

SP 1

- ① Potentiometry
- ② Faradic current, Non Faradic current
- ③ Over potential
- ④ Perfectly non polarized electrode.
- ⑤ Perfectly of Polarized electrode.

Types of Electrodes:-

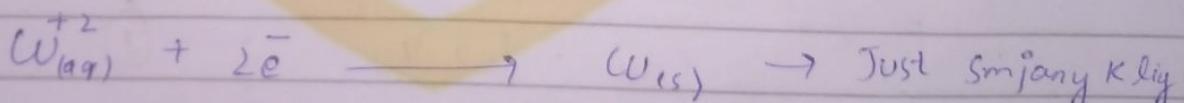
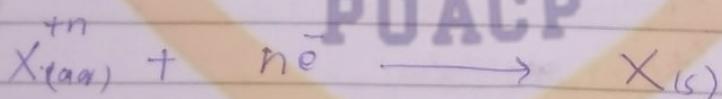
- 1- Electrode of one type → Electrode jis ka bna ho ga us kih estimation/detection kry ga
- 2- Electrode of 2nd type → Ye jis ka bna ho ga os sa alg metal ki detection kry ga
- 3- Redox electrode.

Imp

Electrode of 1st type:

An electrode of 1st type is pure metallic electrode, that is ~~intera~~ indirect contact with cation derived from the metal. A single reaction is involved. For example; the equilibrium b/w metal X^{+n} and its cations.

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By applying Nernst equation

For non-

equilibrium $\leftarrow E_{\text{eff indicator}} = E_{X^{+n}}^{\circ} - \frac{0.0592}{n} \log \frac{[X]}{[X^{+n}]}$

$$E_{\text{cell}} = E_{\text{XO}}^{\circ} - \frac{0.0592}{n} \log \frac{1}{[X^{+n}]}$$

Where E_{ind} is electrode potential of metal electrode. X^{+n} is conc. of metal ions.

Electrode potential of indicator electrode is also expressed in terms of P function

$$E_{\text{ind}} = E_{\text{XO}}^{\circ} - \frac{0.0592}{n} \left[-\log \frac{1}{X^{+n}} \right]$$

$$= E_{\text{XO}}^{\circ} - 0.0592 \left(-\log [X^{+n}] \right)$$

$$E_{\text{indi}} = E_{\text{XO}}^{\circ} - \frac{0.0592}{n} P^x$$

$$\frac{-0.0592 P^x}{n} = E_{\text{indicator}} - E_{\text{XO}}^{\circ} \quad \begin{matrix} \text{Multiply with } -1 \\ \cancel{\text{Multiply with } +1} \end{matrix} \quad \begin{matrix} P^x \\ \cancel{E_{\text{ind}} - E_{\text{XO}}} \end{matrix}$$

$$\frac{-0.0592 P^x}{n} = (E_{\text{ind}} - E_{\text{XO}}^{\circ})$$

$$\boxed{P^x = \frac{E_{\text{XO}}^{\circ} - E_{\text{ind}}}{0.0592} n} \quad \rightarrow \textcircled{1}$$

When metallic indicator electrode is to be used to determine P^x of the soln. it is typically made part of the

Cathode left, anode right

By convention SCE

Cell. The (Standard calomel electrode) is written as anode and is measured cell Potential will be; 1

$$\left. \begin{array}{l} E_{\text{cell}} = E_{\text{ind}} - E_{\text{SCE}} \\ E_{\text{ind}} = E_{\text{cell}} + E_{\text{SCE}} \end{array} \right\}$$

Put values in eq ①

$$P^{\circ} = \frac{n [E_{\text{Xn}}^{\circ} - (E_{\text{cell}} + E_{\text{SCE}})]}{0.0592} \Rightarrow \frac{n (E_{\text{cell}} + E_{\text{SCE}} - E_{\text{Xn}})}{0.0592}$$

$$P^{\circ} = \frac{n (E_{\text{Xn}}^{\circ} - E_{\text{cell}} - E_{\text{SCE}})}{0.0592} \quad \text{--- (2)}$$

This equation permits to calculate the P° of the Cd from the Potentiometric data. The cell $\text{SCE} // \text{Cd}_{\text{part}}^{+2} / \text{Cd}_{\text{ls}}$ develops

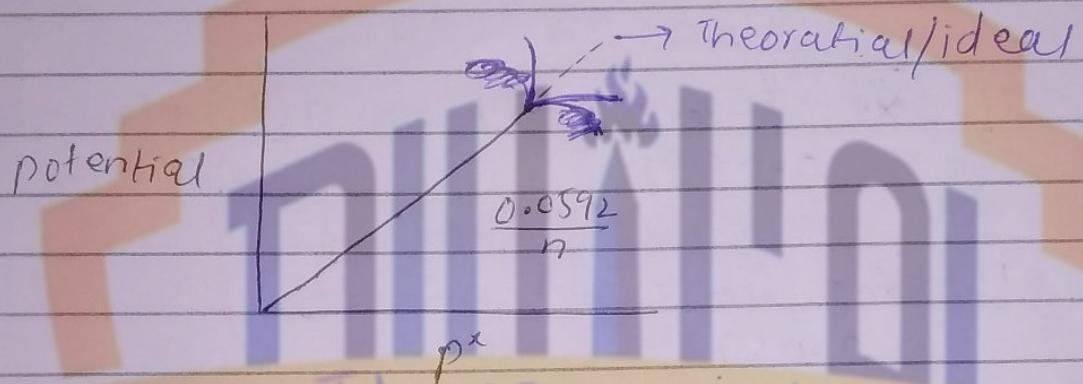
a potential of -0.723 volts. Calculate the P° of the Cd^{+2} solution using -0.403 volt as E° for Cd^{+2} ions.

