

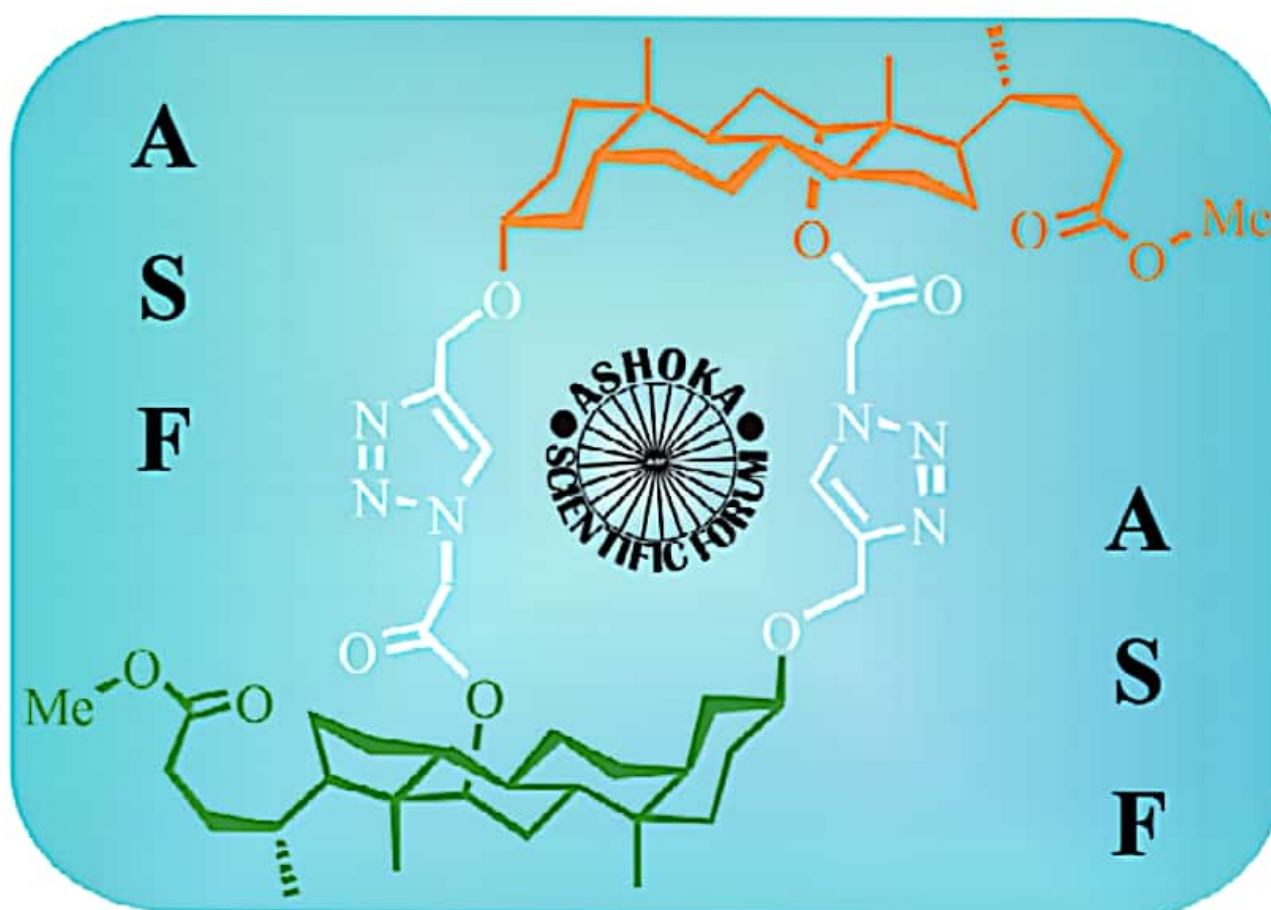


Ashoka Scientific Forum

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Physical chemistry



TOPIC: E I E C T r O C h E m I s T r y

Electrochemistry

ELECTROLYTES

Solid and liquid substances, which are able to conduct the electric current, can be roughly divided into two categories i.e. metallic conductors and electrolytic conductors.

In metallic conductors or electronic conductors, the electric current is carried by the mobile electrons. When an electric potential is applied to metallic conductors, the electrons start moving in one direction while the positive ions remain stationary. Thus, the flow of electricity is not accompanied by any appreciable movement of the matter.

Electrolytic conductors or electrolytes are distinguished from metallic conductors by the fact that the current is carried by ions and not by electrons. The application of an electrical potential causes these charged particles of matter to move, the positive ions move towards the cathode and the negative ions move towards the anode. Thus, passage of an electric current through an electrolyte is always accompanied by transfer of matter. This transfer is manifested by changes in concentration, and also by visible separation of material at the points where the electric current enters and leaves the electrolyte. Electrolytes generally employed are salts in molten form or salts dissolved in water.

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).

An electrode and its electrolyte comprise an **Electrode Compartment**.

