③ Determining pH value using antimony - antimony oxide electrode :

The electrode works as an electrode reversible to hydrogen ions. It consists of a rod of antimony placed in a solution having hydrogen ions. The surface of antimony is cleaned and polished with fine emery paper. Antimony takes up a thin adhering layer of Sb_2O_3 almost instantaneously when exposed to air. This oxide is not dissolved by moderate acid concentrations. The slight solubility of oxide gives an equilibrium concentration of Sb^{3+} ions in in solution.

$$Sb_2O_3 + 3H_2O \rightleftharpoons 2Sb^{3+} + 6OH^-.$$

According to this equation, the solubility product of Sb_2O_3 can be written as:

$$K_{sp} = [Sb^{3+}]^2 [OH^-]^6$$

$$\Rightarrow [Sb^{3+}] = \frac{K_{sp}^{\frac{1}{2}}}{[OH^-]^3}.$$

Also,

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\therefore [OH^-] = \frac{K_w}{[H^+]}.$$

The electrode reaction for antimony electrode can be written as: $Sb^{3+} + 3e^- \longrightarrow Sb$.

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The electrode potential E is given by:

$$E_{Sb^{3+}/Sb} = E^\circ - \frac{RT}{3F} \ln \frac{a_{Sb}}{a_{Sb^{3+}}}$$

$$\Rightarrow E = E^\circ + \frac{RT}{3F} \ln [Sb^{3+}] \qquad \{\because a_{Sb} = 1\}.$$

$$\Rightarrow E = E^\circ + \frac{RT}{3F} \ln \frac{(K_{sp})^{\frac{1}{2}}}{[OH^-]^3}$$

$$\Rightarrow E = E^\circ + \frac{RT}{3F} \ln (K_{sp})^{\frac{1}{2}} - \frac{RT}{3F} \ln [OH^-]^3.$$

$$\Rightarrow E = E^\circ + \frac{RT}{6F} \ln (K_{sp}) - \frac{RT}{F} \ln [OH^-].$$

$$\Rightarrow E = E^\circ + \frac{RT}{6F} \ln K_{sp} - \frac{RT}{F} \ln \frac{K_w}{[H^+]}$$

$$\Rightarrow E = E^\circ + \frac{RT}{6F} \ln K_{sp} - \left\{ \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln [H^+] \right\}.$$

$$\Rightarrow E = E^\circ + \frac{RT}{6F} \ln K_{sp} - \frac{RT}{F} \ln K_w - \frac{2.303\,RT}{F} pH$$

$$\Rightarrow E = E^\circ - 0.0592\, pH.$$

Advantages:

1. Easy to use, cheap and durable
2. It can be used in viscous solutions.
3. It has a low resistance.

Disadvantages:

1. It can only be used with in pH Range 2-8. ~~at Low.~~
2. It can't be used in presence of oxidising agents, reducing agents, complexing agents and nobel metals.

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(4) Determination of pH by using hydrogen electrode:

The hydrogen electrode is dipped in unknown solution and connected suitably with saturated calomel electrode, as shown in the figure. The saturated calomel electrode serves as a cathode with respect to hydrogen electrode in spontaneous cell. Thus, the diagram of the cell set up is represented as

$$Pt \,|\, H_2(g, 1atm) \,|\, H^+(aq_{H^+}) \,||\, KCl\ (saturated) \,|\, Hg_2Cl_2(s) \,|\, Hg.$$

(unknown pH soln)

The EMF of this cell is measured with the help of a potentiometer and is represented as —

$$E_{cell} = E_{calomel} - E_{(2H^+, H_2)}$$

$\because$ At 298 K, $E_{calomel(saturated)} = 0.2415\ V$

and, $E_{(2H^+, H_2)} = -0.0591\, pH$

$\therefore E_{cell} = 0.2415 - (-0.0591\, pH)$.

$\Rightarrow E_{cell} = 0.2415 + 0.0591\, pH.$

$\Rightarrow pH = \dfrac{E_{cell} - 0.2415}{0.0591} = \dfrac{E_{cell} - E_{calomel}}{0.0591}$

Thus, by measuring EMF of the cell, the pH of a given solution can be determined.

Advantages:

(1) It can be used over the total pH range of 0 to 14 and is very reproducible.

(2) It has no salt error and is a fundamental electrode for referring all pH measurements.

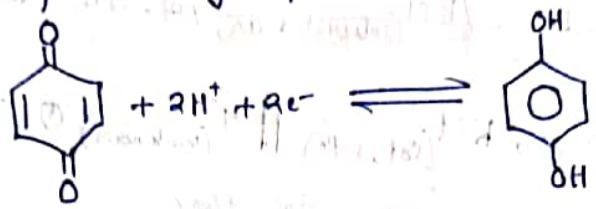
Disadvantages:

(1) It is not conveniently set up as it makes use of hydrogen at 1 atm pressure.