Putting values in eq ② then,

$$\left[P^{\circ} = 2.57 \right]$$

The above eq. accurately describe the behavior of number of common metals that are used as indicator electrode of 1st type

4 g cm^{-3} ~~ki density~~
 heavy metals hoty hain. Transition metals
 Certain heavy metals such as Fe, Cr, Co,
 do not produce reproducible results (potential).
 Moreover, the plot of potential versus
 p^x of the metal yield slopes that
 differ markedly from theoretical / ideal



The non-ideal behavior of this type of electrode is due to the strains and deformations in the crystal structure of metals and presence of oxides films only surface.

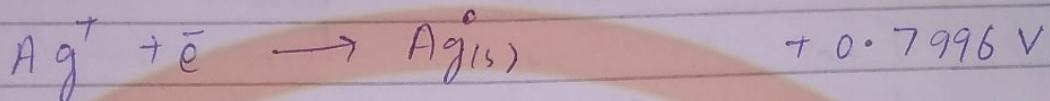
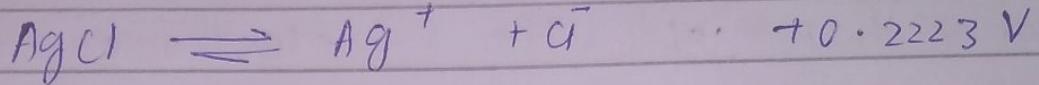
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Electrode of 2nd Type:

Metals not only serve as indicator electrodes of their own kind but also respond to concentration of anions for sparingly soluble precipitate or highly stable complexes with such cations.

For example; The potential of silver electrode correlate reproducibly with

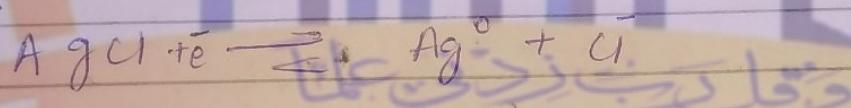
conc. of chloride ions in a soln. which is saturated with AgCl . Here, two equilibrium are involved.



By applying Nernst Equation:

$$E_{\text{ind}} = E_{\text{AgCl}}^\circ - \frac{0.0592}{nF} \log Q$$

Net eq.



$$E_{\text{ind}} = E_{\text{AgCl}}^\circ - \frac{0.0592}{F} \log \frac{[\text{Ag}^\circ][\text{Cl}^-]}{[\text{AgCl}]}$$

$$E_{\text{ind}} = E_{\text{AgCl}}^\circ - 0.0592 \cdot \log [\text{Cl}^-]$$

$$E_{\text{ind}} = E_{\text{AgCl}}^\circ + 0.0592 (-\log [\text{Cl}^-])$$

$$E_{\text{ind}} = E_{\text{AgCl}}^\circ + 0.0592 P^{\text{Cl}} \quad \text{--- (1)}$$

Eq ① shows that potential of Ag/AgCl electrode is proportional to the power of chloride ion concentration that is $-\log$ of Cl^- concentration. Since the solution is saturated with AgCl ,

Silver electrode therefore serves as indicator electrode of 2nd kind for Cl^- concentration.

The sign of log term for the chloride electrode of 2nd kind is opposite to that of the electrode of 1st kind.

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{SCE}} \quad \text{(1)}$$

$$E_{\text{cell}} = E^{\circ}_{\text{AgCl}} + 0.0592 \cdot P^{\text{Cl}} - E_{\text{SCE}}$$

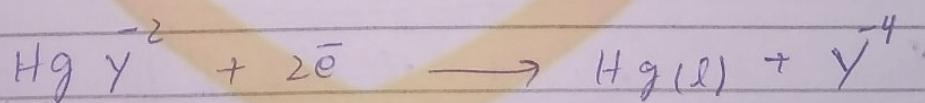
$$E_{\text{cell}} + E_{\text{SCE}} = E^{\circ}_{\text{AgCl}} + 0.0592 P^{\text{Cl}}$$

$$E_{\text{cell}} + E_{\text{SCE}} - E^{\circ}_{\text{AgCl}} = 0.0592 P^{\text{Cl}}$$

$$\boxed{P^{\text{Cl}} = \frac{E_{\text{cell}} + E_{\text{SCE}} - E^{\circ}_{\text{AgCl}}}{0.0592}} \quad \text{(2)}$$

Mercury cell as indicator electrode of 2nd kind for EDTA anion (Y^{4-})

For example, small amount of $\text{Hg}(\text{Y}^2)$ is added to a solution containing (Y^{4-}), the half reaction of Hg cathode is



By applying Nernst equation

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Hg(l)}][\text{Y}^{4-}]}{[\text{Hg Y}^{2-}]}$$

$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Y}^{4-}]}{[\text{Hg Y}^{2-}]}$$

$$E = E^\circ - \frac{0.0592}{2} \log [Y^4] - \frac{0.0592}{2} \log \frac{1}{HgY^2}$$

The formation constant of HgY^2 is very large that is 6.3×10^{21} . So the concentration of the complex remains almost constant over a large range of Y^4 , so by applying Nernst equation to above equilibrium, we can write

$$E = E^\circ - \frac{0.0592}{2} \log \frac{1}{HgY^2} - \frac{0.0592}{2} \log \frac{1}{Y^4}$$

$$E = K - \frac{0.0592}{2} \log Y^4 \quad \therefore K = E^\circ - \frac{0.0592}{2} \log \frac{1}{HgY^2}$$

$$E = K + \frac{0.059}{2} P_Y$$

Thus, actually electrode is valuable electrode of 2nd kind for EDTA titration.

