

By

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ELECTROCHEMISTRY

1. What is electrochemistry? What is its importance?

Ans: Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy into Chemical energy and vice-versa. It is the study of phenomena at electrode solution interfaces. Electrochemistry deals with the relationship between electrical, chemical phenomena and the laws of interaction of these phenomena. The branch of electrochemistry is of major technical importance. The laws electrochemistry forms the basis of electrolysis and electro synthesis. Knowledge of electrochemistry is of immense importance to study about the causes of destruction of materials caused due to corrosion. There are two processes where both are interrelated. Electrolysis is one process where electrical energy causes chemical changes.

E.g. electrolysis of water yields H_2 and O_2 .

In this process, electricity is passed through water (having few drops of an acid) and H_2 and O_2 are collected at different electrodes. The equipment is called electrolytic cell.

In the other process, certain chemical reactions take place in a vessel and produce electrical energy. The device is called electrochemical cell. The specific reaction is called the redox reaction and the vessel is called the cell. This process is also called the electromotive process. Electromotive means motion of electron, i.e. the flow of current.

The two processes above can be summarized as follows:

1. Electrical energy causing chemical reactions \rightarrow Electrolysis (Electrolytic cell)

In redox reactions, electrons are released (oxidation) and consumed (reduction).

In galvanic cells, batteries and fuel cells chemical energy is transformed into electrical energy and in electrolysis, electrical energy is converted into chemical energy

2. What are the differences between metallic and electrolytic conductance?

Metallic conductance	Electrolytic conductance
1. Conductance is due to migration of electrons.	1. Migration of ions to different electrodes takes place in molten salts (or) electrolytic solution
2. It does not result in any chemical change.	2. It involves the decomposition of the conductor.
3. It decreases with increase in temperature.	3. It increases with increase in temperature.
4. It does not involve the transfer of any matter.	4. It involves the transfer of matter.

3. What is specific, equivalent, molar conductance and cell constant?

Ans: The resistance of a uniform conductor is directly proportional to its length (l) and inversely proportional to the cross-sectional area (A). Thus,

$$R \propto \frac{l}{A}$$

Or

$$R = \rho \frac{l}{A} \quad (1)$$

The proportionality constant (ρ) is called the specific resistance. In the equation (1)

if $l = 1 \text{ cm}$ and $A = 1 \text{ cm}^2$, then

$$R = \rho$$

Thus specific resistance (ρ) is defined as the resistance of an electrolyte solution of 1 cm in length and 1 cm^2 cross-section i.e. resistance of one cubic centimeter of the electrolytic solution. The unit of specific resistance is ohm-centimeter.

The reciprocal of specific resistance (ρ) is called specific conductance. This may be defined as the conductance of one centimeter cube of a material and is denoted by K . Thus,

$$K = \frac{1}{\rho} \quad (1.2)$$

From Eqs. (1.1) and (1.2)

$$K = \frac{l}{\rho R} \quad (1.3)$$

Its unit is $\text{ohm}^{-1} \text{ cm}^{-1}$. In SI units, the units of specific conductance (k) are $S\text{m}^{-1}$, where S stands for Siemen.

Equivalent conductance

Equivalent conductance is defined as the conductance of an electrolyte solution containing one gram equivalent of the electrolyte. It is usually denoted by λ . The relation between equivalent conductance (λ) and specific conductance is given as

$$\lambda = V \times K$$

where,

V is the volume of the electrolyte solution in ml containing one gram equivalent of the electrolyte. If the concentration of the electrolyte solution is C grams per liter. Then volume containing 1 gram equivalent of the electrolyte will be $1/c$

liter or $\frac{1000 \text{ ml}}{C}$

Thus by using above equation

$$\lambda = V \times K$$

$$= \frac{1000}{C} \times K$$

The unit of equivalent conductance is $\text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

Molar conductance

Molar conductance is defined as the conductance of electrolytic solution containing one mole of electrolyte. It is denoted by λ_m . If V_m ml is the volume of the solution containing one gram mole of the electrolyte, then $\lambda_m = V_m \times K$.