(2) The experimental solution might contain substances like As, S & Sb which can react with H_2 gas or which might destroy the catalytic activity of platinised surface of the electrode

⑤ By using Quinone - Hydroquinone electrode :

The quinhydrone electrode consists of an inert metal like Pt. or Au dipped into a given solution of unknown pH and saturated with quinhydrone. Quinhydrone is an organic compound which sparingly dissolves in water to give an equilibrium mixture of two non-electrolytic compounds, hydroquinone and quinone, i.e.



Quinone (Q) $C_6H_4O_2$ ... Hydroquinone (QH_2) $C_6H_6O_2$.

The Nernst equation for the electrode potential of quinhydrone electrode is given by,

$$E_{(Q,QH_2)} = E^{\circ}_{(Q,QH_2)} - \frac{RT}{2F} \ln \frac{a_{QH_2}}{a_Q \times a^2_{H^+}} \longrightarrow (i).$$

$\because \frac{a_{QH_2}}{a_Q} = 1$, for pH of the solution less than 7.0,

$$E_{(Q,QH_2)} = E^{\circ}_{(Q,QH_2)} + \frac{RT}{2F} \ln a^2_{H^+}$$

$$\Rightarrow E_{(Q,QH_2)} = E^{\circ}_{(Q,QH_2)} + \frac{RT}{F} \ln a_{H^+} \longrightarrow (ii).$$

At $T = 298\,K$, eqn (ii) becomes,

$$E_{(Q,QH_2)} = E^{\circ}_{(Q,QH_2)} + 0.0591 \log_{10}(a_{H^+})$$

$$= E^{\circ}_{(Q,QH_2)} + 0.0591 \log_{10}[H^+] \longrightarrow (iii).$$

$\because pH = -\log[H^+]$, eqn (iii) becomes,

$$E_{(Q,QH_2)} = E^{\circ}_{(Q,QH_2)} - 0.0591\, pH.$$

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For finding the pH of the solution, the quinhydrone electrode is dipped into solution of unknown pH & is combined with saturated calomel electrode which acts as a reference electrode. In the cell, quinhydrone electrode act as a cathode. So, the cell diagram is,

~~Hg / Hg_2Cl_2(s) / KCl (saturated, aq) / Q, QH_2 / Pt~~

$Hg \,|\, Hg_2Cl_2(s), KCl_{(sat, soln)} \,||\, H^+_{(unknown)} \,|\, Q, QH_2 \,|\, Pt.$

The emf of the cell is thus given by,

$$E_{cell} = E_{cathode} - E_L.$$

$$\Rightarrow E_{cell} = E_{(Q, QH_2)} - E_{calomel}$$

$$\Rightarrow E_{cell} = 0.6996 - 0.0591\, pH - 0.2415 \quad \{At\ 25^\circ C\}.$$

$$\Rightarrow pH = \frac{0.4581 - E_{cell}}{0.0591} \longrightarrow (IV)$$

Thus, by measuring E_{cell} and using eqn (IV), it is possible to find pH of the given unknown solution.

Advantages:

1. It is very ~~convent~~ conveniently set up.
2. It attains the equilibrium rapidly as it needs no special electrode surface or a gas.
3. It can be used for solutions containing reducible ions like Ni^{2+}, Cu^{2+}, which interferes in the case of hydrogen electrode
4. It is not readily poisoned

Disadvantages:

1. It gives satisfactory results only for solution with pH range from 0 to 8.
2. It fails to give reliable results when the soln contains ammonium salts or a protein.
3. The electrode becomes unstable if used for a long time at a temp above 30°C.

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⑥ By using glass Electrode:

The glass electrode is made of a special glass of relatively low melting point and high electrical conductivity. It is blocon in the form of a bulb which is then sealed to the bottom of a glass tube. A solution of 0.1 molar HCl, which furnishes a constant hydrogen ion concentration, is placed in the ~~unknown solution~~ bulb and a Ag, AgCl electrode or simply a platinum coire is inserted to make electrical contact as shown in the figure. The reference electrode used is usually the calomel electrode. The arrangement of the cell is given as.

$$Pt, 0.1\ M\ HCl \mid glass \mid Experimental\ sol^n \mid KCl_{(1M)}\ Hg_2Cl_{2(s)} \mid Hg.$$

The EMF of such a cell can be determined by means of a potentiometer. Since potential of the calomel electrode is known, that of the glass electrode can be easily calculated and the pH of the experimental solution is evaluated. The value of E°_{Gl} is first obtained by working with solution of known pH.

$$\therefore E_{cell} = E_{calomel} - E_{Gl}.$$

$$\Rightarrow E_{cell} = E_{calomel} - (E^\circ_{Gl} - 0.0591\,pH) \quad \{At\ 25^\circ C\}.$$

$$\Rightarrow 0.0591\,pH = E_{cell} - E_{calomel} + E^\circ_{Gl}.$$

$$\Rightarrow pH = \frac{E_{cell} + E^\circ_{Gl} - 0.2416}{0.0591}.$$

Thus, the value of E°_{Gl} for the glass electrode is determined by finding Ecell for a no. of buffer solutions of known pH. and By measuring the EMF of the cell containing an unknown solution potentiometrically. and knowing E°_{Gl}, the value of pH of the given solution can be calculated.