⇒ Electrode of Redox Type:

In a redox electrode an inert metal is in contact with the solution containing soluble oxidize and reduce forms of the half reaction.

Inert metal such as platinum, Au, C, Pd

respond to the potential of the redox system with which it is in contact. The inert metal used is usually Pt. The potential of such electrode is determined by the ratio at electrode surface of reduced and oxidized species in half reactions.



By applying Nernst equation.

$$E = E_{\text{M}^{+}, \text{M}}^{\circ} - 0.0592 \log \frac{[\text{M}^{+(a-n)}]}{[\text{M}^{+n}]}$$



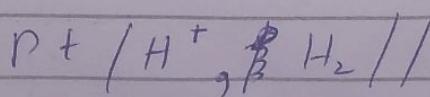
$$E = E_{\text{MnO}_4^-, \text{Mn}^{2+}}^{\circ} - \frac{0.0592}{5} \log \frac{[\text{Mn}^{2+}][\text{H}_2\text{O}]^4}{[\text{MnO}_4^-][\text{H}^+]^8}$$

In terms of activity;

$$E = E_{\text{MnO}_4^-, \text{Mn}^{2+}}^{\circ} - \frac{0.0592}{5} \log \frac{a_{\text{Mn}^{2+}} \cdot a_{\text{H}_2\text{O}}}{a_{\text{MnO}_4^-} \cdot a_{\text{H}^+}^8}$$

$$E = E_{\text{MnO}_4^-, \text{Mn}^{2+}}^{\circ} - \frac{0.0592}{5} \log \frac{a_{\text{Mn}^{2+}}}{a_{\text{MnO}_4^-} \cdot a_{\text{H}^+}^8}$$

Very important type of electrode is hydrogen electrode





By applying Nernst equation

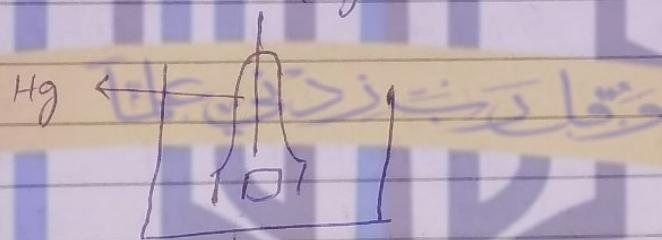
$$E = E_{H^+, H_2}^\circ - \frac{0.0592}{n} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$E = E_{H^+, H_2}^\circ - \frac{0.0592}{n} \log \frac{1}{[H^+]}$$

$$E = E_{H^+, H_2}^\circ - \frac{0.0592}{n} (\log P_{H_2})$$

$$E = E_{H^+, H_2}^\circ - \frac{0.0592}{n} P^H$$

The construction of Hydrogen electrode is shown in fig a



A layer of Pt black must be coated on surface of Pt electrode by cathodically electrolyzing in a H_2 $PtCl_6$ soln. The Pt black provides large surface area for adsorption of H_2 molecule and catalyse their oxidation. The pressure of gases in terms of is used instead of activity.

If H pressure is held at 1 atm then electrode potential from equation can be defined as;

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{1}{a_{H^+}}$$

$$E = E^\circ - \frac{2.303RT}{nF} \log P_{H_2}$$

$P_{H_2} \Rightarrow$ Partial pressure of hydrogen
If partial pressure is H_2 is 1 then

$$E = E^\circ - \frac{2.303RT \log 1}{nF}$$

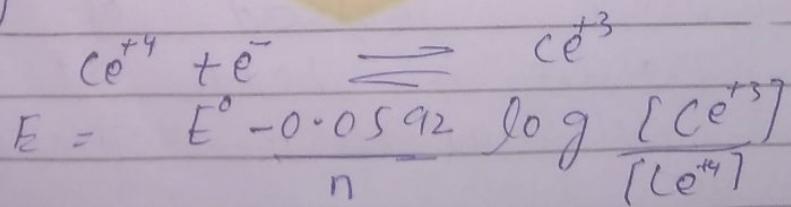
$$E = 0$$

Hydrogen electrode is very important for specificity of H^+ but its use for routine pH measurement is limited because the inconvenience to prepare it and partial pressure of hydrogen must be established at measured temperature. It should not contain either oxidizing or reducing reagents since this will affect the potential of electrode.

The vapour pressure of water above the surface must be subtracted from measured gas pressure.

Application of hydrogen electrode in addition to pH measurement:

Platinum electrode can be used to measure the potential of the solution containing cerium III and cerium species (Ce^{+3}, Ce^{+4})



Hence, a platinum electrode is regarded as

a convenient indicator electrode for titration involving standard cerium (IV) (Ce^{+4}) solution.

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Membrane electrode:

Another type of indicator electrode are membrane electrode. The most convenient method for determination of PH involve measurement of potential envelop across a thin glass membrane that separate two soln. of different H^+ ions concentration. As a result, the sensitivity and selectivity of glass membrane towards H^+ ions are remarkably well understood.

