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Electro Chemistry

The branch of science which deals with the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations is called electrochemistry. The subject is both of theoretical as well as practical importance. The basis of these processes is redox reactions. There are large numbers of chemical and biological reactions which are redox reactions. These are used in burning fuels for obtaining energy for domestic, transport or industrial purposes, digestion of food in animals, photosynthesis to capture energy from the sun, many industrial processes for extracting metals from their ores and manufacture of important chemicals, operation of dry and wet batteries, fuel cell etc. The electrochemical processes are less pollution creating and energy efficient so that these are very important for creating new technologies which are eco friendly. The transmission of sensory signals to brain through cells and vice versa and communication between cells has electrochemical origin. Therefore it is an interdisciplinary subject. In this chapter we will introduces with some initial knowledge of electrochemistry.

Metallic and Electrolytic conductors :

All the substances do not conduct electric current. The substances which allow passing the electric current are called conductors. Metals such as copper, silver, tin etc. are the best conductors. On the other hand, the substances which do not allow passing the electric current through them are called insulators or non conductors, e.g. rubber, glass, wood, plastics etc.

The conductors are mainly classified into two types :-

(1) Metallic or Electronic Conductor :

There are metallic substances which allow the electricity to pass through them without undergoing any chemical change. Metals and their alloys is very god conductor of electricity. In these conductors, the flow of electric current is due to the flow of electrons in valence shell electrons of metals. The conductance in the electronic conductors depends upon :

(i) The nature and structure of metal

(ii) The number of valence electrons per atom

(iii) The density of metal, and

(iv) Temperature (conductance decreases in these conductors with increase in temperature)

As the electrons enter at one end and go out at the other end, the composition of the metallic conductors remains unchanged. Some non-metals like graphite, carbon black, and some organic polymers are also show electric conductance due to some loosely bonded electrons in their structures.

(2) Electrolytes or Electrolytic Conductors :

The substances which allow the electric current to pass through them in their molten state or in their aqueous solutions and undergo any chemical change, are called electrolytes or electrolytic conductors. For example acids bases and salts are electrolytes. The flow of electric current in electrolytic solution is called electrolytic conduction. In this type of conduction, charge is carried by ion in solution. Therefore, these are also called ionic conductors. Thus, the conduction will not occur unless the ions of the electrolyte are free to move. Therefore these substances do not conduct electricity in the solid state. On the other hand, in non-electrolytic conductors do not passes electricity either in their molten state or through their aqueous solutions. For example sugar, glucose, ethyl, alcohol, urea etc.

Table (1) Differences between metallic and electrolytic conductors are shown in the following table.

S.N.	Metallic Conductors	Electrolytic Conductors
1	Metallic conduction is carried by the movement of electrons	Electrolytic conduction is carried out by the movement of electrons
2	There is no any chemical change occur in these conductors	It involves the decomposition of the electrolyte as a result of the chemical reaction
3	It does not involve the transfer of any matter	It involves the transfer of matter as ions
4	Metallic conduction decreases with increase in the temperature	Electrolytic conduction increases with increase in temperature

Classification of Electrolytes :

All the electrolytes do not ionize to the same extent in solution and on this basis; the electrolytes are broadly divided into two types: strong electrolytes and weak electrolytes.

Strong electrolytes are those which are almost completely dissociated into ions in solution like strong acids, strong bases, salts of strong acid and strong bases, salts strong acid and weak base, salts of weak acid and strong bases etc. For example HCl, NaOH, NaCl, NH_4Cl, CH_3COONa etc. These electrolytes dissociates at their general concentrations .

On the other hand, the electrolytes which do not ionize completely in solution are called weak electrolytes like, weak acids, weak bases and salts from weak acid and weak bases. For example CH_3COOH, H_2CO_3, H_2BO_3, NH_4OH, $Al(OH)_3$, CH_3COONH_4 etc. Thus, in case of weak electrolytes, equilibrium is established between the unionized electrolyte and the ions formed are solution. The extend of ionization of a weak electrolyte is expressed in terms of "degree of ionization or degree of dissociation", which is expressed by alpha (α).

Factors affecting Electrical Conductivity of Electrolyte Solution :

The electrical conductivity of the solutions of electrolytes depends upon the following factors :

(1) Interionic Attractions : These depend upon the interaction between the ions of the electrolyte and the molecules of the solvent which are called "solute – solvent interactions". If the solute-solvent interactions are large, the extent of dissociation will be less. The energy of solute-solvent interaction is called 'solvation energy' and if solvent is water then it is called 'hydration energy' If the salvation energy is large than ion-ion interaction energy the solute will not be desolve.

(2) Solvation of Ions : These depend upon the interaction between the ions of the solute and the molecules of the solvent and are called solute-solvent interactions. If the solute-solvent interactions are strong, the ions of the solute will be highly solvated and their electric conductivity will be low.

(3) Viscosity of the Solvent : The viscosity of the solvent depends upon the solvent-solvent interactions. Larger the solvent-solvent interactions higher will be the viscosity of solvent decreases the conductivity.

(4) Concentration of Solution : Conductance of a solution depends upon the number of ions and number of ions depends upon the concentration of the solution. Thus the conductance increases with increase in dilution of the solution due to degree of dissociation of solute molecules increases with dilution.

(5) Temperature : Migration of ions towards the oppositely charged electrode depends on the kinetic energy of conducting ions and the kinetic energy increases with increase in the temperature. This behavior is quite opposite to the metallic conductors. In metallic conductors the conductance decreases with increase in the temperature because the electronic vibration increases which causes barrier to the motion of flow of electrons.

Electrolytic Cells and Electrolysis :

Electrolysis is a process in which chemical changes take place by the passage of electric current in the electrolytic solutions. The cells used to carry out electrolysis are called electrolytic cells. In these processes the electrical energy brings a net chemical change in the electrolytic solution. Thus, in these cells the redox reactions on the electrodes are non-spontaneous processes ($\Delta G > O$).

The process of electrolysis is carried out by taking the solution of an electrolyte in a suitable vessel which is made up of either glass or of a material which is bad conductor of electricity. Two metallic rods or plates are suspended in the electrolytic solution which is connected to the terminals of a battery with the help of metallic wires. These metallic rods allow the passage of current and are called electrodes. The electrode connected with positive terminal of battery is called anode and the other which connected with negative terminal is called cathodes.

When an electrolyte is dissolved in water, it splits up into negative and positive ions for example, if HCl is dissolve in water it splits up into H^+ and Cl^- ions. On passing electric current through the solution, the ions are attracted by oppositely charged electrodes. This movement of ions in solution is known as ionic or electrolytic conduction and constitutes flow of current through the solution.

When electric current (DC voltage is applied to the two electrodes, then H^+ ions discharge at the cathode (negative electrode) and following reaction takes place :

At Cathode : $H^+ + e^- \rightarrow 1/2 H_2$ (Reduction)

At the anode, the Cl^- ions discharge as follows-

At anode : $Cl^- \rightarrow 1/2\, Cl_2 + e^-$ (Oxidation)

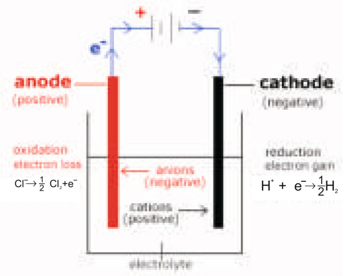


Fig. (1) Electrolysis Process

To make the flow of electricity, electrons flow from anode to cathodes by external circuit while in the internal flow of electricity is due to the flow of ions to oppositely charged electrode. The process will be continuing till the :

(1) Circuit is closed

(2) Concentration of HCl becomes zero in the solution

Faraday's Laws of Electrolysis :

Michal Faraday performed a large number of experiments during 1833-34 on electrolysis and summarized the results in the form of two laws known as Faraday's laws of electrolysis.

(I) Faraday's First law of Electrolysis :

According to this law the amount of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte solution.

Thus, if m grams of substance is deposited on passing Q coulombs of electricity, then :

$m \propto Q$ but $Q = It$

= Electric current x time of passing

$\Rightarrow$ $m = wQ$

w = Chemical equivalent of substance

$\Rightarrow$ $m = wIt$

If $I = 1$ ampere, $t = 1$ second, then

$$\boxed{m = w}$$

Hence the electro chemical equivalent of a substance may be defined as the mass of the substance deposited when a current of one ampere is passed for one second, I. E., a quantity of electricity equal to one coulomb is passed.

Units, $w = m / It$, $gm.amp^{-1} sec^{-1}$

(II) Faraday's Second law of Electrolysis :

According to this law, when same quantity of electricity is passed through different electrolyte solutions connected in series, the weights of the substances produced at the electrodes are directly proportional to their chemical equivalent weights. However, in modern terms, the term equivalent weight is not used.

According to Faraday's law, the amount chemical change occurred i.e. the moles of substances deposited or librated is proportional to the number of moles of electrons exchanged during the oxidation-reduction reactions that occur.

For example the same quantity of electricity is passed through $CuSO_4$, $AgNO_3$ and H_2SO_4 electrolytic solutions which are connected in series as shown in fig.(2). The weights of Cu, Ag and H_2 deposited or librated is found directly proportional to their equivalent weights. If $CuSO_4$ and $AgNO_3$ electrolytes are taking into account :

$$\frac{\text{Wt. of Cu deposited}}{\text{Wt. of Ag deposited}} = \frac{\text{Equi. wt. of Cu}}{\text{Equi. wt. of Ag.}}$$

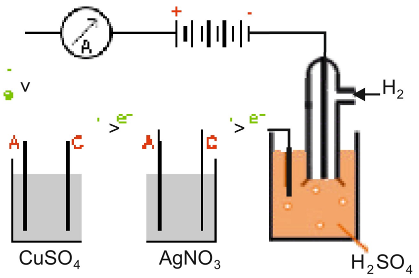


Fig. (2) Electrolytes connected in a series

For example, consider an experiment in which same amount of current is passed simultaneously three electrolyte solutions as shown above figure. It is observed that the deposited weights on the cathodes of above series of electorates were found as :

$H_2 : Cu : Ag = 1 : 31.78 : 107.88$

If m_1 and m_2 are the deposited amount of any two electrolyte of above series and E_1 and E_2 are their equivalent weights respectively, then

$$\frac{m_1}{E_1} = \frac{m_2}{E_2} \Rightarrow \frac{m_1}{m_2} = \frac{E_1}{E_2} \quad ....(1)$$

As we know from the Faraday's law that $m_1 = w_1It$ and $m_2 = w_2It$, where w_1 and w_2 are deposited weights of substances, then

$$\frac{w_1 It}{w_2 It} = \frac{E_1}{E_2} \Rightarrow \frac{w_1}{w_2} = \frac{E_1}{E_2} \quad .... (2)$$

Or $\quad w \propto E$

$\Rightarrow \quad E = Qw \quad .... (3)$

Thus, electro chemical equivalent of any substance is proportional to the equivalent weights of the substance.

Practically it have seen that, if 1 ampere current is passed for 1 second through the electrolytes, then 0.011180 gm of Ag, 0.0003296 of Cu and 0.00001036 gm of H_2 deposited on the cathode of the electrolytes. These amounts are known their respective electro chemicals equivalents of the electrolytes.

Thus, the quantity of electricity Q is required to deposit 1 gm equivalent of Ag. Then :

$$\text{Charge, } Q = \frac{\text{Equi. wt. of Ag}}{\text{Electrochemical equi. of Ag}}$$

$$\Rightarrow \quad Q = \frac{E}{W} = \frac{107.88}{0.0011180} = 96{,}493 \text{ Coulomb}$$

It is obvious from second law of Faraday that 96495C of electricity would yield one gram equivalent of any substance. This quantity of charge is known as "One faraday" and is denoted by F. Therefore Faraday is defined as "This is the quantity of change which deposits of librates one gram equivalent of substance"

1F is taken as equal to 96,500 coulombs.

