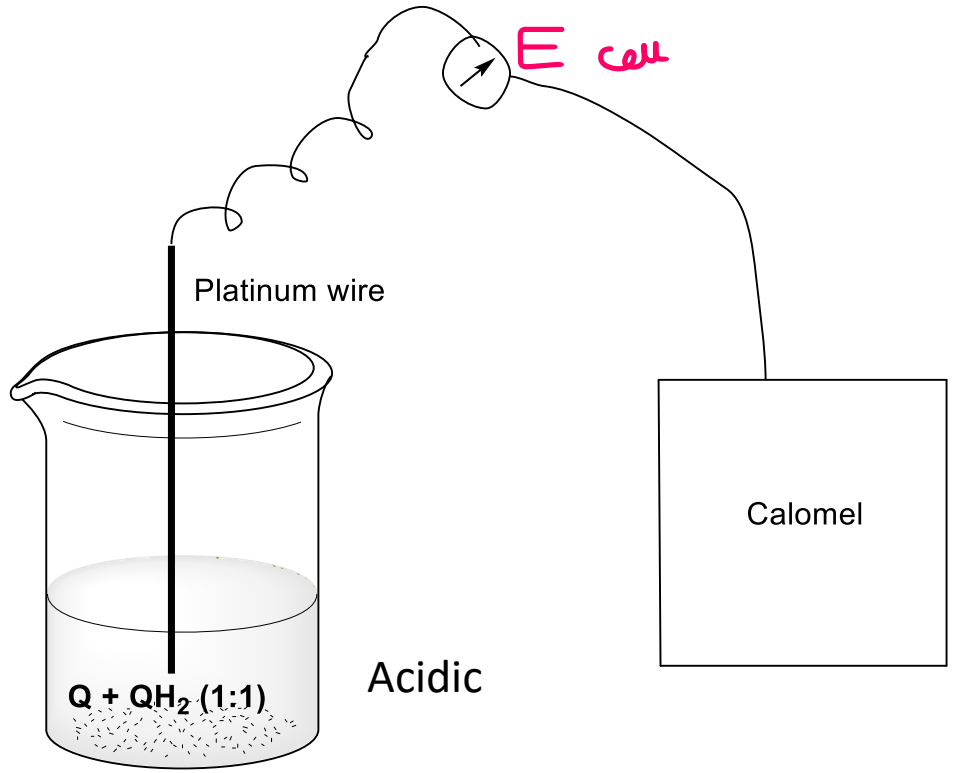
$E_{cell} = E_{cathode} - E_{anode} = E_{QH} - E_{cal} = 0.699 - 0.0591pH - E_{cal}$

For standard calomel electrode $E_{cal} = +0.2422$ V

Therefore , $E_{cell} = 0.699 - 0.0591pH - 0.2422$

$\Rightarrow E_{cell} = 0.4568 - 0.0591\ pH$

$pH = (E_{cell} - 0.4568)/0.0591$



IF the quinhydrone electrode is kept under basic condition, then it acts as anode i.e., oxidation occurs.

$$E_{cell} = E_{cathode} - E_{anode} = +0.2422 - (0.699 - 0.0591\ pH)$$

$$E_{cell} = 0.2422 - 0.699 + 0.0591pH$$

$$E_{cell} = -0.4568 + 0.0591\ pH$$

$$pH = (E_{cell} + 0.4568)/0.0591$$