This understanding lead to the development of other types of membranes that respond selectively to more than two (2) dozen other ions. Membrane electrodes are sometimes called P^{ion} electrode, because of the P function such as P^{Ca} , P^{Cd} , P^{NO_2} , etc. and are classified as crystalline or non-crystalline electrodes.

Types :

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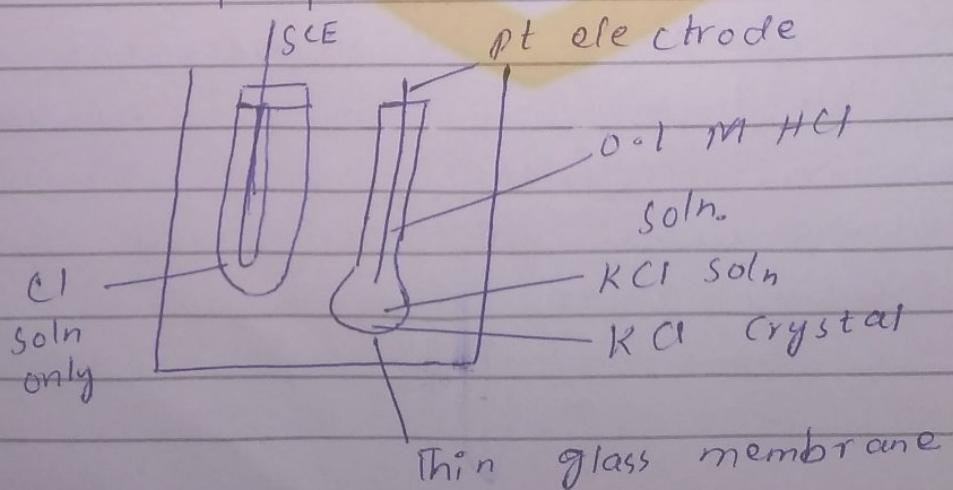
- ① → Glass electrode for PH measurement
- ② Glass electrode for cations other than proton
- ③ combination electrodes
- ④ Liquid - membrane electrodes
- ⑤ Gas - sensing probes.
- ⑥ Ion selective electrode

→ Types of glass membrane electrode.

- (1) Precipitation electrodes
- (2) Solid state electrode
- (3) Liquid-liquid electrodes.
- (4) Plastic membrane or ionophore electrode.
- (5) Coated wire electrodes.

① Glass electrode for pH measurement:

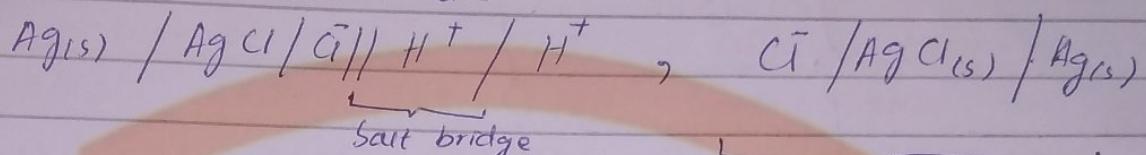
It is consist of glass indicator electrode and SCE (saturated calomel electrode). Both are immersed in a soln. whose pH is to be determined. The glass indicator electrode consist of a thin glass tube, sealed into one end of walls of a glass or a plastic tube. Small volume of dilute HCl saturated with AgCl is present in the indicator electrode. A silver wire in the solution form Ag/AgCl (Ag/AgCl) reference electrode which is connected to one of the terminal of potentiometer device.





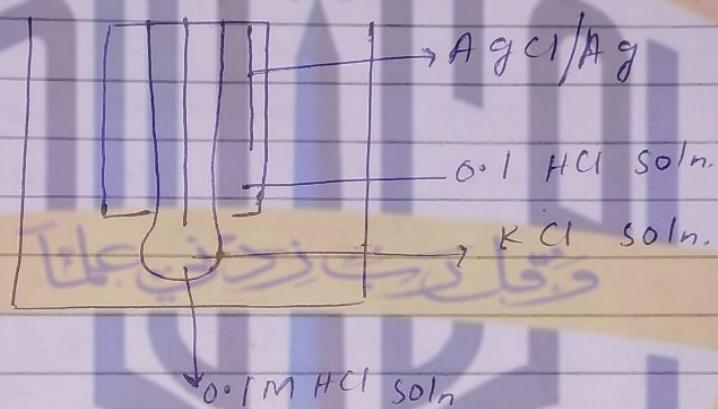
While the Calomel electrode is connected to the other terminal.