If m is the concentration of the solution in moles per litre, then

$$\lambda_m = \frac{1000 \times K}{m}$$

The unit of λ_m is $S\text{m}^2 \text{ mol}^{-1}$.

Cell Constant

It is a constant, characteristic of the cell in which the electrolyte is taken and its value depends on the distance between the electrodes and area of cross section of the electrodes.

$$\text{Cell Constant} = \frac{\text{Distance between the electrodes}}{\text{area of cross-section of each electrode}}$$

$$= \frac{l}{a}$$

And specific conductance, $K = \frac{l}{Ra}$

Therefore, specific conductance = $\frac{\text{cell constant}}{R}$

Or cell constant = Specific Conductance $\times R$

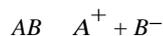
If area of cross-section is in cm^2 and distance between the electrodes is in cm. The unit of cell constant is cm^{-1} .

4. What is the equivalent conductance at infinite dilution? How does it varies with conc. for strong and weak electrolytes?

Ans: On dilution, the volume of electrolyte solution increases. Thus number of ions furnished by electrolyte per unit volume is decreased. Hence the specific conductance decreases on progressive dilution.

Equivalent Conductance

Let us consider a weak electrolyte AB , which is ionized as



when the electrolyte solution is diluted, degree of dissociation increased. As a result conductivity. Is increased If the process of dilution is continued, more and more electrolyte molecule will undergo dissociation. At that point on further dilution, no more ions will produce and equivalent conductance will not increase. This limiting value is known as equivalent conductance at infinite dilution (λ_0 or λ_∞).

For strong electrolyte, equivalent conductance (λ) increases with dilution and cause of this variation is fundamentally different from weak electrolytes.

Conductivity of an electrolyte depends on the speed of ion and concentration of ion. The motion of an ionic species in an electric field is retarded by the oppositely charged ions due to inter ionic attraction. On dilution, the concentration of electrolyte decreases and the retarding influence of oppositely charged ions decreases. Consequently the speed of ion increases and equivalent conductance of electrolyte is increased.

The variation of λ with concentration for strong electrolytes is given by De-bye-Huckel-Onsager conductance equation

$$\lambda = \lambda_0 - [A + B \lambda_0] C \sqrt{C}$$

Where,

λ = Equivalent conductance at concentration C

λ_0 = Equivalent conductance at infinite dilution

$(A + B\lambda_0)\sqrt{C}$ = Retarding influence

A and B include two important properties of solvent i.e. dielectric and viscosity.

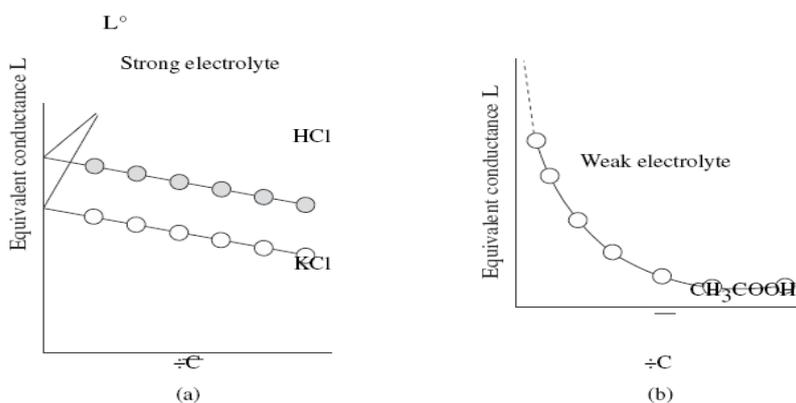


Fig. 1.3 Variation of equivalent conductance (L_m) with square root of concentration C for

(a) Strong electrolytes and (b) Weak electrolytes.

The equivalent conductance when plotted against C yields a straight line.

Molar conductance of an electrolyte increases with increase in concentration because on dilution degree of dissociation of the electrolyte increases.

5. What is Kohlrausch's law? Mention its applications?

Ans: Kohlrausch's law of independent migration of ions At infinite dilution, each ion of an electrolyte makes a definite contribution to the total equivalent conductance of the electrolyte, and this contribution is independent of the presence of the other ionic species.