Electrochemical Cells can be classified as:

- (i) **Electrolytic Cells** in which a non-spontaneous reaction is driven by an external source of current.
- (ii) **Galvanic Cells** which produce electricity as a result of a spontaneous cell reaction

Note: In a **galvanic cell**, cathode is positive with respect to anode.

In a **electrolytic cell**, anode is made positive with respect to cathode.

ELECTROLYSIS

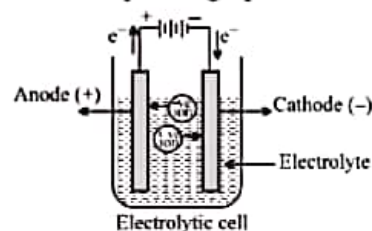
Electrolysis is a process of chemical decomposition of the electrolyte by the passage of electric current. It is carried out in a cell called electrolytic cell.

The electrode at which oxidation takes place is called anode and the electrode at which reduction takes place is called cathode. The electrodes are named anode or cathode depending upon the reaction occurring on them and not on the basis of sign of electrodes.

ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy.

The entire assembly except that of the external battery is known as the electrolytic cell



ELECTRODES

Anode	Positive	Loss of electron or oxidation takes place	Positive current enters
Cathode	Negative	Gain of electron or reduction takes place	Current leaves

FARADAY'S LAWS OF ELECTROLYSIS:

Faraday established the relationship between the quantity of electricity passed through an electrolyte and the amount of material liberated or deposited at the electrode. The quantity of electricity is equal to the product of the current strength and the time for which it is passed. The results of Faraday's findings can be put in the form of two laws of electrolysis.

(i) First Law of Electrolysis

When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electricity passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation: $W \propto Q$

Remember that Q is not the amount of charge passed but it is the amount of charge utilized.

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

$$\begin{aligned} Q &= \text{Current in amperes} \times \text{time in seconds} \\ &= I \times t \end{aligned}$$

$$\begin{aligned} \text{So } W &\propto I \times t \\ \text{or } W &= Z \times I \times t \end{aligned}$$

where Z is a constant, known as electro-chemical equivalent, and is characteristic of the substance deposited.

When a current of one ampere is passed for the one second, i.e., one coulomb ($Q = 1$), then

$$W = Z$$

Thus, electrochemical equivalent can be defined as the mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second.

(ii) Second Law of Electrolysis

The amount of different substances deposited or dissolved by the same quantity of electricity are proportional to their respective chemical equivalent weights.

$$W = Z \times Q$$

$$\text{Thus, } E = Z \times 96500$$

$$\text{or } Z = E/96500; \quad \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Charge and Potential Difference

As one g-equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by one g-equivalent of an ion is 96500 coulomb. If the valency of an ion is 'n', the one mole of these ions will carry a charge of nF coulomb. One g-mole of an ion contains 6.02×10^{23} ions.

Then, the charge carried by an ion = $\frac{nF}{6.02 \times 10^{23}}$ coulomb

For n = 1, The fundamental unit of charge = $\frac{nF}{6.02 \times 10^{23}}$

$$\text{i.e. } \frac{96500}{6.02 \times 10^{23}} = 1.6 \times 10^{-19} \text{ coulomb}$$

$$\text{or } 1 \text{ coulomb}^* = 6.25 \times 10^{18} \text{ electrons}$$

The rate of flow of electric charge through a conductor is called the electric current.

$$1 \text{ coulomb} = 1 \text{ ampere-second}$$

$$\text{Electric current} = \frac{\text{Electric charge}}{\text{Time}}$$

$$1 \text{ ampere} = \frac{1 \text{ coulomb}}{1 \text{ second}}$$

Volt is a unit of electrical potential difference, it is defined as potential energy per unit charge.

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}} = \frac{1 \text{ newton} \times 1 \text{ metre}}{1 \text{ ampere} \times 1 \text{ second}}$$

Electrical energy = potential difference $\times$ Quantity of charge

$$= V \times Q$$

$$= V \times I \times t \quad (I = \text{ampere}; t = \text{second})$$

$$= \text{Watt-second}$$

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

Faraday's Law for Gaseous Electrolytic Product

$$\begin{aligned} \text{We know } W &= ZQ \\ &= ZIt \end{aligned}$$

$$W = \frac{ItE}{96500} \quad \dots(i)$$

$$\text{where } Z = E/96500$$

Equation (i) is used to calculate the mass of solid substance dissolved or deposited at an electrode.

For the gases, we use

$$V = \frac{It V_e}{96500} \quad \dots(ii)$$

where V = volume of gas evolved at S.T.P. at an electrode

V_e = Equivalent volume

= Volume of gas evolved at an electrode at S.T.P. by 1 Faraday charge.

Table 1 : Distinction between metallic and Electrolytic conduction.