Thus, if I ampere current is passes through an electrolyte of E equivalent for t seconds, then the librated amount of substance is :

$$m = I.t.E / F \qquad ....(4)$$

Equation (4) can be used to measure the electric current and apparatus used for this purpose is known as "Coulometer of Voltameter.

1 Faraday charge is actually the charge on one mole of electrons.

Since charge on one electron = 1.66×10^{-9}C

Therefore charge on one mole of electron :

$= 1.66 \times 10^{-19} \times 6.023 \times 10^{23}$

= 96,500C

The both of the Faraday's laws are very important in the study of various electrolytes to understand their behavior. These laws are also very useful in the electroplating processes.

Conductance in Electrolytes :

Metallic as well as electrolytic conductors obey Ohm's law which states that "the amount of current (I) flowing through a conductor is directly proportional to the potential difference (E) applied across the conductor and is inversely proportional to the resistance (R) of the conductor, i.e.:

$$I = E / R$$

Applied voltage is equal to the electromotive force of the cell.

When a voltage is applied to the electrodes dipped in to an electrolyte solution, ions of the electrolyte move and, therefore, electric current flows through the electrolytic solution. The power of electrolyte to conduct electric current is termed conductance or conductivity.

In metallic conductors the resistances are very low as compared to their conductivity, so that the measurement of resistance is logical to study the behavior of metallic conductors. While in electrolyte conductors their resistances are very high as compared to conductance so that it is logical enough to measure the conductivity in them. Conductivity is the reciprocal of resistance.

$$C = 1 / R$$

Units of conductance are also the reciprocal of the units of resistance as Ohm^{-1} or mho and in SI system it is Siemens(S).

Conductivity or Specific Conductance :

The resistance of any conductor is directly proportional to the length (l) and inversely proportional to the area of cross – section (A) of the conductor, thus,

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

$$\Rightarrow \quad R = \rho \frac{l}{A}$$

Here ρ(rho) is a constant and depends on the nature of conductor which is called specific resistance. If l = 1cm and A = 1cm^2, then

$$R = \rho$$

Thus, resistivity or specific resistance (ρ) is defined as the resistance of conductor of 1cm length and having area of cross-section equal to 1cm^2. Actually it is a resistance of 1ml ($=1\text{cm}^3$) of electrolyte solution.

In other words, resistivity or specify resistance is the resistance between opposite faces of one centimeter cube of the conductor.

The units of resistivity are

$$\rho = R\frac{A}{l} = \text{ohm}\left(\frac{\text{cm2}}{\text{cm}}\right) = \text{ohm.cm}$$

The inverse of resistivity is called conductivity or specific conductance. It is represented by the symbol, κ (Greek kappa). It may be defined as the conductance of a solution of 1 cm length and having 1 square centimeter as the area of cross-section in other words, conductivity is the conductance of one cm^3 of a solution of an electrolyte as shown in fig(3)

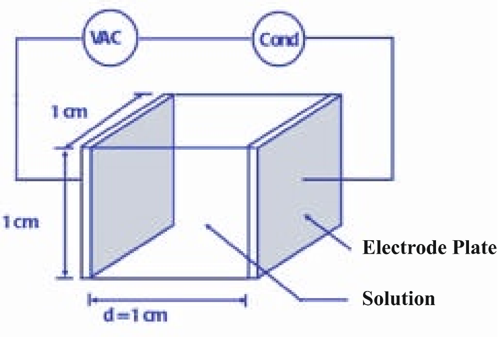


Fig. (3)

Thus, $\kappa = 1/\rho \qquad \therefore \ \kappa =$ kappa

The units of conductivity are

$\kappa = 1/(\text{ohm.cm}) = \text{ohm}^{-1}\ \text{cm}^{-1} = \Omega\text{-1 cm}^{-1}$

In SI units, l is expressed in metre and area is in metre square so that the units of conductivity are Sm^{-1}.

It is very typical to make the cell in which the area of electrode must be 1cm^2 and the distance between both of electrode be kept at 1cm. i.e. the actual cells are large than these dimensions.

Thus, the ratio of the distance of electrodes (l) with the area of cross – section (A) is known as cell constant (X), i.e. –

$X = l/A \qquad$; units is cm^{-1}

So the conductivity of any cell may be given as :

$$\frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{A}$$

$$\Rightarrow \ \kappa = C.\frac{l}{A}$$

$\Rightarrow \ \kappa = C.X$ (Where X = l/A = cell constant)

$\boxed{\text{Conductivity = Conductance x Cell constant}}$

Equivalent Conductance :

Electric current is carried out by ions in electrolytic solutions. Therefore conductance depends upon the concentration of solution. To compare the conductance of different solutions a definite concentration is taken for different electrolytes. For this definite concentration, either equivalent or molecular weight of electrolytes is taken. The conductance of solution containing one gram equivalent of an electrolyte in V ml of solution when placed between two parallel large electrodes which are one cm apart, is called equivalent conductance. It is denoted by λ (lambda).

Relation can be easily obtained between conductivity and equivalent conductance of on electrolyte. Suppose 1 cm^3 of a solution of an electrolyte is placed between two large electrodes of 1 cm^2 area of cross-section which are lying apart 1 cm. The measured conductance of this solution will be its conductivity. Further suppose the one gram equivalent of the electrolyte contains the solution, then measured conductivity of the solution will be equal to its equivalent conductivity (1). This, for this solution containing 1gm equivalent of electrolyte placed between two parallel electrodes of 1 cm^2 area of cross-section and one cm apart,

Conductance (C) = Conductivity (κ)

= Equivalent Condutance (λ)

As we know that it is not possible to dissolve one gram equivalent amount of any electrolyte in 1ml. Now suppose that solution is diluted to 100ml. There are now 100 cm^3 of the solution. The conductance of each one cm cube will be conductivity so that the conductance of the solution will be 100 times of its conductivity. But even now the solution contains one gram equivalent of electrolyte therefore, the measured conductance will be the equivalent conductivity. Thus,

Equivalent conductance (λ) = 100 x Conductivity

Or $\qquad \lambda = \kappa \text{ x } V$

Where, V is the volume of solution in cm^3 containing one gram equivalent of the electrolyte.

If N is the equivalent concentration, then

1 Equivalent electrolyte is present in

= (1000 / C) cm^3 of solution

This, $\lambda = \kappa$ x Volume in cm^3 containing one gram equivalent.

$\Rightarrow \ \lambda = \kappa \text{ x } 1000/C$

$\Rightarrow \ \lambda = \kappa \text{ x } 1000/N$

Where N is the normality of solution.

The units of equivalent conductance can be derived from the formula,

$$\lambda = \frac{\kappa \text{ x } 1000}{N} = \Omega^{-1}\ \text{cm}^{-1} \text{ x } \frac{\text{Cm}^3}{\text{Equ.}}$$

Units of λ is mho cm^2 Equi.^{-1} or $\text{S.cm}^2.\text{Equi.}^{-1}$

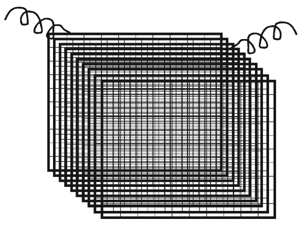


Fig. (4)

Molar Conductivity :

Molar conductivity is defined as the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution. It is denoted by lm. Like equivalent conductivity the molar conductivity is also related to the specific conductance (κ) as the similar manner.

Molar conductivity $\lambda_m = (\kappa \text{ x } 1000) / M$

Where, M is the molar concentration of the solution. The units will be mho cm^2 mol^{-1} or $S.cm^2$ mol^{-1}. The recent trend is to describe electrolytic conductance in terms of molar conductance in place of equivalent conductance.

Measurement :

Measurement of electrical conductance of a solution, in fact, accounts to determination of electrical resistance of the solution because conductance is just the reciprocal of resistance. Generally wheat stone bridge method is employed for this purpose. Solution whose resistance is to be determined is kept in a cell which is called conductivity cell. Now the day's conductivity-meters are being used to measure the conductivity of any electrolyte. These are compact devices.

Effect of Dilution on Conductance :

Specific and molar or equivalent conductance of a solution depends upon the number of ions present in the electrolytic solution. Number of ions in electrolytic solution depends on the concentration. As with dilution, the dissociation of solute molecule in the solution increases and hence the conductance also increases. However, conductivity of an electrolyte decreases with increase of dilution because number of conducting ions per ml decreases. Where the molar or equivalent conductance is increases with increase of dilution because total number of ions will increase with dilution due to more dissociation. Alternatively upon dilution, specific conductance a conductivity decrease while molar conductivity increases.

On dilution, conductivity decreases but volume containing one mole of an electrolyte increases. It has been found that the increase in volume on dilution is much more than the decrease in conductivity. As a result molar conductivity increases with dilution.

In following table molar conductance and conductivities of KCl solution with dilution are given at 25^0c temperature which correlates the above discussion.

Table : At 295.15 K the conductivity and molar conductance are given of KCl

Conc./Molarity		Conductivity (κ)		Molar Conductivity (λm)	
mol L^{-1}	mol m^{-3}	S cm^{-1}	S m^{-3}	S cm^2 mol^{-1}	S m^2 mol^{-1}
1000	1000	0.1113	11.13	111.3	111.3 X 10^{-4}
0.100	100.0	0.0129	1.29	129.0	129.0 X 10^{-4}
0.010	10.00	0.00141	0.141	141.0	141.0 X 10^{-4}

Hence, molar conductance $\lambda \propto$ Dilution

Conductivity $\kappa \propto 1 /$ Dilution

It is to be seen into the above table that the molar conductance goes on increasing with dilution until they reach a certain maximum value. Beyond this value there is no increase in conductance on further dilution this maximum value of molar conductance is known as molar or equivalent conductance at infinite dilution which are represented by λ^∞ or λ^∞_m. This value for the KCl solution is 147 ohm^{-1} cm^2 mol^{-1}.

Variation of Molar Conductivity with Dilution (Strong and Weak Electrolytes) :

It has been started earlier that infinite dilution is meant a solution so dilute that it has maximum conductance which does not increase on further dilution. The molar conductivities of a few electrolytes in water at different concentrations are given in the following table at 298k.

Table : Molar conductivities (Scm^2mol^{-1}) of few electrolytes in water at 298K

Concentration (g mol / lit)	KCl	NaCl	Na_2SO_4	CH_3COONa	CH_3COOH	NH_4OH
0.1	129.0	106.7	90.0	72.8	5.2	3.6
0.01	141.3	118.5	112.4	83.8	16.3	19.3
0.001	146.3	123.7	124.1	88.5	49.2	34.0
0.0005	147.8	124.5	125.7	89.2	67.7	47.0

Inspection of above table reveals that the molar conductivities of strong electrolytes (KCl, NaCl, Na_2SO_4, CH_3COONa) and weak electrolytes (CH_3COOH, NH_4OH) increases with increase in dilution. The variation is however different for strong and weak electrolytes. It is because with dilution, mole ions are produced in solution so conductance also increases on dilution.