Standard electrode



Tes f soln

Indicator electrode



composition of glass membrane:

72% Silica (SiO_2)

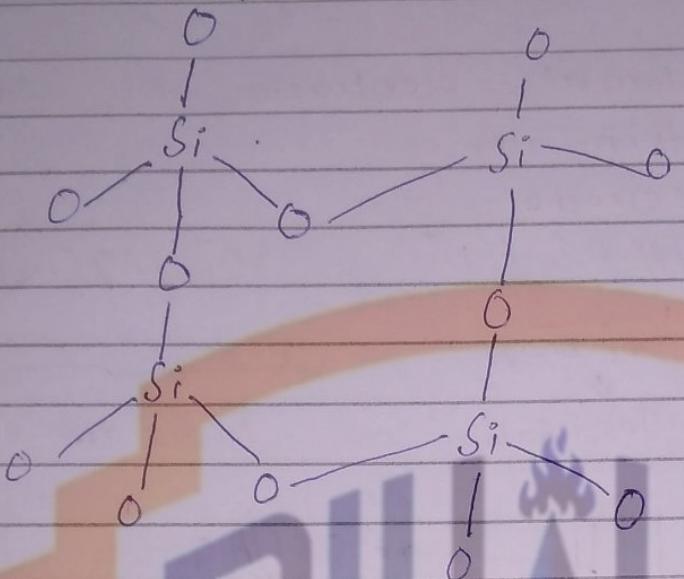
22% Na_2O (Sodium Oxide)

6% CaO

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These membrane show excellent specificity towards H^+ ions upto a pH of about 9. At higher pH value they become somewhat responsive to Na^+ as well as other singly charge cation. In other glass formulation, now sodium and calcium ions are replaced to various degree by lithium and barium ions. These membrane are superior, selective and have much better life time

Structure of membrane:

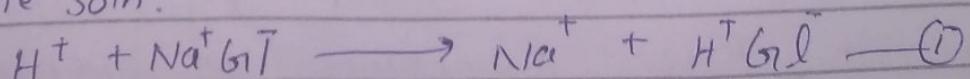


The Silica glass membrane has a finite three dimensional network (Si_4O_8) in which silicon is bonded to four oxygen atom and each oxygen is shared by 2 silicon atoms.

Hygroscopicity of glass membrane:

The surface of glass membrane is must be hydrated before it will function as a pH electrode. The amount of water involve is approximately 50mg/cm^3 of glass membrane. Non-hygroscopic glass do not show any pH function.

The effect is reversible and response of the glass electrode is restored by soaking in water. The hydration of pH sensitive glass membrane involves an ion exchange reaction b/w Singly charged cation in a glass lattice (Li or Na) and proton from the soln.



The process involve univalent cation exclusively because

di and trivalent cation are strongly held within the silicate structure. The ion exchange reaction is shown in eq(1) where $\text{G}\bar{\text{l}}$ represents negatively charged sites of glass surface. The equilibrium constant for this process is so large that the surface of glass membrane ordinarily consist of Silica acid ($\text{H}_2\text{G}\bar{\text{l}}$). In case of highly alkali media there Na^+ concentration is very large. A significant fraction of sites are occupied by Na^+ (cation) in the membrane.

Electrical conductance of membrane:

In order to serve as indicator electrode for cation a glass must be capable of conducting electricity. The conduction within hydrated glass membrane involved movement of Na^+ and H^+ ions. Conduction across the soln. / gel interface occur by the reaction.



This reaction occur b/w the glass and the analyte on the outer surface of glass membrane. While at the internal surface that is b/w the internal solution and glass membrane



Position of these two equilibria is determined by the H^+ ions in the solution on the two sides of the membrane. A boundary potential thus develops across the membrane. The magnitude of this potential depends

upon the difference that serves as an analytical parameter in a potentiometric PH measurement.

Membrane Potential:

There are four potentials that develop in a cell when PH has been determined with the help of glass electrode.

Two of these are $E_{\text{Ag}/\text{AgCl}}$ and E_{SCE} are reference electrode potentials. Third potential exist across the salt bridge that separates SCE from the analyte solution. This junction and its associated junction potential (E_j) are in cell used for potentiometric measurement of ionic species. The fourth and most important potential is boundary potential (E_B) which varies with PH of the solution. A reference electrode simply provide a mean for measuring magnitude of boundary potential. There is another potential called asymmetric potential. It is found in most membrane electrodes and its changes slowly with time.

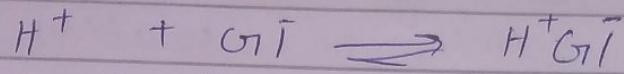
Boundary Layer potential.

The boundary potential (E_B) consist of two potential E_1 and E_2 . The boundary potential is the difference b/w of these two potential

$$E_B = E_1 - E_2$$

The potential of E_1 is the difference is determined by ratio of H^+ activity in

analyte solution to the H^+ activity in gel surface. and can be considered as a driving force for the reaction given



Similarly E_2 is related to H^+ activity in internal solution and corresponding gel surface and is related to the driving force for the reaction given below;



The relationship b/w two H^+ ion activity and the potentials E_1 and E_2 is given by the relation

$$(1) - E_1 = J_1 + 0.0592 \log \frac{a_1}{a'_1} \quad \begin{matrix} a_1 \rightarrow \text{conc. in} \\ \text{solution} \end{matrix}$$

$$(2) - E_2 = J_2 + 0.0592 \log \frac{a_2}{a'_2} \quad \begin{matrix} a_2 \rightarrow \text{conc. in} \\ \text{internal soln.} \end{matrix}$$

Where a_1 and a_2 are H^+ activities in solution, and a'_1, a'_2 are the corresponding electrode in internal side activities of H^+ ions in the surface layer of two gels. If the surface of two gels has same no. of sides available to accomodate protons then constants J_1 and J_2 are identical.