Kohlrausch's law is applicable to calculate:

1. Equivalent conductance of weak electrolytes at infinite dilution.
2. Calculation of absolute ionic mobility.
3. Calculation of Solubility of sparingly soluble salt.
4. Calculation of degree of ionization.
5. Calculation of ionic product of water.

1. A solution of salt (1.0 N) surrounding two platinum electrodes 2.1 cm apart and 4.2 cm² in area was found to offer a resistance of 50 ohms. Calculate the equivalent conductivity of the solution.

Solution:

$$l = 2.1 \text{ cm} \quad C = 1.0 \text{ N}$$

$$a = 4.2 \text{ cm}^2$$

$$R = 50 \text{ ohm}$$

$$\begin{aligned} \text{Specific Conductance (K)} &= \frac{1}{R} \cdot \frac{l}{a} \\ &= \frac{2.1}{4.2 \times 50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Equivalent conductance}(\Lambda) &= \frac{K \times 1000}{c} \\ &= \frac{0.01 \times 1000}{1} = 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1} \end{aligned}$$

2. Specific conductance of a decinormal solution of KCl is 0.0112 ohm⁻¹ cm⁻¹.

The resistance of a cell containing the solution was found to be 56. What is the cell constant?

$$K = 0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$R = 56 \text{ ohm}$$

$$\text{Cell constant} = \text{Specific conductance} \times \text{Resistance}$$

$$= K \times R$$

$$= 0.0112 \times 56 = 0.6272 \text{ cm}^{-1}$$

3. The equivalent conductance of NaCl, HCl and CH₃COONa at infinite dilution are 126.45, 426.16 and 91.0 ohm⁻¹ cm² equiv⁻¹, respectively at 25°. Calculate the equivalent conductance of acetic acid at infinite dilution.

6. Why λ_{∞} for a weak electrolyte cannot be determined experimentally ?

Ans: Equivalent conductance of weak electrolytes increases steadily with dilution and the graph drawn between λ_{eq} and \sqrt{c} is not a straight line. The curve does not meet the equivalent conductance axis. So, the value of λ_{∞} cannot be determined by extrapolation.

Hence equivalent conductance at infinite dilution can be determined indirectly by Kohlrausch's law

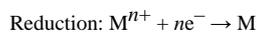
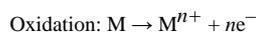
6. The specific conductance of an electrolyte decreases when the equivalent conductance increases with dilution. Explain why?

Ans: When the electrolyte solution is diluted, the degree of dissociation increases but the total volume increases. The number of ions per cm³ decreases, since the volume of the solution increases. The number of ions per cm³

Decreases, since the volume of the solution increases. The number of ions per cm³ overweighs the increase in conductance with increase of dilution. Since the total number of ions / gm .eq. increases with dilution due to increased degree of ionization.

7. What is electrode potential? How is it measured?

Ans: When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction). The process of oxidation or reduction depends on the nature of metal. In this process, there develops a potential between the metal atom and its corresponding ion called the electrode potential.



The tendency of oxidation results in the dissolution of metal and in the release of electron density on the surface of metal with respect to electrolyte solution. Similarly in reduction, the positive charge density is more on the surface of metal with respect to the solution. Consequently, they attract oppositely charged particles and form a double layer of charge called the Helmholtz electrical double layer (Fig. 1.1).

Oppositely charged counter ions close to the surface

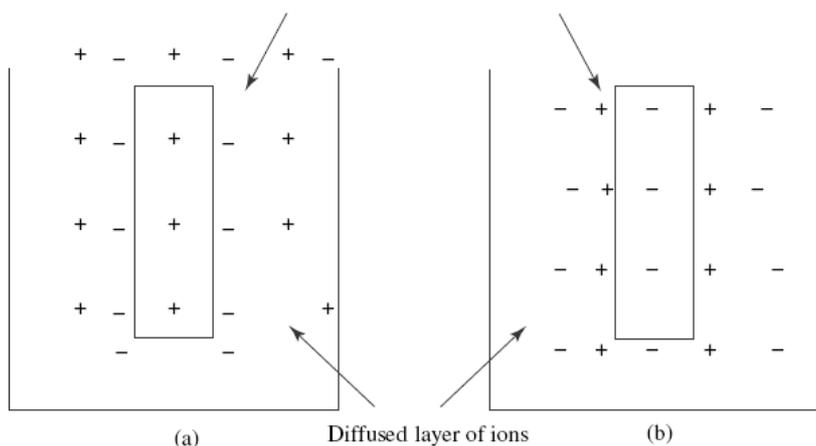
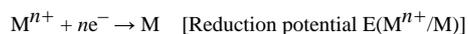
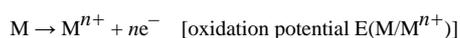