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Advantages:

(i) It is useful for solution of pH range from 0 to 10, even upto 14 in case of a special glass, with an accuracy of ± 0.05 pH.

(ii) It is simple to operate, not poisoned easily and can be used in the presence of both oxidising and reducing agents and without contaminating the given solution.

(iii) It attains equilibrium very rapidly.

Disadvantages:

(1) As the glass electrode has a very high ~~res~~ electrical resistance, electronic potentiometers or electronic voltmeter must be used to find EMF of a given soln.

(2) It is found not suitable for use in presence of pure ethyl alcohol, acetic acid, gelatine and sodium salt solutions with more than pH 9.

(3) Due to highly absorptive nature, a lot of washing is required.

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Concentration cells:

To form a galvanic cell, we bring two half cells together. If the electrochemical cells reactions in the half cells differ, the overall cell reaction is a chemical reaction and we call it a electrochemical cell. e.g. Daniel cell.

If the electrochemical reactions in the two half cells are the same but one species is at a different concentration in each half cells, the cell will have a non-zero emf and its overall reaction will account to transfer of electrolyte from one concentration to another. Such cell is called a concentration cell.

e.g. $Pt.\ H_2(g) \mid HCl\ (m_1) \mid HCl\ (m_2) \mid H_2(g) \cdot Pt.$

LHE : $H^+_{(m_1)} + e^- \rightleftharpoons \frac{1}{2} H_2(g)$

RHE : $H^+_{(m_2)} + e^- \rightleftharpoons \frac{1}{2} H_2(g)$.

(RHE - LHE) $\Rightarrow$ $H^+_{(m_2)} \rightleftharpoons H^+_{(m_1)}$

Concentration cell with transference:

To discuss the working procedure, let us consider the following single cell of this type as follows.

$Pt.\ H_2(g, 1\ atm) \mid HCl_{(a_1)} \mid HCl_{(a_2)} \mid H_2(g, 1\ atm) \cdot Pt.$

Let, 1 Faraday of electricity flows through the cell. then

Left hand electrode :—

$$\frac{1}{2} H_2 \rightleftharpoons H^+_{(a+)_1} + e^-$$

Right hand electrode :—

$$H^+_{(a+)_2} + e^- \rightleftharpoons \frac{1}{2} H_2(g)$$

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i.e. H^+ ions are generated at the LHE and consumed in the RHE as the current flows. As the anion move in the direction opposite to that of cation, Cl^- ions migrate from right to left. Let, t_+ and t_- are the transport of H^+ and Cl^- respectively. Thus, t_- equivalent of Cl^- ions will be ~~transformed~~ transferred from the sol^n of activity a_2 to that of activity a_1.

$$t_- Cl^-_{(a_-)_2} \longrightarrow t_- Cl^-_{(a_-)_1}.$$

Simultaneously,

$$t_+ H^+_{(a_+)_1} \longrightarrow t_+ H^+_{(a_+)_2}$$

Thus, the net result of flow of 1 faraday of electricity may be summed up as follows,

LHE: Gain of 1 gram equivalent of H^+ ions. Step (I)
Loss of t_+ gram equivalent of H^+ ions. Step (II)

Net gain of H^+ ion = $(1 - t_+)$ gram equivalent of H^+ ions.
$= t_-$ gram equivalent.

Net gain of Cl^- ion = t_- gram equivalent.

R.HE: Loss of 1 gram equivalent of H^+ ions.
Again, it gains t_+ gram equivalent
$\therefore$ Net loss of H^+ ions = $(1 - t_+)$ gram equivalent of H^+ ions.
$= t_-$ " " " "
At the same time, net loss of Cl^- ions = t_- gram equivalent.

Thus,

$$t_- (H^+)_{(a_+)_2} \longrightarrow t_- (H^+)_{(a_+)_1}.$$

$$t_- Cl^-_{(a_-)_2} \longrightarrow t_- Cl^-_{(a_-)_1}.$$

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∴ EMF of the cell with transference,

$$E_{cell} = t_- \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + t_- \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1}$$

$$\Rightarrow \boxed{E_{cell} = t_- \frac{RT}{F} \ln \frac{(a_\pm)_2^2}{(a_\pm)_1^2}}$$

where $a_\pm$ is the mean ionic activity and by definition, $(a_\pm)^2 = (a_+)(a_-)$.

For 1:1 electrolyte,

$$a = (a_\pm)^2$$

$$\therefore \boxed{E_{cell} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1}}$$

Concentration cell without transference:

Let us consider the example,

$$Pt.\ H_2(g),\ HCl(a_1) \mid AgCl(s),\ Ag$$

Let, the activity of H^+ ions in the solution is a_1 and that of the Cl^- ion is a_2.