In addition if all the Na^+ on both surfaces have been replaced by the protons the two activities a'_1 and a'_2 are also same. Assuming these two equalities and subtracting eq (1) and (2) we get

$$E_B = E_1 - E_2 = 0.0592 \log \frac{a_1}{a_2}$$

Hence, provided the two gel surfaces are identical. The boundary potential E_B depends only on H^+ activity in solution on either side of glass membrane. For a glass pH electrode the H^+ activity of internal solution (a_2) is held constant. So above equation simplifies to

$$E_B = L + 0.0592 \log a_1$$

$$\therefore L = -0.0592 a_1$$

The potentials of electrodes become a measure of H^+ activity (a_1) of the external solution.

Asymmetric potential

When identical solution and reference electrode (pH of the reference electrode soln, and analyte soln. is same) are placed on the two sites of glass membrane. A potential of zero is expected. In fact a small asymmetric potential that changes with time is frequently encountered. The sources of the potential include a difference in strain on the two surface of the membrane imparted during manufacturing, mechanical abberation on outer surface and chemical itching. In order to eliminate the error caused by asymmetric potential, all membrane electrode must be calibrated against standard analyte soln.

Potential of Glass electrode:

The potential of glass electrode (E_{ind}) has three components.

1) The boundary potential (E_B)

2) A-Symmetric potential (E_{asy})

3) Potential of inner Ag/AgCl electrode.

$$E_B = L' - 0.0592 \log^H$$

$$E_B = L' + 0.0592 \log a_1$$

$$E_{\text{ind}} = E_B + E_{\text{Ag/AgCl}} + E_{\text{asy}}$$

$$E_{\text{ind}} = L' + 0.0592 \log a_1 + E_{\text{Ag/AgCl}} + E_{\text{asy}}$$

$$L = L' + E_{\text{Ag/AgCl}} + E_{\text{asy}}$$

$$E_{\text{ind}} = L + 0.0592 \log a_1$$

Alkaline Error:

A = Corning 015, H_2SO_4

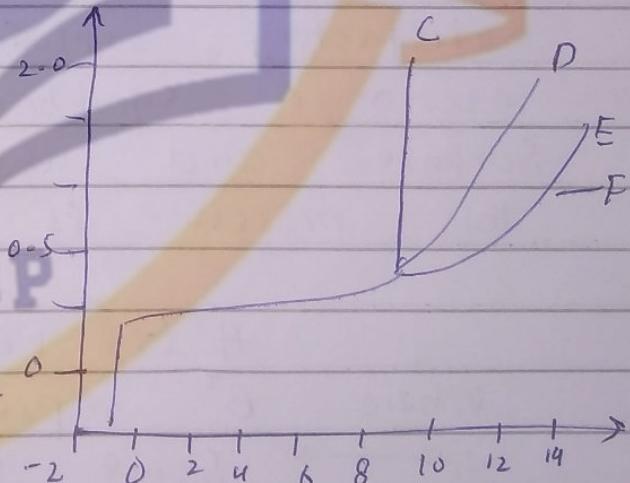
B = Corning 015, HCl

C = Corning 015, 1M NaOH

D = Beckmann GP, 1M Na^+

E = L 8 N Black Dot,
1N/1 Na^+

F = Beckmann type E, 1M Na^+



The glass electrode response to the concentration of both H^+ and alkali metal ions in basic soln.

The magnitude of alkali error for different glass membrane electrode is shown in Fig

These Curves referred to the soln. in which

Sodium ion concentration is held constant at 1 molar while the pH was varied. Note that the error is negative (the measured pH values are lowered than the true values) which suggest that electrode is responding to sodium ions as well as protons.

This observation is confirmed by the data obtained for solution containing different Na^+ concentration. Thus at pH 12 the electrode with corning 015 membrane register a pH of 11.3 when immersed in a soln. of Na ion concentration of 1 mole. All singly charged cation induce error whose magnitude depends upon the cation in equation and composition of the glass membrane. The alkaline error can be satisfactorily explained by assuming an exchange equilibrium b/w H^+ on glass surface and cations in the soln. and this process is reversible



where B^+ represents the activity of H^+ or some singly charged cations such as Na^+ ions. The equilibrium constant for this reaction is $K_{\text{eq}} = a_1 b_1 / a'_1 b'_1$ where a_1 and b_1 represents the activity of H^+ and B^+ in soln. and a'_1 and b'_1

represents H^+ and B^+ activities of these ions in the gel surface. For the glasses used for PH electrode K_{eq} is so small that activity ratio b'_i/a'_i is neglected but the situation is different in strongly alkaline media. In strongly alkaline media the activity ratio b'_i/a'_i for an electrode immersed in pH 11 soln. that is 1 molar Na^+ . The activity ratio is 10^{42} . In this case the activity of Na^+ relative to H^+ become so large that the electrode respond to species.

Next →

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In the strongly alkaline media the activity ratio b_1/α for an electrode immersed in pH 11 solution that is 1 molar ~~soak~~ Na^+ . The activity ratio is 10^{11} . In this case the activity of Na^+ relative to H^+ become so large that the electrode respond to both species.

Selectivity co-efficient.

The effect of alkaline metal ion on potential across the membrane can be accounted for by inserting an additional term in equation.

$$E_b = L + 0.059 \log \alpha, \quad \text{--- (1)}$$

$$E_b = L + 0.0592 \log \alpha + K_{HB} b_1 \quad \text{--- (2)}$$

K_{HB} = Selective co-efficient

Eq. (2) applies not only to glass electrode but all other types of membrane electrode. Selectivity co-efficient ranges from 0 (lower interference) to the values greater than unity.