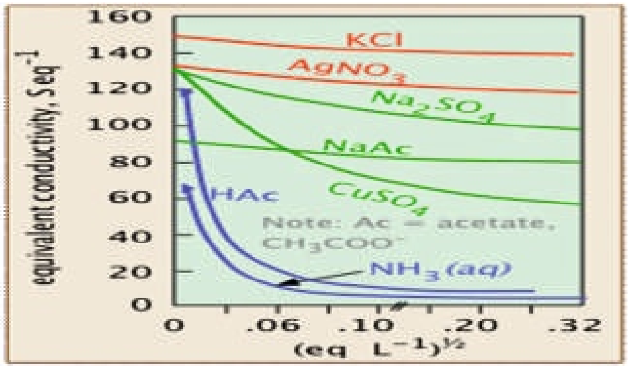
It is also to be noticed from the above table that for the strong electrolytes the molar conductivity is sufficient high at higher concentrations and there is no shape change with dilution. The strong electrolytes get sufficient dissociation at their normal concentrations. While the weak electrolytes dissociates to a much lesser extent as compared to strong electrolyte. Therefore, their molar conductivities at normal concentration are very low and increasingly sharply with the increase in dilution. For example :

Strong	**Weak**
0.1 M KCl = 129.0	0.1 M CH_3COOH = 5.2
0.001 M KCl = 146.3	0.001M CH_3COOH = 49.2
0.1 M CH_3COONa = 72.8	0.1 M NH_4OH = 3.6
0.001 M CH_3COONa = 88.5	0.001 M NH_4OH = 34.0

Weak acid, weak, weak base and salts of weak acids and bases are called weak electrolytes while the remaining all acid, base or salts are strong electrolytes.

Kohlrausch's Law :

The variation of molar conductivity with concentration of various electrolytes was studied by kohlrausch (1875) and plots are drawn between molar conductivities against the square root of concentration. Interesting results are obtained as follows:



It has been observed by kohlrausch that the molar (or equivalent) conductivity with concentration may be given by the expression. This is based on the above observations.

$$\lambda_c = \lambda^{\infty} - b\sqrt{c}$$

Where b = Constant

c = Concetration

λ_c = Molar Conductance

λ^{∞} = Molar conductance at infinite dilution

There was no any theoretical background of above kohlrausch's relation. On the basis of electro statics Debye-Huckel and Onsager gave a theoretical back ground to the above equation and the obtained the following expression.

$$\lambda_c = \lambda^{\infty} - \left[\frac{82.48}{(DT)^{1/2}n} + \frac{8.20 \text{ X } 10^5}{(DT)^{3/2}}\lambda^{\infty}\right]\sqrt{c}$$

Where D is the dielectric constant of the solvent, r is viscosity of electrolytic solution, c is molar concentration and T is the absolute temperature. This expression may be given as.

$$\lambda_c = \lambda^{\infty} - [A + B\lambda^{\infty}]\sqrt{c}$$

Following results are obtained by the plots :

(1) Graphs of strong electrolytes (KCl, NaCl, Na_2SO_4, CH_3COONa) are almost straight line at lower concentrations whereas these graphs are non-linear for weak electrolytes (CH_3COOH, NH_4OH etc.) Therefore the electrolytes which give straight or linear line are called strong electrolytes, whereas the electrolytes which give non-linear line are called weak electrolytes. For strong electrolytes, limiting value of molar conductivity can be determined by 'extra plotting' the line up to zero concentration.

(2) Equivalent conductance increases with dilution due to increase in the degree of dissociation of the electrolyte. Since, dissociation is almost complete at infinite dilution so we get constant value of molar conductance at infinite dilution. After this dilution, there does not occur any increase in conductivity with increase in dilutions, so that it is a constant molar conductivity at the given temperature. If to be the molar conductivity at any concentration and to be the molar conductivity at infinite dilution, then the degree of dissociation for weak electrolytes is given as :

$$\text{Degree of dissociation } (\propto) = \lambda_c / \lambda^\infty$$

$$\Rightarrow \propto = \frac{\text{Molar conductance at given dilution}}{\text{Molar conductance at infinite dilution}}$$

However, the concept of degree of dissociation (α) has its validity as for as weak electrolytes. Since there is almost completely dissociation occurs for strong electrolytes so that for strong electrolytes the 'α' is only ratio of conductivities.

(3) Weak electrolytes give non-linear plots, so that extra flotation is not possible for these and we cannot determine the molar conductivity at infinite dilution for weak electrolyte by plots.

Implications of Kohlrausch's Law :

(i) Kohlrausch's law of free migration of ions :

In the case of weak electrolytes there is no indication that a limiting value can be attained even when the concentration approaches to zero. It is not therefore convenient to obtain the limiting value by extra-plotation in the case of weak electron as show in above figure (5). Therefore, Kohlrausch's law of 'independent migration of ions' employed to determine λ^∞ or weak electrolytes.

Molar conductance of some of the electrolytes which have common coin (anion or cation) are given in the following table:

Electrolyte [Common anion]	Molar Cond. at infinite dilution λ_∞	$\lambda^\infty_{k^+} - \lambda^\infty_{Li^-}$	Electrolyte [Common anion]	Molar Cond. at infinite dilution λ_∞	$\lambda^\infty_{Cl^-} - \lambda^\infty_{NO_3^-}$
KCl LiCl	149.86 115.03	34.83	LiCl $LiNO_3$	115.03 110.10	4.93
KNO_3 $LiNO_3$	144.96 110.13	34.83	KCl KNO_3	149.86 144.96	4.90
KOH LiOH	271.50 236.70	34.80	HCl HNO_3	426.16 421.30	4.86

It is evident from the table that electrolytes having common ion have constant difference of molar conductivities of infinite dilution. For example KCl and LiCl having common Cl^- ion and KNO_3 and $LiNO_3$ having common NO_3^- ion have constant difference of 34.83 in their molar conductivities. Similarly electrolytes of Cl^- and NO_3^- having common cation have constant difference of 4.90 in their molar conductivities at infinite dilution. It may be assumed that the difference in the conductivities of any two cations appears to be same, irrespective of the nature of anion with which they are associated. The same is true for anions also.

This led Kohlrausch to state that "At infinite dilution when dissociation is almost complete, each ion makes a definite contribution towards equivalent a molar conductance of the electrolyte irrespective the nature of the co-ion with which it is associated. Thus, it is evident that the equivalent or molar conductivity at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. This is known as "Kohlrausch's law of independent migrations of ions". Therefore :

$$\lambda^\infty = \lambda^\infty{}_c + \lambda^\infty{}_a$$

Where $\lambda^\infty{}_c$ and $\lambda^\infty{}_a$ are the molar conductance of cation and anion respectively at infinite dilution. For example the equivalent conductivity of Na_2SO_4 may be calculated as :

$$\lambda^\infty \frac{1}{2}(Na_2SO_4) = \lambda^\infty [Na^+] + \lambda^\infty \frac{1}{2}[SO_4^{2-}]$$

$$(129.9) = (50.1) + (79.8)$$

Molar conductivities at infinite dilution for weak electrolyte can also be determined by using "Kohlsausch's law" of independent migrations of ions.

(A) By Molar Conductivities of Ions :

We have learnt that it is not possible to determine the value of λ^{∞} for weak electrolytes by extrapolation of λ_c versus √c graph. However, this can be calculated easily by using Kohlrausch's law of free migration of ions.

Let us calculate the limiting molar conductivity for CH_3COOH.

According to Khlrausch's law.

$$\lambda^{\infty} CH_3COOH = \lambda^{\infty} CH_3COO^{-} + \lambda^{\infty} H^{+} \quad \text{........(1)}$$

This equation can be obtained by the knowledge of molar conductivity at infinite dilution for some strong electrolytes. For example, consider the strong electrolytes HCl, NaCl and CH_3COONa. From Kohlrausch's Law.

$$\lambda^{\infty}[CH_3COONa] = \lambda^{\infty}[CH_3COO^{-}] + \lambda^{\infty}[Na^{+}] \quad \text{....................(ii)}$$

$$\lambda^{\infty}[HCl] = \lambda^{\infty}[H^{+}] + \lambda^{\infty}Cl^{-} \quad \text{....................(iii)}$$

$$\lambda^{\infty}[NaCl] = \lambda^{\infty}[Na^{+}] + \lambda^{\infty}[Cl^{-}] \quad \text{....................(iv)}$$

It is clear that

$$\lambda^{\infty}[CH_3COONa] + \lambda^{\infty}[HCl] - \lambda^{\infty}[NaCl]$$

$$= \lambda^{\infty}[CH_3COO^{-}] + \lambda^{\infty}[Na^{+}] + \lambda^{\infty}[H^{+}] + \lambda^{\infty}[Cl^{-}] - \lambda^{\infty}[Na^{+}] - \lambda^{\infty}[Cl^{-}]$$

$$= \lambda^{\infty}[CH_3COO^{-}] + \lambda^{\infty}[H^{+}]$$

$$= \lambda^{\infty}[CH_3COOH]$$

Similarly, we can determin the infinite conductance of weak electrolyte NH_4OH.

By putting the λ^{∞} Values of strong electrolyte as above we can easily calculate the λ^{∞} of weak electrolytes.

(B) By Transpose Numbers of Ions :

The fraction of the total current carried by each ion is called its transport number which is depending upon the speed or ion and nature of coin. Ionic conductance of ion can be determined by its transport number.

Transport number of any ion is the ratio of the molar conductance of that ion at infinite dilution with molar conductance of an electrolyte at in infinite dilution which contains the ion under consideration.

Ionic conductance of any ion can be determined by its transport numbers as follows.

Transport number of cation $n_c = \lambda^{\infty}_c / \lambda^{\infty}$

Transport number of anion $n_a = \lambda^{\infty}_a / \lambda^{\infty}$

Hence,

$$\lambda^{\infty}_c = n_c \lambda^{\infty}$$

and $\quad \lambda^{\infty}_a = n_a \lambda^{\infty}$

Where n_c and n_a are the transport numbers of cation and anion repsectively. And

$$\lambda^{\infty} = n_c \lambda^{\infty} + n_a \lambda^{\infty}$$

(ii) Calculation of Degree of Dissociation of Weak Electrolytes:

Molar conductance of a weak electrolyte depends upon its degree of dissociation. Higher the degree of dissociation, larger is the molar conductance. With increase in dilution, the conductance increases and at infinite dilution, the electrolyte is completely dissociated so that the degree of dissociation becomes on i.e.

$$\lambda_c = \lambda^{\infty} \qquad (\text{at } c \rightarrow 0)$$

Then, degree of dissociation at any concentration is :

$$\lambda = \lambda_c / \lambda^{\infty}$$

Where λ_c = Molar conductance at c concentration

λ^{∞} = Molar conductance at infinite dilution

Electrochemical Cells

We have learnt above electrolyte cells. These constitute the electrochemical reactions in which electrical energy is converted in to chemical energy. In these cells electric current is used to drive redox reactions which have positive Gibbs energy change (+ΔG) and are non-spontaneous. By redox reactions the ions on electrodes discharge to give chemical products.

The process of electrochemical cells is quite opposite. These cells constitute the electrochemical reaction in which chemical energy is converted into electrical energy. In this cell, spontaneous redox reaction is used to generate an electric current.

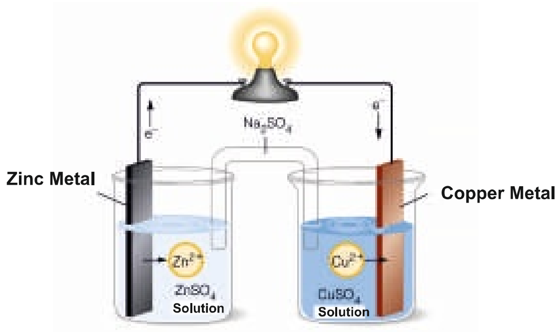
The devices in which chemical energy of a spontaneous redox reaction is converted into electrical energy are called electrochemical cells. In these devices, the Gibbs free energy of the spontaneous redox reaction converted into electrical energy which may be used as an electric source. These cells are very important because of their practical applications. These cells are introduced by their founder Luigi Galvani (1780) and Alesandro Bolla (1800) and initially modified form of these cells is given by British chemist John Daniell in 1836. Now after successive development these are said to be 'electrochemical cells'.