Reduction half cell reaction –

$$AgCl_{(s)} + e^- \rightleftharpoons Cl^-_{(a_-)_1} + Ag_{(s)} \longrightarrow (I)$$

Oxidation half cell reaction –

$$\frac{1}{2} H_2(g) \rightleftharpoons H^+_{(a_+)_1} + e^- \longrightarrow (II)$$

The net reaction is taking place by adding (I) and (II).

$$(I) + (II) \Rightarrow \frac{1}{2} H_2(g) + AgCl_{(s)} \rightleftharpoons H^+_{(a_+)_1} + Cl^-_{(a_-)_1} + Ag_{(s)} \longrightarrow (III)$$

Now, consider the same cell with the difference that the activity of HCl is now a_2.

$$Pt.\ H_2(g),\ HCl(a_2) \mid HCl(s),\ Ag.$$

The net cell reaction for passing 1 faraday electricity will now be

as follows —

$$\frac{1}{2}H_2(g) + AgCl_{(s)} \rightleftharpoons H^+_{(a+)_2} + Cl^-_{(a-)_2} + Ag_{(s)} \longrightarrow (iv)$$

Finally consider the situation in which the two cells are connected to each other in such a way that the current pass in opposite direction. Thus,

$$Pt.\ H_2(g) | HCl_{(a_1)} | AgCl_{(s)} | Ag | AgCl_{(s)} | HCl_{(a_2)} | H_2(g), Pt.$$

The overall reaction for passage of 1 F of electricity.

$$H^+_{(a+)_2} + Cl^-_{(a-)_2} \rightleftharpoons H^+_{(a+)_1} + Cl^-_{(a-)_1}$$

Thus for flow of 1 F of electricity, the overall reaction is the transfer of 1 mol of each of H^+ and Cl^-.

$$E_{cell} = \frac{RT}{F} \ln \frac{(a+)_2}{(a+)_1} + \frac{RT}{F} \ln \frac{(a-)_2}{(a-)_1}$$

$$\Rightarrow \boxed{E_{cell} = \frac{RT}{F} \ln \frac{(a\pm)_2^2}{(a\pm)_1^2}}.$$

Activity and Mean Ionic Activity of an electrolyte:

When an electrolyte is dissolved in water, the no. of ions actually present (effective concentration of the ions) is less than the actual concentration. This is because of the fact that due to presence of a large no. of ions in the solution, the freedom of moment of each ion is hindered and thus interionic forces can't be neglected. This effect becomes more significant at higher concentrations and increasing valency of ions. To explain the departure of electrolyte solution from ideal behaviour, Gr. N. Lewis,

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proposed a term 'activity' in place of the concentration term (molarity, molality or mole fraction). Thus,

Activity can be defined as, the effective concentration of an ion or the electrolyte in a solution. It is denoted by 'a' and is related to the actual concentration expressed in molarity molality m by the equation,

$$a = \gamma \times m$$

where γ is called activity coefficient.

$$\therefore \gamma = \frac{a}{m} = \frac{\text{Effective concentration}}{\text{Actual Concentration}}$$

Thus, activity coefficient may be defined as the ratio of effective concentration to the actual concentration of the solution.

For real solutions, $m > a$

$$\therefore \gamma < 1.$$

It is because, in case of strong electrolytes, strong electrostatic forces leads to the formation of ion pairs.

For ideal solutions, $a = m$.

$$\therefore \gamma = 1$$

Mean Ionic Activity coefficient of uni-univalent electrolyte:

Let us consider a uni-univalent electrolyte, like HCl, in aqueous solution. Let, a_+ and a_- be the activities of H^+ and Cl^- ions respectively, in a solution of a given concentration. The activity a of the electrolyte is defined as,

$$a = a_+ a_- \longrightarrow (1)$$

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While mean ionic activity $a_\pm$ of the electrolyte is ~~simply~~ defined by the expression,

$$a_\pm = \sqrt{a_+ a_-} \longrightarrow (i)$$

ie. The mean ionic activity of the electrolyte is the geometric mean of activities of the component ions.

Squaring eqn (i), we get.

$$(a_\pm)^2 = a_+ a_- \longrightarrow (ii).$$

From eqn (i) and (ii), we get,

$$a = a_+ a_- = (a_\pm)^2$$

Mean Ionic Activity ~~of~~ coefficients of electrolytes:

Let us consider an electrolyte, M_xA_y ionising as,

$$M_xA_y \longrightarrow xM^+ + yA^-.$$

$\therefore$ Activity, $a = (a_+)^x (a_-)^y$

$$= (a_\pm)^{x+y}$$

where,

a_+ is the activity of the cation

a_- is the activity of the anion.

$a_\pm$ is the mean ionic activity.

Again, let m be the concentration of the electrolyte in terms of molality then, ~~no of moles per~~ molality of

cations, $m_+ = xm$

Molality of anions, $m_- = ym$

$\therefore a = \gamma m$.

where γ is the activity coefficient.