If an electrode for ion A respond 20 times more strongly to ion B then K_{HB} value will be equal to 20. The product of $K_{HB} \cdot b_1$ for glass electrode is ordinarily small relative to α , provided that pH is less than 9. Under

these conditions, eq ② simplifies to eq ①.
At high PH values and high conc. of
Singly charge ions. Eq ② become more
Significant and an alkaline error is
encountered.

Acidic Error: /water activity error

Acidic Error oblique can be described
as water activity error. It is a 2nd type of
error which cause Non-Nernstian response.
Such errors occurs because the potential of
the membrane depends on the activity of
water with which it is in contact. If the
activity is unity, then their response is
Nernstian. In very acidic Solutions the activity of
water is less than unity because appreciable
amount used in solvating proton and a positive
error in PH reading reserved. A similar
type of error is reserved if activity of
water is decreased by higher conc. of
dissolved salts or by addition of non-
aqueous solvents like ethanol

like ethanol

→ Ion Sensing electrodes: / Glass membrane for other
than H^+

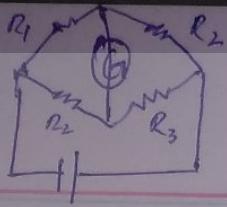
Glass membrane for determination of ion other than protons. Studies have been directed towards discovery of glass composition other than that permits the determination of cations other than H^+ . This application realises that H^+ activity (a_1) in the equation equilibrium be negligible relative to $K_{HB} b_1$.

$$a_1 K_{HB}$$

$$E_b = L + 0.0592 \log(a_1 K_{HB} b_1)$$

Under such circumstances the potential will be independent of pH and will be a function of p^B . Several investigators have demonstrated that p^B permits the direct potentiometry measurement of singly charged species such as $Na^+, K^+, NH_4^+, Li^+, Cs^+, Rb^+, Ag^+$, have been developed and are commercialized. Several investigators demonstrated that the incorporation of alumina (Al_2O_3 and B_2O_3) in the glass membrane has produced the desired effect and enhanced the response of Na and other singly charged cations.

→ Instrumentation and measurement of cell (EMF) Potential:- Poggendorff compensation method is used for the measurement of cell EMF. The principle of the method is to balance the unknown EMF against the non EMF, which can be easily varied, when these two EMF are equal, no current will flow.

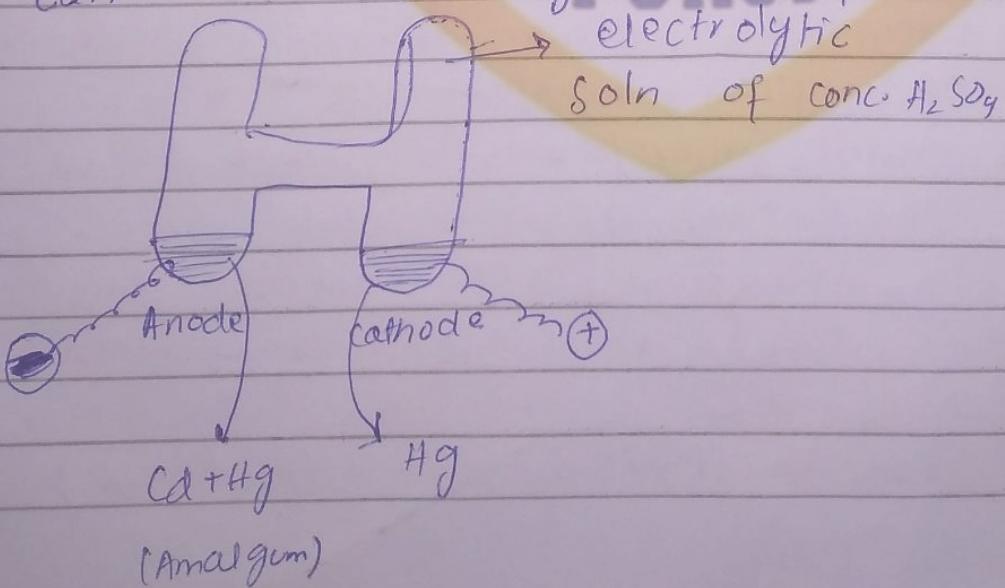


through the galvanometer placed in the circuit. The galvanometer is therefore employed as null instrument. A Null instrument as shown in Fig. A_2/A_4 furnishes opposing EMF which is connected in the series with Rheostat and the terminals of the slide wire AB.

A_2/A_4



A thin wire of uniform cross section named as potentiometer wire (AB). The cell the EMF of which is to be determined is connected to the one end (A) of the slide wire and through the galvanometer (G) and S_2 (switch) connected with slide wire C which can moved along the potentiometer wire AB.



A special double through switch S_1 may be provided to permit standard cell to be placed in circuit. In connecting battery and cell to the bridge it is essential that the +ve pole should be connecting to same end of the wire bridge, so that the

unknown cell will send current through the circuit in the direction opposite to that furnished by battery/accumulator. If we assume that potentiometer wire has uniform cross section and resistance

then fall of potential along slide wire will be uniform. The difference b/w potential at A and any point C will be proportional to the fraction length AC/AB , of the total fall of potential along wire.

The standard cell is now placed in circuit and position of C is adjusted to say C'. So that when switch S_2 is pressed no current will pass through galvanometer G_1 and EMF of the cell will be equal to that of battery multiplied by AC'/AB .

For each potentiometric work only changes in potential are required, so only variation of length AC is all which is required during titration. However the EMF of the battery is not quite constant, therefore a standard cell is required to calibrate the slide wire.