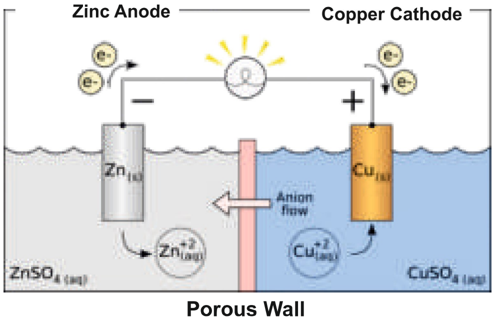
Galvanic Cell or Daniell Cell :

The device in which electrical energy is produced from chemical reactions is called electrochemical cell or galvanic cell or voltaic cell or daniell cells. In this cell the oxidation and reduction reactions occur in separate vessel which is called half cell and the redox reactions are spontaneous. Electrical energy is produced during the redox reactions.

The arrangement consists of two vessels made by bad conductor material like glass. One of which contains 1.0 M solution of zinc sulphate and a zinc rode is placed in it. The other vessel contains 1.0m solution of copper sulphate and a copper rode is placed in it as shown in the figure (6). These metallic rods called electrodes where Zn-electrode is here acts as anode and the c4-electrode is as cathode. The solutions in the two vestals are connected by an inverted U-tube containing saturated solution or moist salts like KCl, Na_2SO_4 etc. and both of the mouth of U tube are packed with glass wool. The saturated solution is generally taken in ager-ager jelly or gelatin. This U tube is called salt bridge and ions of electrolytes from the vessels can travel from this tube to cone-another to maintain electro neutrality.

The arrangement of the electrochemical or galvenic cell is show in the following fig(6) :





Every metal or hydrogen has a tendency to covert into their cation by loosing electrons when they are placed either in water or in their solution. In daniell cell Zn an Cu are in contact with their solutions. So they also have tendency to liberate electrons and acquire following equilibrium :

$$Zn \rightleftharpoons Zn^{+2} + 2e^-$$

$$Cu \rightleftharpoons Cu^{+2} + 2e^-$$

Due to its higher electrolytic pressure Zn has more tendencies to liberate electrons than Cu; therefore, Zn-electrode has higher density of electrons. When two electrodes are connected with a metallic wire, electrons start to flow from Zn to Cu electrode. Following reactions take place due to movement of electrons :

At anode $Zn\ (S) \rightleftharpoons Zn^{+2}\ (aq) + 2e^-$ [Oxidation]

At cathode $Cu^{+2}(aq.) + 2e^- \rightleftharpoons Cu\ (s)$ [Reduction]

Total cell Reaction : $Zn\ (S) + Cu^{+2}(aq.) \rightleftharpoons Zn^{+2}(aq.) + Cu\ (s)$

The reaction take place at any electrode is termed as "Electrode reaction or half cell reactions". These reactions are classified as oxidation and reduction reactions or simply, these are redox reactions. Hence in Gavenic cell the current is produced due to these redox reactions which are a spontaneous process.

Conventionally, the electrode at which oxidation takes place is known as anode. In Daniell cell, Zn rod acts as anode and the electrode at which reduction takes place is known as cathode, Cu-rod acts as cathode in Daniell cell. When the ectrodes are connected with voltmeter, the deflection in voltmeter shows “potential defference”. When the potential difference is measured in open circuit (i.e. no current is flowing) it is called: electromotive force (emf) of the cell. Electromotive force of Daniell cell at 298K is 1.0988 volt.

When the circuit is completed, it is observed that electric current flows through external circuit and sulphate ions flow through salt bridge or porous wall from $CuSO_4$ to $ZnSO_4$ solution. The following observations are made:-

(i) Zinc rod gradually dissolving

(ii) Copper gets deposited on the electrode

(iii) The concentration of $ZnSO_4$ is increases

(iv) The concentration of $CuSO_4$ is decreases

(v) Zinc electrode gets negative while copper rod gets positive charge

It has to be note that the galvanic cells are the initial concept of electrochemical cells. Now the days various types of ‘concentration cells’ are developed. In these cells the both of electrolytes may be in direct content to each other without any salt bridge and having the different concentrations of same electrolyte in contact. The electrode may be the same with different concentrations in the same electrolyte and more. You will study about these in higher classes.

Representation of Cells by Cell Notation :

It is more convenient to represent a cell by some notations rather than by a diagram. There are some sign conventions and notation to represent a cell which is known as ‘cell diagram’. These are summarized below.

(1) A galvanic cell is represented by writing the anode on the left hand side and cathode on the most right hand side.

(2) The anode of the cell (where oxidation occurs) is represented by writing metal or solid phase first and then the electrolyte (or cation of electrolyte) white cathode is represented by writing the electrolyte first (or cation) and then metal and solid phase. The metal and the cation are separated by a vertical line. Further, the concentrations of electrolyte may be given in the bracket after the electrolyte or cation. For example :

$Zn\,(s)\,|\,Zn^{+2}\,(aq.),\quad AgNO_3(a_1)\,|\,AGNO_3(a_2),$

$Ag\,|\,Ag^{+},\ Pt\,|\,H_2\,|\,H^{+}\ .\ Pt\,|\,Cl_2\,|\,C^{-}$

(3) The salt bridge or porous wall which separates the two half cells is indicated by two vertical line. For example :

$ZnSO_4\,(aq.)\,||\,Cu_4SO_4\,(aq.)\,,$

$AgNO_3\,(a_1)\,||\,AgNO_3$

(4) Some times negative and positive sign are written of the superscript of anode and cathode respectively

$Zn\,|\,Zn^{+2}\ ||\,Cu^{+2}/Cn\,|\,Cn$

(5) Since the emf of the cell depends upon the temperature, activities or concentration of the solutions, pressure of gases, so they must also be shown to represent a complete cell. Example are :

$Zn\,(s)\,|\,Zn^{+2}\,(aq.,\ a = 0.35)\,||\,Cu^{+2}\ (aq.,\,a = 0.49)\,|\,Cu\,(s)$ at 298K

Development of Electrode Potential :

The flow of electric current in an electrochemical cell indicates that a potential difference exists between two electrodes. To understand the potential deference between two electrodes or electrode potential let us consider the redox reactions occurring at these electrodes.

It Zn-electrode is immersed in a solution of its ions, then either of the three possibilities can take place –

(i) The metal ions (Zn^{+2}) may collide with the electrode and do not undergo any change.

(ii) Zn^{+2} ions may collide with the electrode, gain electrons and get converted into metal ions i.e. the reduction takes place

$Zn^{+2} + 2e^{-} \rightarrow Zn$ (Reduction)

(iii) Zn atoms on the electrode may lose electrons to the electrode and become Zn^{+2} ions and go into solution i.e. the oxidation takes place.

$$Zn(s) \rightarrow Zn^{+2} + 2e^-$$

These possibilities are shown in the following figure (7)

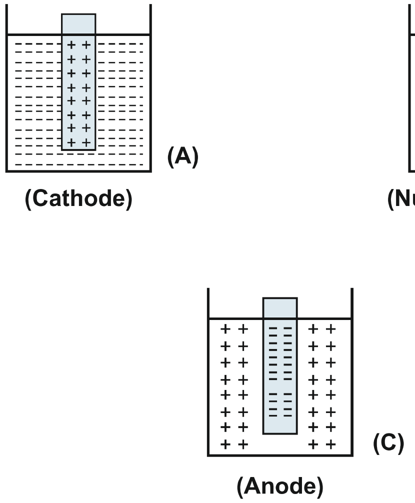


Fig. (7)

Now, if the metal has relatively high tendency to get oxidized, its atoms will lose electrons readily and form Zn^{+2} ions, which go into the solution. The electrons lost on the electrode would be accumulated on the metal surface of electrode and the electrode acquires a slight negative charge with respect to the solution. After some time equilibrium is established as:

$$Cu\ (s) \rightleftharpoons Cu^{+2}\ (aq.) + 2e^-$$

When such equilibrium is attained, it results in separation of charges.

Similarly, if the metal ion have relatively greater tendency to get reduced, they will take electrons from the electrode. As a result, a net positive charge will be developed on the electrode with respect to the solution. This will also result into separation of charges.

$$Zn^{+2}(aq) + 2c^- \rightleftharpoons Zn\,(s)$$

Due to this charge separation between the electrode and the solution, an electrode potential difference set up between the metal and its solution is known as electrode potential. Thus, the electrode potential is a measure of tendency of an electrode in a half cell to gain or lose electrons.

Cell Potential or Electromotive Force of Cell :

Electrochemical cell consists of two half cells. The electrodes in these half cells have different reduction potentials. Therefore, they have different tendency to lose or gain electrons. The electrode having higher reduction potential will have high tendency to gain electrons whereas the electrode having lower reduction potential will have lesser tendency to fain electrons, rather it loses electrons. As a result of this potential difference there is a flow of electrons from the electrode with a lower reduction potential (higher tendency to lose electrons) to the electrode with higher reduction potential "The difference between the electrode potentials of the two electrodes constituting an electrochemical cell is known as electromotive force or cell potential of the cell". This acts as a driving force for the cell reaction and it is expressed in volts.

As we know that reduction occurs at cathode and oxidation at anode. Therefore,

e.m.f. = Reduction potential of cathode - Reduction potential of anode.

or $E_{cell} = E_{(cathode)} - E_{(anode)}$

or $E_{cell} = E_{(Right)} - E_{(Left)}$

Thus, the e.m.f. of a cell is the potential difference between the electrodes of the cell when there is no current is allowed to flow in the circuit. The e.m.f. of the cell is measured with the help of a potential meter. It depends upon the nature of electrodes, temperature and the concentration of electrolyte solutions in both of the half cells. Voltmeter can measure the potential difference but cannot measure the e.m.f. of cell.

In the following table, the differences between e.m.f. (cell potential) and potential difference of a cell are given here :

Cell Potential (Volt)	Potential Difference (Volt
1. It is the potential difference between the electrodes of a cell when these are no any current flowing through the cell.	1. It is the potential difference between the electrodes of a cell when the cell is sending current through the circuit.
2. It is the maximum voltage obtained from the cell.	2. It is less than the maximum voltage obtained from the cell.
3. It cannot be measured by voltmeter because as the circuit is closed a small amount of current flows from the cell before the reading obtained into the voltmeter	3. It is measured by voltmeter.

Standard Electrode Potential :

Since a half cell in an electrochemical cell can work only in combination with the other half cell and does not work independently, it is not possible to determine the absolute electrodes potential of an electrode. We can, therefore, find out the relative electrode potential.

The difficulty can be solved by selecting one of the electrodes as a reference electrode and arbitrarily fixing the potential of this electrode as zero. For this purpose, reversible hydrogen electrode has been universally accepted as a reference electrode. It is called "Standard Hydrogen Electrode (SHE) or normal hydrogen electrode (NHE).

Standard Hydrogen Electrode :

It consists of platinum wire seated in a glass tube and platinum foil attached to it as shown if figure (8). The foil is coated with finely devided platinum which acts as platinum electrode. It is dipped into acid solution (say HCl). Containing H^+ ions in 1M concentration (say 1m-Hcl). Pure hydrogen gas at 1 atmosphere pressure is constantly bubbled in solution at constant temperature of 298K. The surface of the foil acts as a site for the reaction. The electrode may be given as :

$Pt(s) / H_2(g) / H^+(aq)$

If the SHE acts as anode, where Pt. foil adsorb the hydrogen gas which is in content to H^+ ions.