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∴ Activity of the electrolyte is given by,

$$a = (\gamma_+ m_+)^x (\gamma_- m_-)^y$$

$$\Rightarrow a = (\gamma_+ x m)^x (\gamma_- y m)^y$$

$$\Rightarrow a = x^x y^y (\gamma_\pm m)^{x+y}$$

where, $\gamma_\pm$ is the mean ionic activity coefficient related with γ_+ and γ_- by the expression.

$$(\gamma_\pm)^{x+y} = (\gamma_+)^x (\gamma_-)^y$$

For a uni-univalent electrolyte, e.g. HCl or NaCl, $x = 1$ and $y = 1$.

$$\therefore a = (a_\pm)^2$$

and, $a = (\gamma_\pm m)^2$

For a uni-bivalent electrolyte, e.g. Na_2SO_4, $x = 2$ and $y = 1$.

$$\therefore a = (a_\pm)^3.$$

and, $a = 2^2 \times 1 (\gamma_\pm m)^3$.

$$= 4\gamma_\pm^3 m^3.$$

Ionic Strength (I):

Ionic Strength is the measure of the electrical intensity due to the presence of ions in the solution. Mathematically,

$$I = \frac{1}{2}\left[m_1 z_1^2 + m_2 z_2^2 + m_3 z_2^2 + \ldots\ldots\right] \longrightarrow (1)$$

where, $m_1, m_2, m_3, \ldots$ are molalities of various ions and $z_1, z_2, z_3, \ldots$ are the valencies of various ions in solution.

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Eqn (1) $\Rightarrow I = \frac{1}{2}\sum_i m_i z_i^2$.

i.e. Ionic strength is the half of the sum of the products of the molalities and square of the valence of each ion in solution.

For uni-univalent electrolyte, e.g. KCl

$$I = \frac{1}{2}\left(m_+ z_+^2 + m_- z_-^2\right).$$

Determination of activity coefficient of an ion:

Let, the activity coefficient of Ag^+ ion is to be determined. Let, the concentration cell be,

$$(-)\,Ag \;|\; AgNO_3(aq)_{m_1} \;||\; \text{salt bridge: Sat. } NH_4NO_3 \text{ agar-water} \;||\; AgNO_3(aq)_{m_2} \;|\; Ag\,(+)$$

where, $m_2 > m_1$

The emf of this concentration cell without transference is,

$$E = \frac{2.303}{F} RT \log_{10}\left[a_{Ag^+(2)}/a_{Ag^+(1)}\right] \longrightarrow (i)$$

Putting, $a_{Ag^+(1)} = m_1(\gamma_\pm)_1$

$a_{Ag^+(2)} = m_2(\gamma_\pm)_2$ in eqn (i), we get,

At 25°C,

$$E = 0.05916 \log_{10} \frac{m_2(\gamma_\pm)_2}{m_1(\gamma_\pm)_1} \longrightarrow (ii)$$

where $(\gamma_\pm)_1$ and $(\gamma_\pm)_2$ are mean activity coefficients of the solution at molalities m_1 and m_2 respectively.

The emf of the cell is measured by keeping m_2 constant and varying m_1 by dilution of that solution.

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Determination of Transport no.:

We know, the EMF of a concentration cell with transference,

$$E_{w.t} = 2t_- \frac{RT}{F} \ln \frac{a_2}{a_1} \longrightarrow (I)$$

Again,
The EMF of the same cell with the same solutions but without transference is,

$$E_{w.o.t} = \frac{RT}{F} \ln \frac{a_2}{a_1} \longrightarrow (II)$$

$\therefore$ (I) $\div$ (II) $\Rightarrow$ $\boxed{\frac{E_{w.t}}{E_{w.o.t}} = 2t_-}$.

Thus, the ratio of the EMFs of the two concentration cells, one with transference and the other without transference, gives the transference no. of the anion, if the end electrodes are reversible with respect to the cation.

If the end electrodes are reversible w.r.t. the anion, then the ratio of the two EMFs will give the transference no. of the cation of the electrolyte.

Liquid Junction Potential (L.J.P):

In a cell when two electrolyte solutions of different concentrations are kept in direct contact with each other, a potential develops at the junction (boundary) of the two solutions due to difference in the rates of diffusion of the two ions. This potential is called liquid junction potential.

If a cell acquires a liquid junction potential, then the emf of the cell is given by,

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$$E_{cell} = E_1 + E_2 + E_{L.J.P}$$

where E_1 and E_2 are the oxidation and reduction potential of the cell.

Calculation of Liquid Junction Potential :

We know,

$$E_{w.t} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1} \longrightarrow (1)$$

$$E_{w.o.t} = \frac{RT}{F} \ln \frac{a_2}{a_1} \longrightarrow (11)$$

Eq^n (1) includes the potential at the junction of the two solutions & can also be written as,

$$E_{w.t} = 2t_- \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \longrightarrow (111)$$

Eq^n (11) does not include the potential at the junction of the two solutions or the liquid junction potential. and can also be written as,

$$E_{w.o.t} = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$\therefore$ The liquid junction potential is given by,

$$E_{L.J.P} = E_{w.t} - E_{w.o.t}$$

$$= 2t_- \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} - \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$= \left[2t_- - 1\right] \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$= \left[2t_- - (t_+ + t_-)\right] \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$$

$$\Rightarrow E_{L.J.P} = (t_- - t_+) \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \longrightarrow (iv)$$

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From eqn (iv) it is clear that the magnitude as well as sign of $E_{L.J.P}$ depends upon the transference numbers of cations and anions.