Fig. 1.1 Electrical double layer at the metal–solution interface:

(a) positively charged metal and (b) negatively charged metal

There is a dynamic equilibrium between metal and metal ion and the potential difference between the two is called the electrode potential or the equilibrium potential. It is measured in volts.

The potential difference for oxidation reaction is called the oxidation potential and that of reduction is called the reduction potential.



For any system, its oxidation and reduction potentials are numerically same with the opposite sign, i.e. $E(M/M^{n+}) = -E(M^{n+}/M)$

The value of electrode potential depends upon (i) the nature of the metal, (ii) the temperature and (iii) the concentration of the electrolyte. Nernst equation gives the idea for the same.

$$E = E^0 - \frac{RT}{nF} \log [M^{n+}]$$

where E = electrode potential,

E^0 = standard electrode potential,

R = gas constant,

T = absolute temperature,

F = Faraday constant,

n = number of electrons under redox process, and

M^{n+} = concentration of electrolyte.

Substituting the values of R , T and F , the above equation is modified as

$$E = E^0 - \frac{0.0591}{n} \log[M^{n+}]$$

For an electrode–electrolyte system, if the concentration of the electrolytic solution is 1 mol/L, the above relationship can be written as

$$E = E^0 - \frac{0.0591}{n} \log[M^{n+}]$$

For an electrode–electrolyte system, if the concentration of the electrolytic solution is 1 mol/L, the above relationship can be written as

$$E = E^0 - \frac{0.0591}{n} \log 1 \quad \text{Or} \quad E = E^0 \quad (\text{as } \log 1 = 0)$$

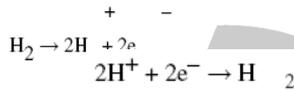
Hence, the standard electrode potential of a metal is the electrode potential when the metal is dipped in its electrolytic solution of unit concentration at room temperature.

Measurement of Electrode Potential

In no way, one can measure directly the electrode potential of an electrode. It is possible with the help of a reference electrode. The most common is the standard hydrogen electrode (SHE).

SHE has a cylindrical glass vessel dipped in 1 M HCl. A platinum wire is fitted inside the glass vessel. Hydrogen gas is passed in it at 1 atmospheric pressure. SHE acts as anode and cathode, both as per need.

At anode



At cathode

SHE is a reversible electrode and can be represented as shown in Fig. 1.2



The electrode potential of SHE is zero. To measure the electrode potential of any electrode, it is connected to SHE and the system acts like a cell. The electro-motive force (EMF) of the cell is measured with the potentiometer

$$E_R = \text{electrode potential of the right side electrode}$$

$$E(\text{cell}) = E_R - E_L$$

$$E_L = \text{electrode potential of the left side electrode}$$

Since the electrode potential of the SHE is zero, the reading of the potentiometer will be the electrode potential of the electrode. Other reference electrodes are chlorine electrode, calomel electrodes, etc.

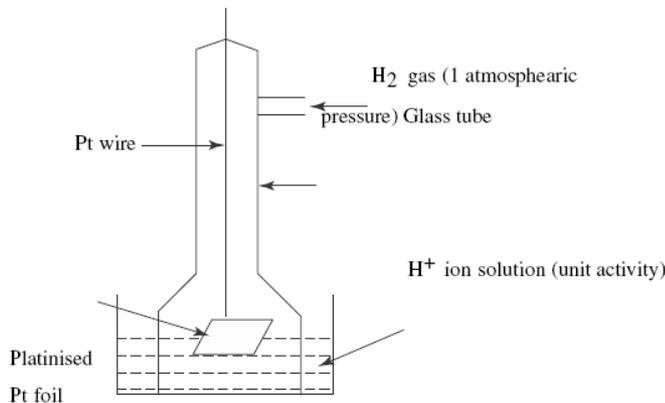


Fig. 1.2 Standard hydrogen electrode

8. What is a galvanic cell? Describe galvanic cell with a neat diagram? Write the cell reaction?

Ans: The galvanic cell is made of two half cells. One is oxidation or anodic half cell and the other one is reduction or cathodic half cell.