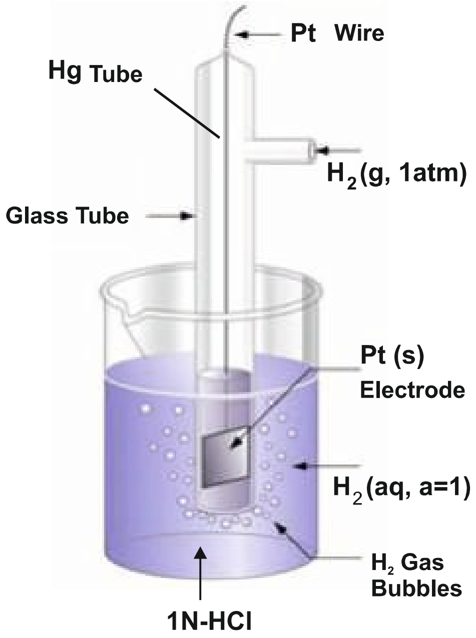
$H^2(g) \rightarrow 2H^+(aq) + 2e^-$ (Oxidation)

If SHE acts as cathode,

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ (Reduction)

This standard hydrogen electrode is also regarded as reversible electrode for cations.

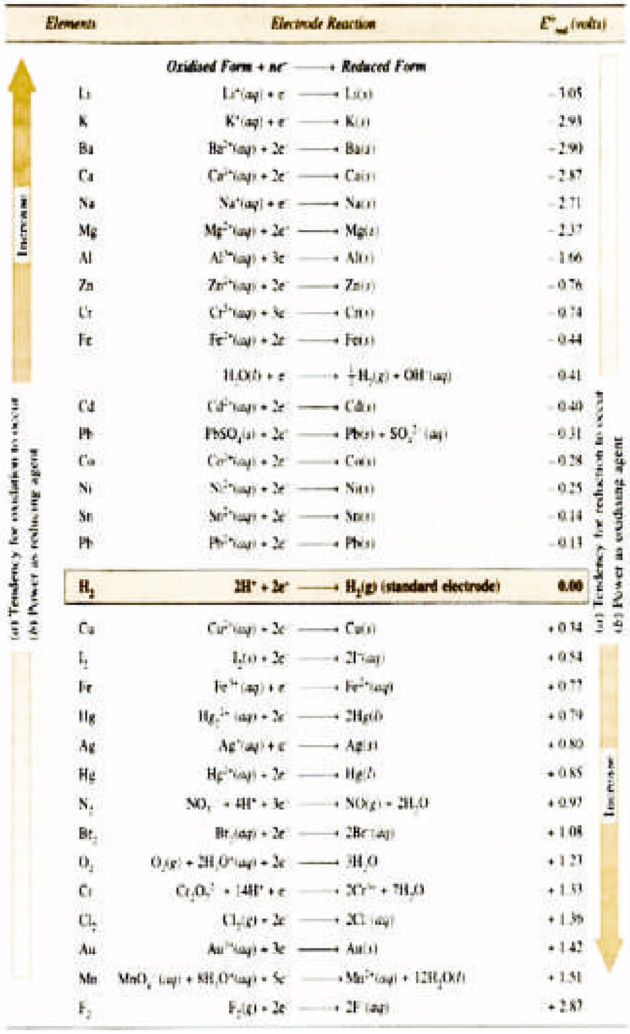
$1/2\, H_2(g) \rightleftharpoons H^+(aq) + e^-$



The electrode whose potential is to be determined is couples with SHE to form a cell. The e.m.f. of this cell is determined which the electrode potential of the electrode because the potential of SHE is zero.

The handling of SHE is very sensitive as well as typical for practical use because concentration of H+ ions must kept constant (1M) throughout the experiment. Also the pressure must to kept 1 am. of hydrogen. Due to this a second kind of reference electrode are developed with careful experiment and their potentials are tabulified. Calomel electrode and silver-silver chloride electrodes are second type electrode.

To compare the reduction potentials of various electrodes are shown in the following electrochemical series :



Elements	Electrode Reaction	E°_{red} (volts)
	Oxidised Form + ne^- $\longrightarrow$ Reduced Form	
Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05
K	$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
Ba	$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
Ca	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
Mg	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
Al	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
Zn	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
Cr	$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
Fe	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
	$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	−0.41
Cd	$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
Pb	$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
Co	$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
Ni	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
Sn	$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
Pb	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
H_2	**$2H^+ + 2e^- \longrightarrow H_2(g)$ (standard electrode)**	**0.00**
Cu	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
I_2	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.54
Fe	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
Hg	$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.79
Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
Hg	$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	+0.85
N_2	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.97
Br_2	$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.08
O_2	$O_2(g) + 2H_3O^+(aq) + 2e^- \longrightarrow 3H_2O$	+1.23
Cr	$Cr_2O_7^{2-} + 14H^+ + e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
Cl_2	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
Au	$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.42
Mn	$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 12H_2O(l)$	+1.51
F_2	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87

For example the electrode potential of Zn | Zn^{+2} electrode is measured by using S H E, the cell is shown if the following figure (9).

In this cell the zinc rod is placed in 1M-ZnSO4 and it acts as anode which can be seen in the electrochemical series. SHE is hear acts as cathode in this cell. In this case, the electrons flow from zinc electrode to hydrogen electrode. The cell diagram is as follows:

$$Zn \mid Zn^{+2}(1M) \parallel H^+(1M) \mid H_2(1\ atm.) \mid Pt$$

The cell potential has been measured to be 0.76v.

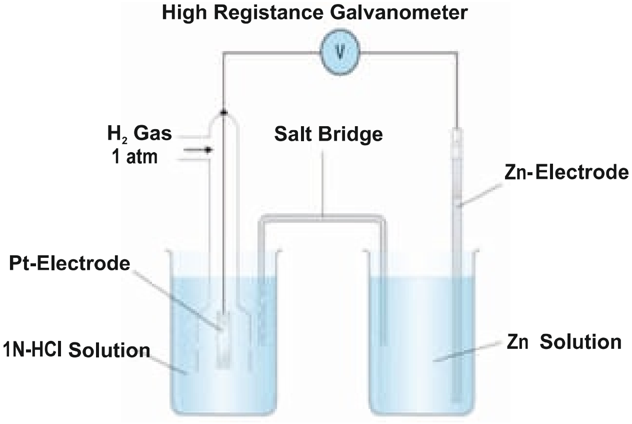


Fig. (9)

Now e.m.f. of cell

$$E_{cell} = E_R - E_L$$

$$0.76\,V = 0 - E_L \quad \Rightarrow \quad E_L = E_{Zn/Zn^{+2}} = -0.76\,V$$

Thus the reduction potential of Zn-half cell is – 0.76v whether the concentration Zn^{+2} is 1M.

Measurement of EMF of a Cell :

The following problems arise with the application of electrochemical cell to measure its cell potential.

(i) As the cell started working the concentration near the electrode changes. Due to which the emf of cell does not remain constant i.e. the cell does not give reproducible electromotive force throughout.

(ii) The most of cells are irreversible but the cell must be reversible.

(iii) The temperature coefficient of cell must be low.'

To measure the cell potential, above problem must not be these in the cell. The standard cell which plays an important role in the accurate determination of emf of any cell, due to following characteristics –

(i) Its emf should be reproducible and should not change with time.

(ii) It should be reversible.

(iii) It should preferably have a low temperature coefficient of emf (it is – 0.00005 volt K^{-1})

(iv) It should not be damaged permanently as a result of small passage of current through it.

Standard Weston Cell :

The most widely used standard cell, which satisfies the all above conditions are the standard western cell.

As shown in figure (10) it consists of an H-shaped glass vessel, the positive electrode of which consists of mercury covered with solid mercurous sulphate. The negative electrode is made of 12.5 percent cadmium amalgam. The connection to the mercury and cadmium amalgam electrode is made by platinum wises seated through the glass. The cell is then filled with a solution of cadmium sulphate kept saturated with solid $CdSO_4$. 8/3 H_2O, which acts as an electrolyte. A small air space is left over the solution in both the limbs for expansion. The upper both limbs are seated with wax.

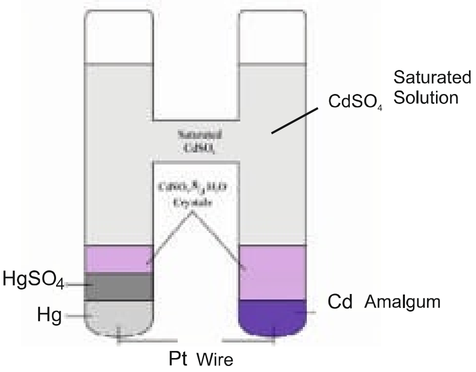


Fig. (10) Standard Weston Cell

The cell diagram is as follows –

$Cd(Hg) \mid CdSO_4\ 8/3H_2O\ (s) \mid Cd\ SO_4(Satu.) \mid Hg_2SO_4(s) \mid Hg(l)$

When the cell is working the cell reactions are as follows –

At anode : $Cd\ (s) \rightleftharpoons Cd^{+2} + 2e^-$ (Oxidation)

At cathode : $Hg_2SO_4(s) + 2e^- \rightleftharpoons 2Hg + SO_4^{2-}$ (Reduction)

Net cell reaction : $Cd(s) + Hg_2SO_4(s) \rightleftharpoons Cd^{+2} + SO_4^{2-} + 2Hg$

Thus, at 298K the e.m.f. of this cell is 1.01832 volt.

E.M.F. Measurement :

As discussed earlier that the potential difference that causes a flow of current from electrode of higher oxidation potential to the electrode of lower oxidation potential is known as the emf or cell potential of the cell. In other words the actual potential difference of the electrodes when there is no any current is flowing through the cell. So That for accurate measurement of cell potential, voltmeter cannot be used since it withdraws appreciable current from the cell.

"Pogganderf's compensation principle" is used to determine the emf or cell potential of any cell. According to the principle, if an opposite and equal cell potential is applied by same external cell to the given cell then no current will flow in the cell. In such a situation the potential applied by the external cell equal to the emf of the given cell.

The principle can explained by a basic circuit diagram of potentio meter shown if figure (11)

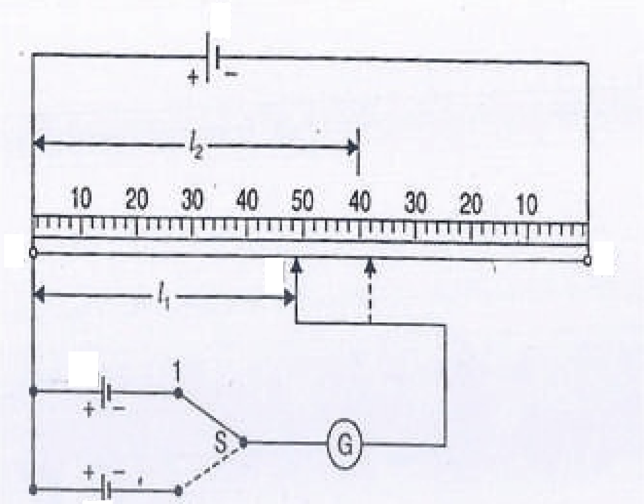


Fig. (11)

AB is the slide wire of Pt-Ir alloy of uniform cross section are having high resistance and hard material, which does not get any scratches by the fractions of sliding key. So that its cross section area remain constant. Electric source c is a battery of constant emf larger than the emf of cell, is connected in series across the terminals of the AB wire on meter scat.

The given cell X whose emf is to be measured is connected to A with poles in the same direction as the battery C. The other terminal of cell X is connected through a galvanometer G to the sliding wire by a double pole-double throw (DPDT key). Position of the terminal is moved along the sliding wire until position D is obtained when no current is flow through the galvanometer. At this position the potential difference between A and D just balances the emf of cell X. Now the standard cell is connected in DPDT key. Again null point D' on the sliding wire is determined. The emf Es of standard cell is balanced with the potential difference between A and D.