Case I: If $t_- = t_+$, then $E_{L.J.P} = 0$

eg. Examples of this type are provided by the electrolytes KCl and NH_4NO_3.

Case II: If $t_+ > t_-$, then $E_{L.J.P} = -ve$

Case III: If $t_- > t_+$, then $E_{L.J.P} = +ve$.

Qualitative Discussion of Potentiometric titrations:

The potential of an electrode depends upon the concentration of the ion with which it is reversible. In a titration, there is continuous change in ionic concentration of the electrolyte solution (analyte) in the cell after each addition of small volume of the titrant, which can be followed by measuring the potential of the cell formed by the electrolyte sampled with a suitable electrode. The potentiometric titrations are thus, those titrations which involves the measurement of electrode potentials with the addition of the titrant. Therefore, the equivalence point can be found by plotting a graph between measured potentials of solution versus volume of titrant added.

The potentiometric titrations generally fall into the following three categories:

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(a) Acid-Base titrations

(b) Oxidation-Reduction (Redox) Titrations

(c) Precipitation Titrations.

(a) Acid-Base titrations:

In case of acid-alkali titrations, e.g. HCl vs NaOH, the emf of the solution is measured by immersing in the given volume of acid solution an electrode reversible to hydrogen ions. This electrode is coupled with a suitable reference electrode to form a complete cell. Generally, the acid solution is kept in contact with the quinhydrone or glass electrode. This forms one half cell which is connected to the calomel electrode to give a complete cell. The whole assembly is connected to the potentiometer and the variation of emf with changes in pH of the solution on each addition of alkali is recorded. The pH varies as, $E = E^{\circ} + 0.0591$ pH at 25°C.

If a plot of E versus the volume of alkali added is made, the following graph is obtained.

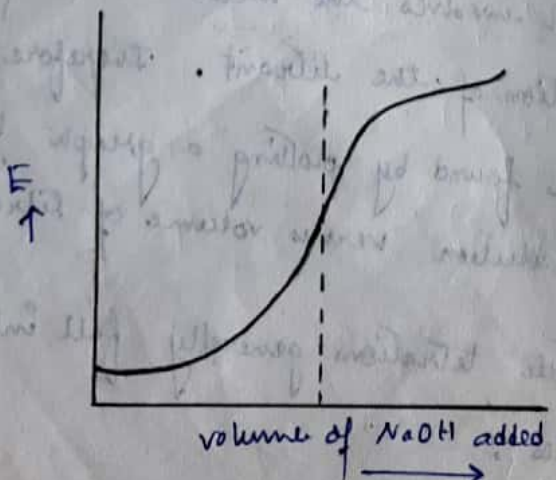

Fig: Plot of E vs volume of alkali added

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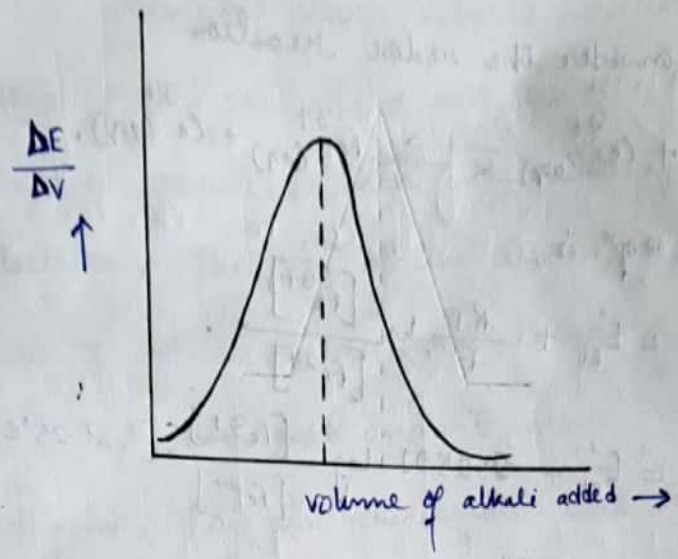
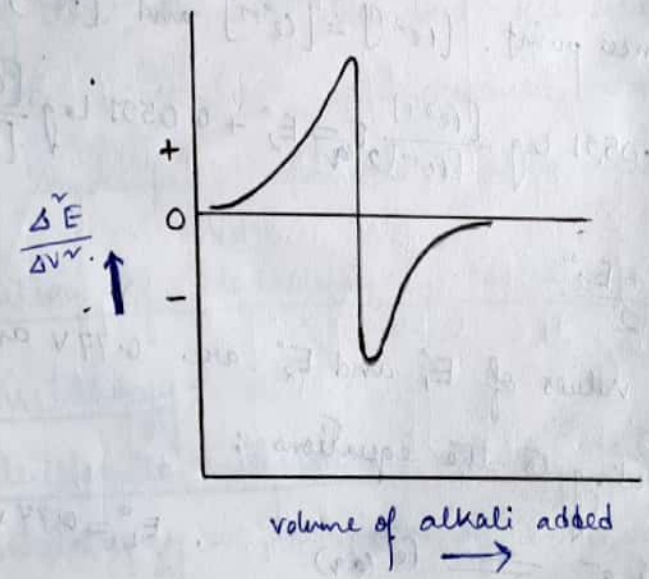
If a plot of $\frac{\Delta E}{\Delta V}$ is placed instead of emf of the cell versus the volume of alkali added, a maximum is observed at the end point as shown below:



~~(b) Oxidation~~

If a plot of $\frac{\Delta^2 E}{\Delta V^2}$ is placed versus the volume of alkali added, the following graph is obtained.



(b) Oxidation-Reduction (Redox) Titrations:

The redox titrations are also carried out potentiometrically. Here, the electrode reversible with respect to H^+ ions is replaced by an inert metal, such as platinum wire,

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immersed in a solution of containing both the oxidised and reduced forms of the same species. The electrode acts as an oxidation - reduction electrode.

Let us consider the redox reaction

$$Fe^{2+}_{(aq)} + Ce^{4+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ce^{3+}_{(aq)}.$$

The Nernst eqn is,

$$E_{el} = E^{\circ}_{el} + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}.$$

$$= E^{\circ}_{el} + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad \text{at } 25^{\circ}C.$$

If the ratio $\frac{[Fe^{3+}]}{[Fe^{2+}]} = 0.01$,

$$E_{el} = E^{\circ}_{el} + 0.0591 \log (0.01).$$

$$= E^{\circ}_{el} - 0.1182.$$

At the equivalence point, $[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = [Ce^{3+}]$.

$$\therefore E_{eq} = E^{\circ}_1 + 0.0591 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}, \quad E_{eq} = E^{\circ}_2 + 0.0591 \log \frac{[Ce^{4+}]}{[Ce^{3+}]}.$$

$$\therefore E_{eq} = \frac{E^{\circ}_1 + E^{\circ}_2}{2}$$

The numerical values of E°_1 and E°_2 are 0.77 V and 1.61 V respectively, according to the equations :

$$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}, \quad E^{\circ}_1 = 0.77\ V$$

$$Ce^{4+}_{(aq)} + e^- \rightleftharpoons Ce^{3+}_{(aq)}, \quad E^{\circ}_2 = 1.61\ V.$$

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© Precipitation reactions:

In precipitation reaction like $AgNO_3$ with KCl, AgCl gets precipitated. In such a case, a silver rod is dipped into in a given volume of silver nitrate solution. When KCl soln is added, AgCl is precipitated and we get Ag-AgCl electrode. This half cell is connected with a reference electrode like calomel electrode. The emf of the cell is recorded for each concentration of Ag^+ in contact with electrode. On progressive addn of KCl, $[Ag^+]$ decreases and E values decreases. At the equivalence point, $[Ag^+]$ is very small. Therefore, near about the end point, there is a great change in potential values. The plot of E versus the volume of KCl added is similar to the one obtained for acid-alkali titration. Knowing the volume of standard KCl solution from the graph, the $AgNO_3$ soln is standardised, mixture of halides can also be successfully estimated by this method.

Applications of Electrolysis in Metallurgy and Industry:

(1) In Metallurgy:

(a) Electrolytic extraction of metals (Electrometallurgy):

Electrometallurgy is the process of extraction of metals from ore by electrolysis.

The metals like sodium, potassium, Mg, Ca, Al, etc. are obtained by electrolytes of fused electrolytes.

Let us consider the extraction of sodium by the electrolysis of fused sodium chloride.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

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At cathode : $Na^+ + e^- \longrightarrow Na$

At anode : $Cl^- - e^- \longrightarrow Cl$.

$Cl + Cl \longrightarrow Cl_2$.

(b) Electro-refining :

As the metals obtained from their ores usually contain impurities, these metals like Cu, Fe, Pb, etc. are usually purified by electrolysis.

The anode is the impure metal and any impurities are removed during the process of electrolysis when the metal ~~oxide~~ travels from anode to cathode.