Daniel cell is an example of galvanic cell having zinc and copper electrodes. The first half cell consists of zinc electrode dipped in $ZnSO_4$ solution and the second half cell is made of copper electrode dipped in copper sulphate solution. Both half cells are connected externally by metallic conductor (connecting wire) and internally by a bent glass tube having saturated solution of a strong electrolyte (K_2SO_4) called salt bridge. It acts as a bridge between the two half cells (Fig. 1.3).

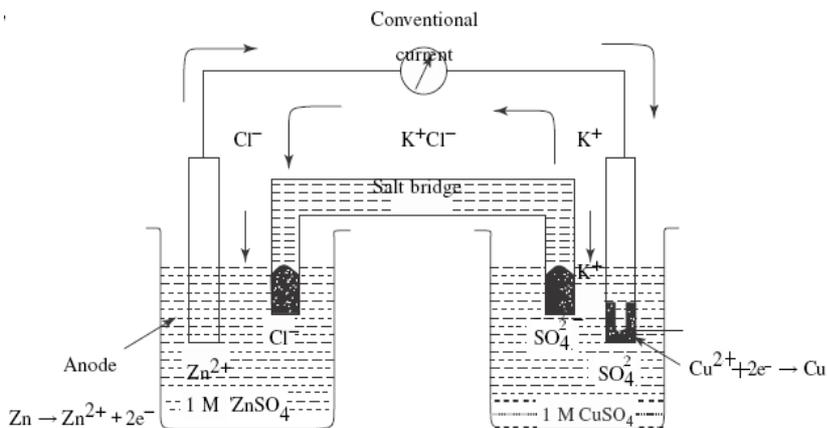


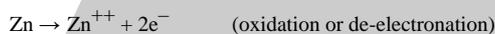
Fig. 1.4 A galvanic cell (Daniel cell)

A zinc or a copper galvanic cell can be represented as



The double bar shows salt bridge, i.e. electrolyte–electrolyte junction. The chemical reactions taking place at both electrodes may be given by as follows:

At anode:



At cathode:



The overall reaction is



The electrode showing oxidation reaction is anode and the next where reduction occurs is cathode. As per IUPAC convention, the anode is always on the left and the cathode is always on the right.

As the connection is complete, the flow of electron will be externally from anode to cathode and internally from cathode to anode through the salt bridge. The flow of current is due to the difference in electrode potentials of both the electrodes. The potential difference in the cell is called the EMF that is measured in volts. It can be measured by the potentiometer.

Because of the polarisation of the electrodes, the flow of the current becomes slow after using them for a long time

9. What is the importance of reference electrodes? Describe the standard hydrogen and saturated calomel electrode.

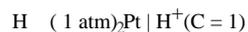
Ans: The determination of the potential of a single electrode is not possible. Since any circuit necessarily contains two electrodes. A reference electrode is an electrode which has a stable and well known potential. It is used as half cell to build an electrochemical cell, to determine the potential of the other electrode. A fixed potential difference is applied between the working electrode and the reference electrode this potential drives the electrochemical reaction at the working electrode surface. The current produced from the electrochemical reaction at the working electrode is balanced by a current flowing in the opposite direction at the counter electrode. The example of reference electrodes are standard hydrogen electrode, calomel electrode, silver-silver chloride electrode etc.