Thus, $E_x \propto$ Drop of potential from A to D

$E_s \propto$ Drop of potential from A to D

or $E_x \propto$ Length AD

and $E_s \propto$ Length AD

or $$\frac{Ex}{Es} = \frac{AD}{AD'}$$

$$\Rightarrow \quad Ex = \frac{AD}{AD'} \times Es$$

A D and 'A D' can be determined with potentio meter scale. E_s of standard cell is known, and then Ex can be calculated.

Gibb's Free Energy and EMF of Cell :

When a chemical reaction is reversibly conducted the work done by the system at a constant temperature under a given pressure is always equal to decrease in Gibb's free energy ($-\Delta G$) because such processes are spontaneous in nature. The electrical energy produced by a galvanic cell is given by the product of its electromotive force and the quantity of electricity is passed. In other words a quantity of electricity is transported across a potential difference, an electric work is done.

The electrical work is equal to the product of the quantity of electricity and the potential difference. Suppose the cell reaction under consideration involves n chemical equivalent, means n number of electrons are librated or absorbed on the electrode, then nF quantity of electricity has to be passed. Where, F is one Faraday of electricity which is associated with one chemical equivalent. If the emf of cell is E, the electric work is nFE. Therefore,

Decrease in free energy = Electrical work done by cell

$$\Rightarrow \quad -\Delta G = nFE$$

As we know that ΔG is negative for spontaneous reactions, therefore, emf of the cell will be positive. If ΔG is positive emf will be negative and the cell reaction will be non-spontaneous. In the state of equilibrium ΔG will be zero and the cell reactions are stopped.

For example if the following cell is considered:

$$Zn\ (s)\ |\ Zn\ \ (aq.)\ ||\ Cd\ \ (aq.)\ |\ Cd\ (s)$$

The emf of this cell at 299K is found +0.3590 volt so that the ΔG will be negative and following cell reaction will accrue spontaneously

$$Zn\ (s) + Cd^{+2}(aq.) \rightleftharpoons Zn^{+2}(aq.) + Cd\ (s)$$

Now the cell is connected in the following manner

$$Cd\ |\ Cd^{+2}\ (aq.)\ ||\ Zn^{+2}(aq.)\ |\ Zn$$

Then the cell potential of this cell will be -0.3590 volt and the ΔG will be positive, means this the following cell reaction of this cell is non-spontaneous.

$$Cd + Zn^{+2} \rightleftharpoons Cd^{+2} + Zn$$

Now, again $-\Delta G = nFE$

or $E = -\Delta G / nF$

The emf of cell is proportional to decrease in the Gibb's free energy.

Nernst's Equation for Cell Potential :

The standard electrode potential are given in the electrochemical series are measured in their standard states when the concentration of the electrolyte solution are fixed as 1M and temperature is 298K. However, in actual practice electrochemical cells do not have always fixed concentrations of the electrolyte solutions. W.Nernst have a relationship between electrode potentials and concentration of electrolytes known as 'Nernst's Equation.'

Let us suppose a reversible galvanic cell is represented by a following general cell reaction :

$$aA + bB \rightleftharpoons cC + dD$$

According to 'law of mass action' equilibrium constant of above cell reaction may be given as their active concentrations;

$$K = \frac{[a_C]^c \ [a_D]^d}{[a_A]^a \ [a_B]^b} \quad .... (i)$$

Where a_A, a_B, a_C and a_D are the active concentration (activities) of reactants and products.

Gibb's free energy is related with equilibrium constant as follows :

$$\Delta G = \Delta G^{\circ} + RT \ lnk \ ....(ii)$$

If k = constant, then lnk = 0

ΔG^0 is the Gibbs free energy change when the activities of all reactants nd products are unity.

According to the relation between Gibb's free energy and cell potential :

$$\Delta G = -nFE \quad ....(iii)$$

By equations (ii) and (iii) we get:

$$-nFE = -nFE^0 + RT \ lnk$$

(Where E^0 is standard cell potential)

$$\Rightarrow \quad E = E^0 - \frac{RT}{nF} \ lnk$$

$$\Rightarrow \quad E = E^0 - \frac{2.303 \ RT}{nF} \log K \quad .... (iv)$$

(lnx = 2.303 log x)

At 298K,

$$\frac{2.303 \ RT}{F} = \frac{(2.303) \ (8.314 \ JK^{-1} mol^{-1}) \ (298 \ K)}{96500 \ C \ mol^{-1}}$$

$$= 0.591 \ V \quad \because \frac{JK^{-1} mol^{-1} K}{C \ mol^{-1}} = \frac{J}{C} = Volt$$

Using eq. (1) in (V), we get-

$$E = E^{\circ} - \frac{0.0591 \ V}{n} \log \frac{[a_C]^c [a_D]^d}{[a_A]^a [a_B]^b} \quad ....(vi)$$

If all the reactants and product are their unit activities, then

$$E = E^0 \qquad [\quad \log 1 = 0]$$

Thus, all the reactants and products are taken into their unit active concentrations, the cell potential is called 'standard cell potential.'

Implication of Nernst' Equation :

The Nernst's equation may be used to determine the cell potential of any cell and electrode potential of any electrode. For example, consider the following galvanic cell:

$$Zn \ (s) \ | \ Zn^{+2} \ (aq.) \ || \ Cu^{+2} (aq.) \ | \ Cu \ (s)$$

Cell reaction of this cell is as follows :

$$Zn \ (s) + Cu^{+2} (aq.) \rightleftharpoons Zn^{+2} (aq.) + Cu \ (s)$$

Applying the Nernst's equation-

$$E = E^0 - \frac{0.0591 \ V}{2} \log \frac{[a_{Zn^{+2}}] \ [a_{Cu}]}{[a_{Zn}] \ [a_{Cu^{+2}}]}$$

But the active concentrations of solid and pure liquids are unity, thus,

$$[a_{Cu}] = [a_{Zn}] = 1$$

So that,

$$E = E^0 - 0.02955 \ V \ \log \frac{[a_{Zn^{+2}}]}{[a_{Cu^{+2}}]}$$

Hence, the cell potential of this cell depends on the concentrations of Zn^{+2} and Cu^{+2} ions in the electrolyte solutions.

Batteries or Common Cells

One of the main uses of galvanic cells is the generation of portable electrical energy. These cells are also properly known as batteries. The term battery is generally used for two or more galvanic cells connected in a series. The basis of an electrochemical cell is and oxidation – reduction reactions. However, for the practical purposes there is some limitations use of redox reactions.

A useful battery should also fulfill the following requirements:

(i) It should be light and compact so that it can be easily transported.

(ii) It should have responsibly long life both when it is being used and when it is not used.

(iii) The voltage of the battery not varies appreciably during its use.

Primary Cell or Battery :

In these batteries, the electrode reactions cannot be reversed by an external energy source. In these cells, reactions occur only once and after use they become read or useless, ie these are not chargeable. The most familiar commercial cells are dry cells. These are used in torches, toys, calculators, watches and many other devices. These are based on Leclanche cell invented by G. Leclanche in 1868. A dry cell is shown in the following figure (12) :

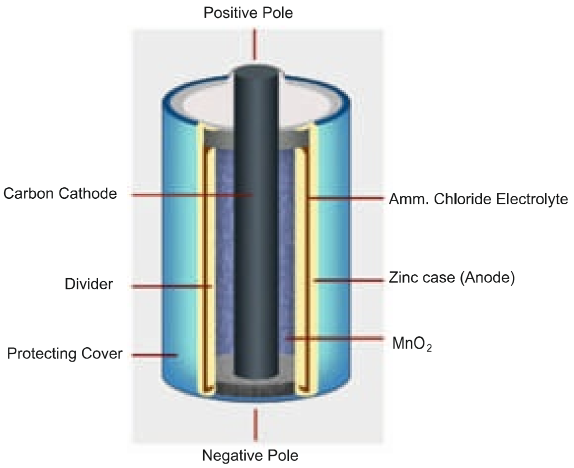


Fig. (12) Leclanche Cell

It consists, zinc cylinder which is fitted with a paste of NH_4OH and little $ZnCl_2$. The zinc cylinder acts as a anode. The cathode is a graphite (carbon) rod which is surrounded by a black paste of manganese dioxide and carbon powder. The zinc case has an outer insulation of cardboard case. During use, zinc case gets consumed and at the end, it will develop holes which are responsible for leakages.

When the cell is working, zinc loses electrons and Zn^{+2} ions produced are dissolving in the electrolyte the electrons pass through the external circuit and are taken up at cathode. This causes discharge of NH^+_4 ions from the electrolyte. The reactions taking place at the electrodes are:

Anode : $Zn\ (s) \longrightarrow Zn^{+2}\ (aq.) + 2e^-$

Cathode :

$NH_4^+\ (aq.) + MnO_2\ (s) + 2e^- \longrightarrow MnO\ (OH) + NH_3$

Overall :

$Zn + NH_4^+\ (aq.) + MnO_2\ (s) \longrightarrow Zn^{+2}\ (aq.) + MnO\ (OH) + NH_3$

In the cathode reaction, manganese is reduced from +4 to +3 oxidation states. Ammonia is not liberated as a gas but it combines with Zn^{+2} ions produced from the anode and form $[Zn(NH_4)_2]^{2+}$ complex ions. It gives about 1.2 to 1.5 volts.

A new type of cell in this type is mercury cell which is used in small circuits such as hearing aids, watches cameras etc. It consists, Zn anode and mercuric and mercuric oxide cathode.

The mercury cell is shown in the following figure (13) :

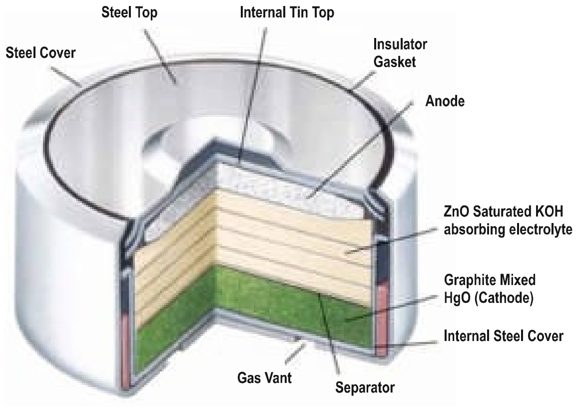


Fig. (13) Mercury Cell

The electrolyte is a past of KOH and ZnO and the reactions in the cell are as follows:

Anode : $Zn\ (Hg) + 2OH^- \longrightarrow ZnO\ (s) + H_2O + 2e^-$

Cathode : $HgO + H_2O + 2e^- \longrightarrow Hg\ (l) + 2OH^-$

Overall : $Zn\ (Hg) + HgO\ (s) \longrightarrow ZnO\ (s) + Hg\ (l)$

In this case, the overall cell reaction does not involve any ion in solution whose concentration can change. Therefore, it has the advantage that its potential remains almost constant throughout its life. The voltage of this cell is about 1.35 volts.

Secondary Cells or Batteries :

As we know that the ordinary cells are not chargeable. However, there are some cells which can be recharged. These are called accumulators or storage cells. These can be recharged and used again and again as a source of electric current. The most popular example is of lead storage cell which is used in cars, buses, trucks etc.