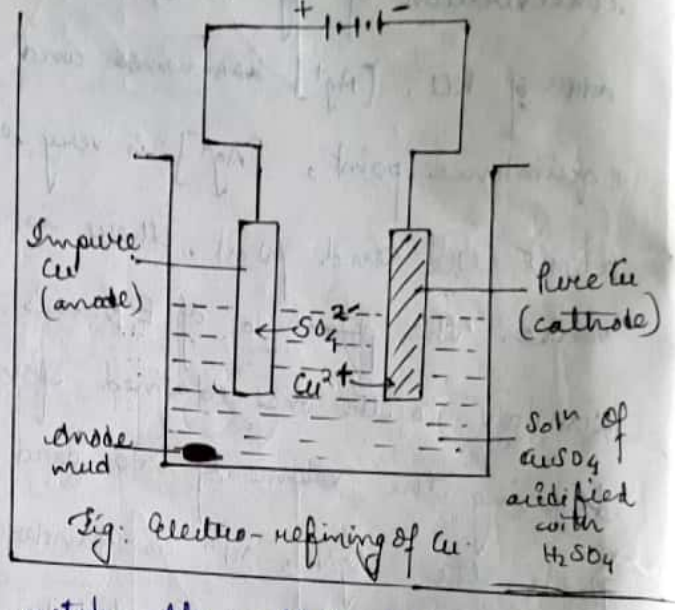

Fig: Electro-refining of Cu

During electrorefining of metals, the cathode has a decomposition of pure metals from a solution containing metal ion. ~~Eg~~ e.g. During the electrorefining of copper, the cathode is a pure piece of copper, while the anode is an impure piece of copper. The electrolyte is an aqueous solution of $CuSO_4$ acidified with dil. H_2SO_4. On passing the electric current, the Cu^{2+} from the anode moves ~~through~~ towards the cathode where it becomes solid copper. The leftover residue in this process is called anode mud.

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu(s)$.

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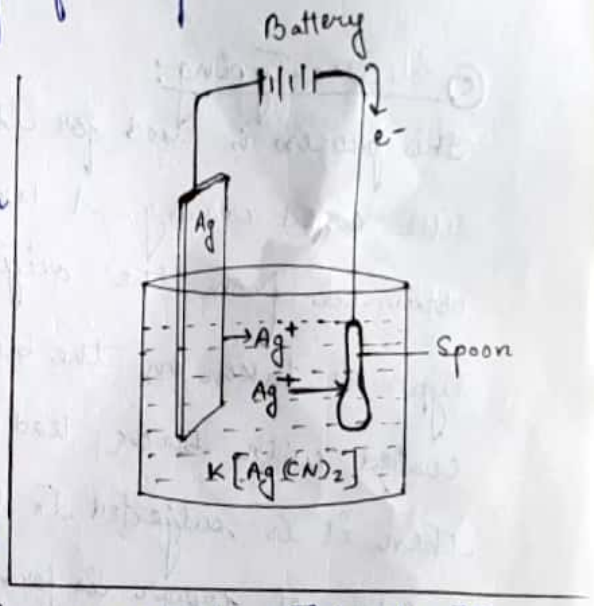
② In Industry:

ⓐ Electroplating: This is the process of covering the articles made up of cheap metals by a thin covering of precious metal such as iron with Ni, Cr, Ag or Au with one or more of the following aim of view:

(i) Protection of metal against corrosion.
(ii) giving shining appearance to articles.
(iii) Replacing work-out material
(iv) giving reflecting properties to reflectors.

e.g. Let us consider the coating of a spoon with silver.



Here the spoon will act as cathode and silver bar as anode. The electrolyte is a solⁿ of AgCN. When a direct current is passed through the cell, Ag^+ ions from AgCN solⁿ migrate to the cathode (spoon) where they are neutralised by e⁻s and stick to the spoon as silver metal. Meanwhile, the silver anode bar loss electrons to become silver ions. Thus, the anode bar ~~gives up~~ gradually dissolves to replenish the silver ions in the solution. The net result is that silver metal has been transferred from the anode to the cathode. This process continues until the desired coating thickness is built upon the spoon.

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(b) Electrosynthesis:

A method which uses electrolysis reactions to produce certain products is called electrosynthesis.

e.g. MnO_2 needs to undergo electrolysis in order to be used for alkaline batteries. The electrolyte is a soln of $MnSO_4$ acidified with H_2SO_4. The anode is graphite, where Mn^{2+} is oxidised. While the cathode hydrogen is reduced from H^+ to H_2. The overall reaction is —

$$Mn^{2+}_{(aq)} + 2H_2O_{(l)} \longrightarrow MnO_{2(s)} + 2H^+_{(aq)} + H_{2(g)}.$$

(c) Electro-Typing:

This process is used for the reproduction of the work of art like wood craving. A large no. of printing plates are obtained from the original type. The impression of the type is taken on the block of wax, ~~the imp~~ which is then coated with black lead to give it metallic surface and then it is subjected to the process of electro deposition. Thus a film of copper is formed on the prepared surface.

(d) Electro-forming:

Reproduction of objects by electro-deposition on some sort of mould or form is called electro-forming.

In the reproduction of coins, medles, engraving, etc. a mould is first made by impressing the object, say in wax. The surface of the wax, which bears exact impression of the object, is coated by powdered graphite in order to make it conducting the mould is then dipped in an electroreforming cell as a cathode. After obtaining coating of desired thickness, the article and the wax core is melted out of the metal shell.

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