This is usually Weston cell which has an EMF of 1.0183 volts at 20°C or at any temp. $t^\circ\text{C}$

$$\text{emf} = 1.0183 - 0.0000466(t-20)$$

t = required Temp.

If the Standard cell is placed by means of switch S_1 and point of balance 'C' on bridge is determined, then unknown EMF can be calculated by the expression given below

$$\frac{AC}{AC'} = \frac{\text{emf of unknown cell}}{\text{emf of Std. cell (weston cell)}}$$

emf of the standard cell. In commercial potentiometer a rheostat is provided in series with 2V battery which can be adjusted. So that the effective emf applied across potentiometer is such that scale reading is volt or mV.

The membrane also respond to the activity S_2 with a cell potential of

$$E_{\text{cell}} = K - 0.0592 \log A_S$$

If we combine an insoluble silver salt such as AgCl with Ag_2S then membrane potential will also respond to the conc. of ~~the~~ Chloride with the cell potential

$$E_{\text{cell}} = K - 0.0592 \log a_i^-$$

By mixing Ag_2S with Cadmium (cds) copper sulphate (CuS) and lead sulphate (PbS). we can make an ion reactive electrode that respond to activity of

Cd^{2+} , Cu^{2+} and Pb^{2+} . In this case cell potential is $E_{\text{cell}} = K + \frac{0.0592}{2} \log A_M^{2+}$. The selectivity of this ion selective electrode depends upon the relative solubility of compounds.

- A chloride ion sensitive electrode using a $\text{Ag}_2\text{S}/\text{AgCl}$ membrane is more selective for bromide ($K_{\text{Cl}/\text{Br}} = 102$) and for iodide ($K_{\text{Cl}/\text{I}^-} = 106$) because AgBr and AgI are less soluble than AgCl . If the activity of bromide ion (Br^-) is sufficiently high, AgCl at the membrane / solution interface is replaced by AgBr and electrode response decreases substantially. Most of the polycrystalline ion selective electrodes operate over an extended range of pH levels. The equilibrium b/w Sulphide (S^{2-}) and HS^+ limits the analysis for S^{2-} to a pH range of 13 to 14. The membrane of fluoride ion selective electrode is fashioned from a single crystal of LaF_3 - which usually is doped with a small amount of EuF_2 to provide enhanced conductivity. Because EuF_2 provides only two fluoride ions compared to the three fluoride ions in LaF_3 , each EuF_2 produces a vacancy in the crystal lattice. Fluoride ion passes through the membrane.

by moving into adjacent vacancy. The LaF_3 membrane is sealed into the end of a non-conducting plastic cylinder which contains a standard solution of F^- , typically 0.1M NaF and a Ag/AgCl reference electrode.

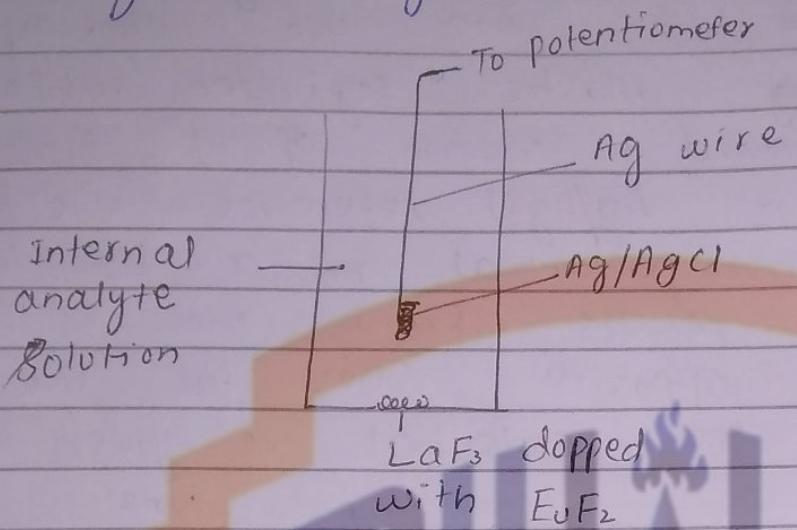
The membrane potential for a fluoride ion electrode results from the solubility of LaF_3 on opposite sides for the membrane and its potential is given by

Note:-

$$E_{\text{cell}} = K - 0.0592 \log \alpha_F \quad [K_{\text{F}/\text{OH}} = 0.1]$$

The only significant exception is negative ($K_{\text{F}/\text{OH}} = 0.1$) which imposes a max. pH limit for the successful analysis. Below a pH of 04 F^- predominantly exists as HF in soln, which does not contribute to the membrane potential. For this reason the analysis of Fluoride is carried out at pH greater than 4. Unlike a glass membrane ion selective electrode, a solid state ion selective electrode does not need to be conditioned before it is used and may be stored dry. The surface of the electrode is subject to poisoning as described above for a Cl⁻ ion selective electrode in contact with an excessive concentration of Br⁻. If an electrode is poisoned, it can be returned to its original condition by sanding and

Polishing the crystalline membrane



Liquid based ion selective electrode:-

Another class of ion selective electrode uses a hydrophobic membrane that contains a liquid organic complexing agent that reacts selectively with the analyte. Three types of complexing agent has been used namely cation exchangers, anion exchangers and neutral ionophores. A membrane potential exist if the analyte activity is different on the two sides of the membrane.