Lead Storage Cell :

This is the most commonly used battery in automobiles and invertors. It consists of a lead anode and grid of lead packed with lead dioxide (PbO_2) as cathode about 38% solution of sulfuric acid is used as an electrolyte. Each battery consists of a number of voltaic cell connected in a series as shown in the figure (14) :

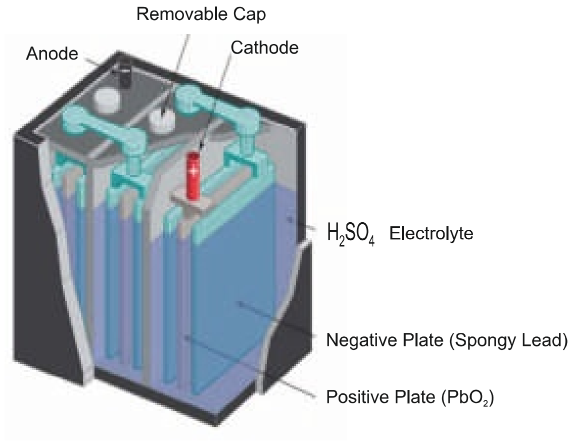


Fig (14) Lead Storage Battery

The following reactions take place in the lead storage cells.

At anode :

$$Pb\ (s) \longrightarrow Pb^{+2}\ (aq.) + 2e^-$$

$$Pb^{+2}\ (aq.) + SO^{2-}\ (aq.) \longrightarrow PbSO_4\ (s)$$

The overall anode reaction may be given as :

$$Pb\ (s) + SO_4^{2-}(aq.) \longrightarrow PbSO_4(s) + 2e^-$$

At cathode :

$$PbO_2\ (s) + 4H^+ + 2e^- \longrightarrow Pb^{+2}(aq.) + 2H_2O$$

$$Pb^{+2}\ (aq.) + SO_4^{2-}\ (aq.) \longrightarrow PbSO_4\ (s)$$

The overall cathode reaction is as follows :

$$PbO_2\ (s) + 4H^+\ (aq.) + SO_4^{2-}\ (aq.) + 2e^- \longrightarrow PbSO_4\ (s) + 2H_2O\ (l)$$

Thus, the complete cell reaction is:

$$Pb\ (s) + PbO\ (s) + 2H\ SO\ \ (aq.) \longrightarrow 2PbSO\ \ (s) + 2H\ \ O\ (l)$$

It is clear from the above reactions that during the working of the cell, $PbSO_4$ is formed at each electrode and H_2SO_4 is used up. As a result the concentration of H_2SO_4 decreases and density falls below 1.2g. ml^{-1}, the battery needs recharging.

The cell can be charged again by passing electric current of a suitable voltage in the opposite direction. The electrode reaction gets reversed. As a result, the flow of electrons gets reversed and lead is deposited on anode and PbO_2 on the cathode. The density of H_2SO_4 also increases. The reaction is :

$$2PbSO_4(s) + 2H_2O \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4$$

It is clear that during the charging it becomes an electrolytic cell.

Nickel – Cadmium Storage Cell :

These cells are also rechargeable cells and have longer life than the lead storage cells. These are more expensive than the lead storage battery; however, due to smaller size and lighter these are more useful. This cell consists of a Cd-anode and a metal grid containing NiO_2 acting as a cathode as shown in the following figure (15) :

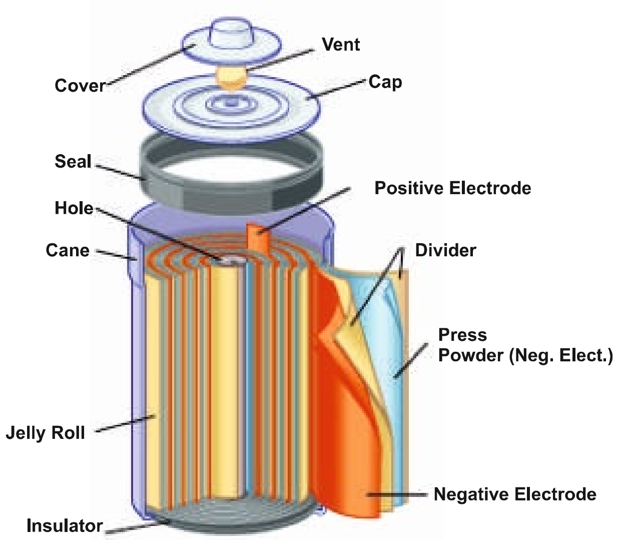


Fig. (15) Nicke-Cadmium Storage Cell

KOH is the electrolyte in this cell and the reactions are as follows:

Anode :

$$Cd\ (s) + 2OH^- \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} CdO\ (s) + H_2O\ (l) + 2e^-$$

Cathode :

$$2Ni\ (OH)_3\ (s) + 2e^- \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} 2Ni\ (OH)_3\ (s) + 2OH^-(aq.)$$

Overall :

$$Cd\ (s) + 2Ni\ (OH)_3(s) \underset{Charge}{\overset{Discharge}{\rightleftharpoons}} CdO\ (s) + 2Ni\ (OH)_2\ (s) + H_2O\ (l)$$

In these reactions there is no any gas formation occur. It produces a potential of about 1.4 V and is longer life than lead storage battery.

Fuel Cell :

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy of fossil fuels (coal, gas or oil) is first used for converting water into vapour of high pressure. This steam is then used to run a turbine to produce electricity. We know that a galvanic cell density converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactions are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment.

Galvanic cells that are designed to convert the energy of combustion of fuel like hydrogen, methane, methanol etc. directly into electrical energy are called fuel cells.

The common example is hydrogen – oxygen fuel cell. In this cell, hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated NaOH or KOH as shown in the following figure (16) :

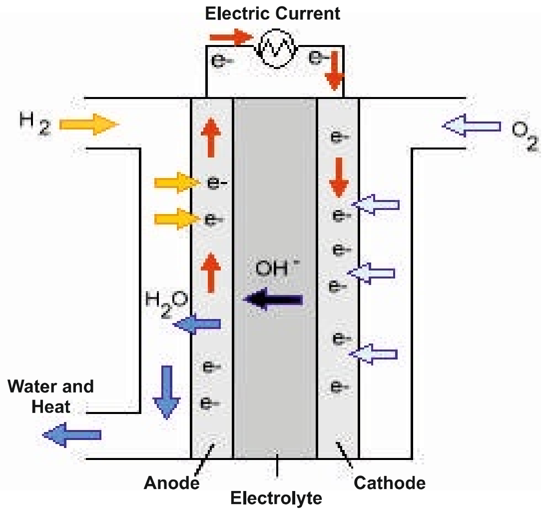


Fig. (16) Fuel Cell

Hydrogen (the fuel) is fed into the anode compartment where it is oxidised. The oxygen is fed into cathode compartment where it is reduced. The diffusion rates of the gases into the cell are carefully regulated to get maximum efficiency. The net reaction is the same as burning of H_2 and O_2 to form H_2O.

The reactions are as follows:

Anode : $O_2(g) + 2\,H_2O\,(e) + 4e^- \longrightarrow 4OH^-\,(aq.)$

Cathode : $2H_2(g) + 4\,OH^-\,(aq.) \longrightarrow 4\,H_2O\,(l) + 4e^-$

Overall : $2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$

This cell runs continuously as long as the reactants are fed. These fuel cells are more efficient than conventionally used methods of generating electricity on a large scale by burning hydrogen, carbon fuel because these fuel cells convert the energy of the fuel directly into electricity. Fuel cells are pollution free and in view of their future importance a variety of fuel cells have been fabricate and tried.

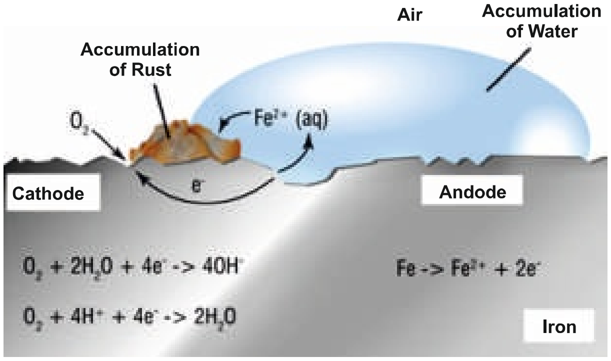
Corrosion :

When the metals are exposed to atmospheric, they react with air or water in the environment to form undesirable compounds (usually oxides). This process is called corrosion. Almost all metals are attached by atmosphere undergo corrosion. Some metals are least active towards corrosion such as gold, platinum, palladium etc. Due to this corrosion process silver tarnishes, copper develops a green coating, lead or stainless steel lose their luster. Corrosion causes enormous damage to buildings, bridges, ships and many other articles made of iron.

The phenomenon of corrosion can be explained with the help of electrochemical theory which involves oxidation and reduction reactions. According this theory of corrosion, it is believed that non-uniform surface of metal or impurities present in iron behave like small electric cells in the presence of water containing dissolved oxygen or carbon dioxide. A film of moisture with dissolved CO_2 constitutes electrolytic solution covering the metal surface at various places. The iron is shown in the following figures (17) and (18) :

(Rusted Iron Material)

Fig. (17)



(Mechanism of Rusting)

Fig. (18)

Oxidation occurs at the anodes of each electrochemical cell. Therefore, at each anode neutral iron atoms are oxidized to ferrous ions:

At anode : $\mathbf{2Fe\ (s) \longrightarrow 2Fe^{2+} + 4e^-}$

$$E^- (Fe^{2+}/Fe) = -0.44V$$

Thus, the metal atoms in the lattice pass into the solution as ions, leaving behind electrons on metal surface. These electrons move towards the cathode region through the metal. At the cathode of each cell, these electrons are captured by hydrogen ions i.e. reduction takes place. The H^+ ions are obtained either from water or from acidic substances like CO_2 etc in water.

At cathode :

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O\ (l); \quad E\ (H^+/O_2/H_2O) = 1.23\ V$$

Overall :

$$2Fe\ (s) + O_2(g) + 4H^+\ (aq.) \longrightarrow 2Fe^{+2}\ (aq.) + 2H_2O\ (l): \quad E\ \text{सेल} = 1.67\ V$$

After that the atmosphere oxygen oxidizes the Fe^{+2} into Fe^{+3} and then ferric oxide ($Fe_2O_3.xH_2O$) which is seen as corrosion on the surfaces of iron materials as shown figure (17).

Prevention of Corrosion :

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collage or failure of key components due to corrosion. This can be prevented or retarded by some methods like:

(I) A barrier is placed between iron and atmosphere air like pain, galvanizing the iron objects.

(ii) Iron is protected by rusting by covering it with a layer of a metal more active than iron. This prevents loss of electron from iron.

Numerical Problems

(1) The resistance of a conductivity cell containing 0.001M KCl solution at 298K is 1500 ohm. What is the cell constant if the conductivity of 0.001M KCl solution at 298K is 0.146×10^{-3} Scm^{-1}.

Solution :

Conductivity, $\kappa = 0.146 \times 10^{-3}\ S\ cm^{-1}$

Resistance, R = 1500 ohm

Cell constant = Conductivity, (κ) x Resistance (R)

Cell constant = $0.146 \times 10^{-3}\ ohm^{-1}\ cm^{-1}\ 1500\ ohm$

$= 0.219\ cm^{-1}$

(2) The conductivity of 0.20M KCl solution at 298K is 0.0248 Scm^{-1}. Calculate its molar conductivity.

Solution :

Molar Conductivity

$\lambda_m = (\kappa \times 1000) / C$

$\therefore \kappa = 0.0248\ S\ cm^{-1}, C = 0.20\ M$

$\Rightarrow \lambda_m = (0.0248 \times 1000) / 0.20$

$= 124.0\ S\ cm_2\ mol^{-1}$

(3) Calculate the equivalent conductivity of 1M - H_2SO_4 solution whose conductivity is $26 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$

Solution :

Conductivity = $26 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$

Concentration = 1M - H_2SO_4 = 98 gm Lit-1

Equivalent weight = 49

Gram Equivalent per litre = 98 / 49 = 2 gm Eq. Lit^{-1}

Eqvivalent Conductivity = $(\kappa \times 1000) / C$

$= (26 \times 10^{-2} \times 1000) / 2$

$= 130\ ohm^{-1}\ cm^2\ Equi^{-1}$

(4) The molar conductivities at infinite dilution for sodium acetate, hydrochloric acid and

sodium chloride are 91.0, 425.4 and 126.4 S.cm^2 mol^{-1} respectively at 298K. Calculate the molar conductivity of acetic acid at infinite dilution.