Standard Hydrogen Electrode (Normal Hydrogen Electrodes)

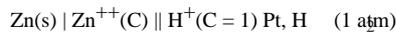
It is redox electrode which is widely used as reference electrode. It can be used either anode or cathode depending upon the nature of the half cell for which it is used. The SHE consists a platinum electrode immersed in a solution with a hydrogen ion concentration of 1.0 M. The platinum electrode is made of a small square of platinum foil which is platinized and known as platinum black. (platinum black provides a surface on which the

hydrogen gas can be in contact with the hydrogen ions (aq.)

A stream of pure hydrogen is bubbled around the platinum foil at a constant pressure of one atmosphere. The SHE may be represented as



Let us consider the zinc electrode whose potential is to be determined, combined with a standard hydrogen electrode to form a complete cell.



In this case reduction occurs at hydrogen electrode and oxidation takes place at zinc electrode as shown below.

1. Platinized platinum electrode
2. Hydrogen blow
3. Solution containing hydrogen ion concentration of unit molarity
4. Seal for prevention of the oxygen interference

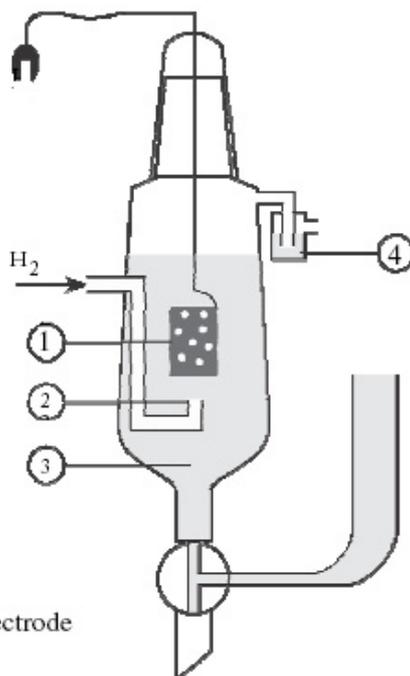
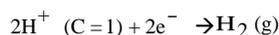


Fig. 1.5 Standard hydrogen electrode

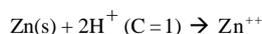
Hydrogen electrode



Zinc electrode



The overall cell reaction become

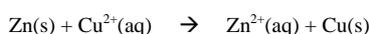


10. What is Nernst equation? Explain with an example

Ans: Nernst equation for a cell reaction:

The emf of a cell is the algebraic sum of the single electrode potentials of the cell.

Ex: Consider the cell



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nf} \log_{10} \frac{C_{\text{Zn}^{2+}}}{C_{\text{Cu}^{2+}}}$$

$$\text{At } 25^{\circ}\text{C} \quad E^{\circ} = \frac{0.0591}{n} \log K$$

$$E^{\circ} = \frac{0.0591}{n} \log K - \frac{0.0591}{n} \log_{10} \frac{C_{\text{Zn}^{2+}}}{C_{\text{Cu}^{2+}}}$$

Nernst equation is used to calculate the potential of standard electrode nernst eq is given as
 $E = E^0 - \frac{2.303RT}{nF} \log_{10}[H^+]$

Where, E^0 = Standard electrode potential
 R = gas constant (8.313)
 T = absolute temp. (298K)
 F = Faraday (96500 coulombs)
 n = valency of the ion and
 E = single electrode potential

Substituting the values
 $E = E^0 - 0.0591 \log H^+$
 $E = E^0 - 0.0591 \text{ pH}$

Using the Nernst equation, the EMF of the complete cell, E may be expressed as

$$E = E^0 - \frac{2.303 RT}{2F} \log \frac{C_{Zn^{++}} \cdot \frac{1}{2} C_{H_2}}{C_{Zn} \cdot \frac{1}{2} C_{H^+}^2} \quad (1)$$

Concentration of hydrogen gas by convention is taken to be unity when passed at one atmosphere pressure. The concentration of solid is also taken to be unity and $C_{H^+} = 1$.