Solution :

Molar conductivity at infinite dilution for acetic acid can be calculated as :

$$\lambda^0 CH_3\,COOH = \lambda^0 H + \lambda^0 CH_3COO^-$$

$$\lambda^0 CH_3\,COOH = \lambda^0 CH_3COO\,Na + \lambda^0 HCl - \lambda^0 NaCl$$

$$= \lambda^0 CH_3COO^- + \lambda^0 Na^+ + \lambda^0 H^+ + \lambda^0 Cl^- - \lambda^0 Na^+ - \lambda^0 Cl^-$$

$$= \lambda^0 H^+ + \lambda^0 CH_3\,COO^-$$

$$\lambda^0 CH_3\,COOH = 91.0 + 425.4 - 126.4$$

$$= 390.5\ cm^2\ mol^{-1}$$

(5) A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? (IF=96487c)

Solution :

Current Strength (I) = 1.5 A

Time (t) = 10 min = 10 x 60 = 600 sec.

Quantity of electricity passed = I x t

= (1.5 A) x (600 S)

= 900 C [∴ A x S = C]

Copper is deposited as

$Cu^{+2} + 2e^- \rightarrow Cu(s)$

2 mol of electrons or 2 x 96487 C of current deposited copper = 63 gm

900 C of current deposited copper

= (63 gm mol^{-1} x 900 C) / (2 x 96487 C mol^{-1})

= 0.2938 gm

(6) Resistance of a conductivity cell filled with 0.1M KCl solution is 100 ohm. If the resistance of the same cell when filled with 0.02M KCl solution is 520 ohm, calculate the conductivity and molar conductivity of 0.02M KCl solution. (The conductivity of 0.1M KCl solution is 1.29 Sm^{-1})

Solution :

Let us first calculate the cell constant.

Cell constant (X) = Conductivity (κ) x Resistance (R)

Resistance of 0.1 M KCl solution = 100 ohm.

Conductivity of 0.1 M KCl solution = 1.29 Sm^{-1}

∴ Cell constant (X) = 1.29 (Sm^{-1}) x 100 (ohm)

= 1.29 m^{-1}

⇒ Cell constant (X) = 1.29 cm^{-1}

Calculation of conductivity of 0.02 M KCl solution

Resistance of solution (R) = 520 ohm

Cell constant (X) = 1.29 cm^{-1}

Conductivity (κ) = X / R

= (1.29 cm^{-1}) / (520 ohm)

⇒ (κ) = 0.248 x 10^{-2} S cm^{-1}

Calculation for molar conductivity

λ_m = (1000 x κ) / C

C = 0.02 M, κ = 0.248 x 10^{-2} S cm^{-1}

⇒ λ_m = (1000 x 0.248 x 10^{-2} S cm^{-1}) / 0.02

= 124 S cm^2 mol^{-1}

(7) The molar conductance of ammonium hydroxide at concentrations 0.1M and 0.001M are 3.6 and 34.0 S.cm^2. mol^{-1} respectively. Calculate the degree of dissociation of NH_4OH at this concentration. Molar conductance at infinite dilution for NH_4OH is 271.1 ohm^{-1} cm2 mol^{-1}.

Solution :

Degree of dissociation is given as $\alpha = \lambda_c / \lambda^\infty$ where λ_c is the molar conductance at concentration C and λ^∞ is the molar conductance at infinite dilution.

I. At concentration C = 0.1 M, λ_c = 3.6 ohm^{-1} cm^2 mol^{-1}, λ^∞ = 271.1 ohm^{-1} cm^2 mol^{-1}

⇒ α = 34.0 / 271.1 = 0.125

i.e. 12.5 % dissociated

(8) Calculate the standard electrode potential of Ni^{+2} | Ni electrode if the cell potential of the

cell. $Ni / Ni^{+2}\ (1M)\ //\ Cu^{+2}\ (1M) / Cu$

is 0.59 V. Given that $E_{Cu^{+2}/Cu} = 0.34$ V.

Solution : Cell diagram is-

$Ni / Ni^{+2}\ (1M)\ //\ Cu^{+2}\ (1M) / Cu$

Cell reaction is,

$$Ni\,(s) + Cu^{+2}\,(aq) \rightarrow Ni^{+2}\,(aq) + Cu\,(s)$$

$$E = E^{0} - \frac{0.0591}{n} \log \frac{[\,Ni1^{+2}\,(aq)]}{[Cu^{+2}\,(aq)]}$$

$$0.59 = E^{0} - \frac{0.0591}{2} \log \frac{0.01}{0.1} \qquad \therefore n = 2$$

$$\Rightarrow \quad 0.59 = E^{0} + 0.0295 \ \log\ [10] \qquad \therefore \log 10 = 1$$

$$\Rightarrow \quad 0.59 = E^{0} + 0.0295$$

$$\Rightarrow \quad E^{0} = 0.59 - 0.0295 \ = \ 0.5605\ V$$

Now, $E^{0}_{cell} = E^{\circ}\,(Cu^{+2} / Cu) - E\,(Ni^{+2} / Ni)$

$$\Rightarrow \quad 0.5605 = 0.34 - E\,(Ni^{+2} / Ni)$$

$$\Rightarrow \quad E^{0}\,(Ni^{+2} / Ni) = 0.34 - 0.5605 = -0.2205\ V$$

(9) If the standard electrode potential copper electrode is +0.34V. Calculate electrode potential of 0.1M electrolyte containing copper ions. (log 10 = L)

Solution : The copper electrode reaction will be as follows :

$$Cu^{+2}\,(aq) + 2e^{-} \rightarrow Cu\,(s)$$

As we know that $E = E^{\circ} - \frac{0.059}{2} \text{ Log } \frac{1}{[\,Cu^{+2}\,]}$

When $[Cu^{+2}] = 0.1$ M

Thus, $E = 0.34 - \frac{0.059}{2} \text{ Log } \frac{1}{0.1}$

$\Rightarrow E = 0.34 - \frac{0.059}{2} \times 1 = 0.31\ V \quad (\therefore \text{Log } 10 = 1)$

Multiple Choice Question

(1) Which of the following is not a good conductor ?

(a) Cu – metal (b) NaCl (aq.)

(c) NaCl (molten) (d) NaCl (s)

(2) If the conductivity and conductance of a solution is same -

(a) 1 (b) 0

(c) 10 (d) 1000

(3) The unit of cell constant is -

(a) $ohm^{-1}\ cm^{-1}$ (b) cm

(c) $ohm^{-1}\ cm$ (d) cm^{-1}

(4) The unit of conductivity (specific conductance) is -

(a) ohm^{-1} (b) $ohm^{-1}\ cm\text{-}^{1}$

(c) $ohm^{-1}\ cm^{2}$ equi (d) $ohm^{-1}\ cm^{-2}$

(5) For a redox reaction proceed in a cell, the emf must be -

(a) Positive (b) Negative

(c) Zero (d) Fixed

(6) Which of the following statement is true for a cell is made by zinc and copper on the basis of electrochemical series –

a- Zinc acts as cathode and copper as anode

b- Zinc acts as anode and copper as cathode

c- Election flows from copper to zinc electrode

d- Copper electrode dissolves and zinc accumulated on zinc electrode

(7) How many coulombs are required for the oxidation of one mole of H_2o to O_2 ?

(a) 1.93×10^{5} C (b) 9.65×10^{4} C

(c) 6.023×10^{23} C (d) 4.85×10^{4} C

(8) Which of the following are used in electro plating of iron seat?

(a) C (b) Cu

(c) Zn (d) Ni

(9) Which of the following mixture causes corrosion -

(a) FeO and $Fe(OH)_3$

(b) FeO and $Fe(OH)_2$

(c) Fe_2O_3 and $Fe(OH)_3$

(d) Fe_2O_3 and $Fe(OH)_2$

(10) When the lead storage battery discharges -

(a) SO_2 librated (b) $PbSO_4$ decomposes

(c) Lead forms (d) H_2SO_4 decomposes

Ans : 1(d), 2(a), 3(d), 4(b), 5(a)

6(b), 7(b), 8(c), 9(c), 10(d)

Very Short Answer Questions :

(1) Can you put the copper sulphate solution in a zinc pot?

(2) Give the three examples on the basis of electrochemical series which can oxidise to ferrous ions appropriate conditions.

(3) Why the conductivity of an electrolyte decreases with dilution?

(4) Give some examples of metals which can be extracted electrochemically?

(5) Except hydrogen, give two other examples of compounds which may be used in fuel cells.

(6) Arrange the following metals in the order which may displace one another from their salt solutions – Al, Cu, Fe, Mg and Zn.

Short Answer Questions :

(1) How will you determines the standard electrode potential of $Mg^{+2} | Mg$ system ?

(2) Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

(3) Calculate the emf of the cell in which the following reaction takes place :

$Ni(s) + 2Ag^{+}(0.002\,M) \rightarrow Ni^{+2}(0.160\,M) + 2Ag(s)$

Given that $E^{0}_{cell} = 1.05V$.

(4) Following cell reaction occurs in cell :

$2Fe^{+3}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{+2}(aq) + I_2(s)$

At 298K the standard cell potential of this cell E^{0}_{cell} = 0.236V. Calculate standard Gibb's free energy and the equilibrium constant of the cell reaction.

(5) Suggest a way to determine the λ^{0}_{m} value of water.

(6) The molar conductivity of 0.025 mol methanoic acid is 46.1 $ohm^{-1}\ cm^{2}\ mol^{-1}$. Calculate its degree of dissociation. Given,

$(H^{+}) = 349.6\ S\ cm^{2}\ mol^{-1}$ and $\lambda^{0}\ (HCOO^{-})$ = $54.6\ S\ cm^{2}\ mol^{-1}$l

(7) Suggest a list of metals that are extracted electrolytically.

(8) Consider the reaction : $Cr_2O^{2-}_7 + 14\,H^{+}\ 6e^{-} \rightarrow 2\,Cr^{+3} + 7\,H_2O$. What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O^{2-}_7$

(9) Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

(10) With the help of given standard electrode potentials of some metals. Average in the increasing reducing power to them.

K^{+}/K = -2.93V, Ag^{+}/Ag = 0.80V

Hg^{2+}/Hg = 0.79v

Mg^{2+}/Mg = -2.37V, Cr^{3+}/Cr = -0.74v

(11) Calculate the standard cell potential of galvanic cells in which the following reactions take place:

(i) $2Cr(s) + 3\,Cd^{+3}(aq) \rightarrow 2\,Cr^{+3}(aq) + 3\,Cd(s)$

(ii) $Fe^{+2}(aq) + Ag^{+}(aq) \rightarrow Fe^{+3}(aq) + Ag(s)$

Given : $E^{0}(Cr^{+3} | Cr) = -0.74$ V, $E^{0}(Cd^{+2} | Cd) = -0.40$ V, $E^{0}(Ag^{+} | Ag) = 0.80$ V, $E^{0}(Fe^{+3} | Fe) = 0.77$

Long Answer Question :

(1) Explain the charging process of lead storage battery with chemical reactions.

(2) Explain that corrosion of iron is due to formation of an electrochemical cell.

(3) Give the cell diagram of the electrochemical cell in which following reaction occurs :

$Zn(s) + 2\,Ag^{+}(aq) \rightarrow Zn^{+2}(aq) + 2Ag(s)$

Now explain :

1) Which electrode is negative?

2) Which are responsible for electric current flow in the cell? What the reactions on electrodes