The Eq. (1), becomes

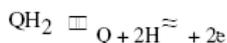
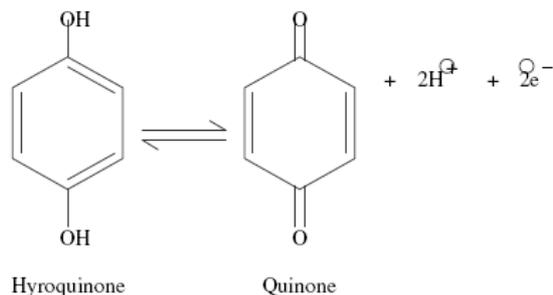
$$E = E^0 - \frac{2.303 RT}{2F} \log C_{Zn^{++}} \quad (2)$$

The EMF of the cell, E is a measure of potential of the zinc electrode because the electrode potential of SHE is assigned zero.

11. What is quinhydrone electrode? What are its advantages and disadvantages?

Ans: It is type of redox electrode which can be used to measure the H^+ ion concentration of a solution. The electrode consists of an inert metal electrode (a platinum wire) in contact with quinhydrone crystals and a water based solution. Quinhydrone is slightly soluble in water, formed by equimolar mixture of hydroquinone and quinone.

The each one of the two substances can be easily oxidised or reduced to the other. In this case the electrode reaction may be represented as follows:



Using Nernst equation, the potential of quinhydrone electrode E_Q may be written as

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

E^0 = standard potential of the electrode

Since $(Q) = [QH_2]$, concentration of quinone and hydroquinone are equal.

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

or

$$E_Q = E_Q^0 - 0.05915 \log [H^+] \text{ at } 25^\circ\text{C}$$

$$E_Q = E_Q^0 - 0.05915 \text{ pH}$$

The above equation can be used in the calculation of pH if E_Q^0 and E_Q values are known. The standard electrode potential E_Q^0

has been found to be -0.06944 volts and for determination of E_Q , the quinhydrone electrode is coupled with calomel electrode and EMF of cell is measured.

Advantages:

1. The electrode is very easy to setup.
2. The pH value obtained is very accurate.
3. Very small quantities of solution is sufficient for the measurement.

Disadvantages:

1. The electrode cannot be used in more alkaline solution (pH>8.5) and also with solutions that react with quinone or hydroquinone (Ex: Fe^{2+} , MnO_2).

12. Explain why a glass electrode is preferred to quinhydrone electrode in measuring pH of a solution ?

Ans.: Glass electrode is not easily oxidized and attains equilibrium rapidly. It can be safely used up to pH of 10. But quinhydrone electrode can be used up to a pH of 8 only. It cannot be used in a redox system.

13. What is the role of salt bridge in the galvanic cell?

Ans.: Salt bridge provides a mechanism by which the ions not directly involved in the redox reaction can migrate to anodic and cathodic compartment to maintain electrical neutrality in the solution.

14. A dry cell stops functioning if left idle for some time why?

Ans.: As the products of the reaction accumulates near the electrodes, the electrode reaction becomes slow and stops functioning. After leaving idle for sometime the products diffuse away and the cell starts functioning again.

15. A fuel cell is considered better than an electrical power plant using same fuel Why?

Ans: The fuel cells are considered better since the reaction takes place under nearly reversible conditions and the efficiency is higher.

16. Describe the construction and working of a glass electrode?

Ans: A glass electrode is a type of ion selective electrode consists of a thin walled glass bulb attached to a glass tube. A very low melting point and high electrical conductivity glass is used for the construction of this bulb. The glass tube contains a dilute solution of constant pH of HCl (0.1 N) solution. A silver-silver chloride electrode or platinum wire is immersed as reference electrode in the HCl solution. The working of glass electrode is based upon the observation that when a glass surface is in contact with a solution, there exists a potential difference between the glass surface and the solution, the magnitude of which depends upon the H^+ ion concentration of the solution and the nature of glass. The glass electrode may be represented as



The electrode potential of the glass electrode depends upon the concentration of H^{\sim} ions contained in the experimental solution and is given by

$$E_g = E_g^0 - \frac{2.303 RT}{F} \log H^{\sim}$$

$$= E_g^0 - 0.059 \log H^{\sim}$$

$$E_g^0 = 0.059 - 11$$

E_g^0 is the standard electrode potential i.e. the potential of the glass electrode when the solution contains unit concentration of H^+ ions. The value of E_g^0 depends on the nature of the glass used in the construction of the glass bulb.

The pH of the solution can be determined if the potential of the glass electrode is known. To determine the value of glass electrode (E_g), the glass electrode is combined with a reference electrode such as calomel electrode. The EMF of this cell will be given by

$$E_{\text{cell}} = E_C - E_g$$

$$= E_C - E_g^0 - 0.059 \text{ pH}$$

$$\text{pH} = \frac{E_C - E_g^0 - E_{\text{cell}}}{0.059}$$

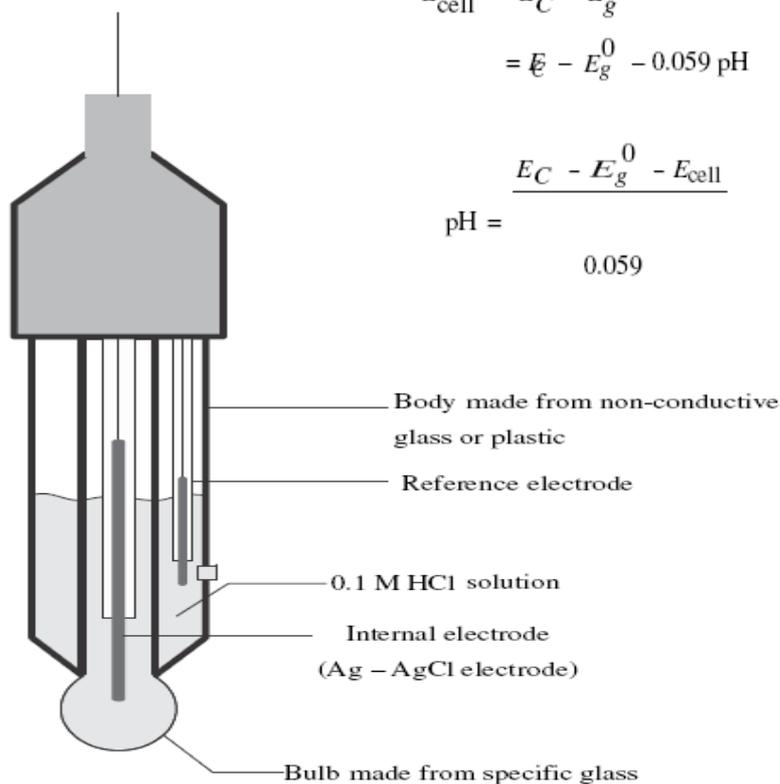


Fig. 1.6 Glass electrode

E_C is the electrode potential of calomel electrode and is constant for a particular concentration of HCl solution. Thus, measuring the EMF of the cell using experimental solution, the pH of the solution can be calculated.

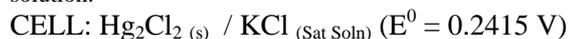
The commercial pH meters are based on potentiometric circuits capable of measuring the EMF of cell consisting of the glass electrode and reference electrode and indicate the pH of solution directly in a digital display.

There are different type of pH glass electrode and almost all electrodes are working in the most popular pH range from pH = 1 to pH = 12.

17. How does the saturated calomel electrode acts as a reference electrode?

Ans: It consists of a glass tube having side tube on each side (Fig:1) Pure sample of mercury is placed at the bottom of the tube and connected to the circuit by a platinum wire, sealed in a glass tube. A paste mercurous chloride (Hg_2Cl_2) or calomel and mercury in KCl solution is placed on the surface of mercury. Potassium chloride solution is used as electrolyte.

The electrode whose potential is to be determined is connected to this electrode through salt bridge. The potential of electrode depends upon the concentration of KCl solution.



17. What are the for the conditions for the standard cell?

Ans: One of the important condition for the standard cell is that ,the cell must be

- 1) Capable of giving constant, reproducible emf.

It must have negligible temperature coefficient of the emf (i.e. change in emf should be very small with change in temperature). Most widely used standard cell is Weston cell, which consists of an H-shaped glass vessel. One limb contains mercury which serves as + ve electrode in contact with a paste of sparingly soluble Hg_2SO_4 and another arm contains the electrode 12.5% Cd amalgam which serves as -ve electrode

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