S.No.	Metallic conduction	Electrolytic conduction
1	Electric current flows by movement of electrons.	Electric current flows by movement of ions.
2	No chemical change	Ions are oxidised or reduced at the electrodes.
3	It does not involve the transfer of any matter	It involves transfer of matter in the form of ions.
4	Ohm's law is followed	Ohm's law is followed
5	Resistance increase with increase of temperature	Resistance decreases with increase of temperature
6	Faraday law is not followed	Faraday law is followed

CONDUCTANCE

Specific Conductance

Molten electrolytes and the aqueous solutions of electrolytes contain free ions and conduct electricity due to the movement of ions.

We know that Ohm's law is applicable to metallic conductors as well as electrolytic conductors. According to the Ohm's law, the resistance of a conductor is directly proportional to the length and is inversely proportional to the area of cross-section of the conductor.

$$\therefore R \propto \frac{l}{a}$$

$$R = \rho \times \frac{l}{a}$$

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

$$K = G \cdot \frac{l}{A}$$

where 'l' is the distance between the electrodes, 'a' is the area of cross-section of electrodes, ρ is the resistivity of the solution, K is conductivity (specific conductance) of the solution and G is conductance.

$$\frac{l}{A} \text{ is cell constant.}$$

Now, if $l = 1$ unit of length and $a = 1$ unit of area, then

$$K = G$$

i.e., K is conductance of the solution which is placed 1 unit length apart between the electrodes of 1 unit area.

Thus, specific conductance is the conductance of a conductor which is observed when it is 1 cm in length and 1 sq. cm in cross-sectional area. In other words, it is the conductance of 1 cc of the electrolyte.

The unit of resistance is ohm (Ω) so unit of conductance will be ohm^{-1} or Ω^{-1} and expressing l in cm and a in cm^2 , the unit of specific conductance are Sm^{-1} where S stands for Semen.

Molar Conductance (Λ_m)

The conductance of all the ions furnished by one mole of an electrolyte in any solution is termed as its molar conductivity".

Thus, molar conductance is expressed as

$$\text{Molar conductance } (\Lambda_m) = \frac{\text{Conductivity}}{\text{Concentration in moles per unit volume } (C_m)} = \frac{k}{C_m}$$

Expressing molar conductance in unit of $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, mathematical expression assumes the form

$$\Lambda_m = \frac{k}{C_m} \times 1000$$

Si units of Λ_m is $\text{S m}^2 \text{mol}^{-1}$

Here Λ_m is molar conductance

K is conductance of solution

C_m is concentration of solution in terms of molarity.

Equivalent Conductance

Equivalent conductance is the conducting power of all the ions produced by one g-equivalent i.e. one equivalent of an electrolyte in a given solution. The equivalent conductance may, therefore, be defined as the conductance which is observed when two sufficiently large electrodes are dipped into solution at unit distance so as to enclose in between them the entire volume of solution containing one equivalent of the electrolyte.

$$\Lambda_{eq} = \frac{k}{\text{Normality}}$$

Expressing Λ_{eq} in $\text{S cm}^2 \text{equiv}^{-1}$.

$$\Lambda_{eq} = \frac{k}{\text{Normality}} \times 1000$$

Relationship Between Molar and Equivalent Conductivities

$$\Lambda_m = n \times \Lambda_{eq}$$

Where $n = n$ factor of electrolyte = total charge carried by either of the positive or negative ion.

Variation of Conductance with Dilution

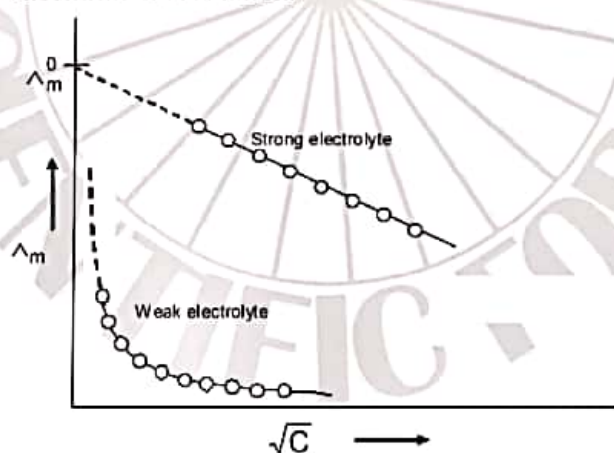
Upon dilution i.e. lowering concentration, specific conductance decrease while equivalent and molar conductances increase. At infinite or almost zero concentration equivalent conductance and molar conductance attain their respective limiting values called equivalent conductance at infinite dilution (Λ_{∞}) or zero concentration (Λ_0) and molar conductance at infinite dilution (Λ_m^{∞}) or zero concentration (Λ_m^0), respectively. The increase of Λ or Λ_m with dilution of a weak electrolyte is attributable to increase of degree of dissociation with dilution resulting into more number of ions in solution. Note that ions are carriers of electricity. The increase of Λ and Λ_m of a strong electrolyte which remains completely ionised at all dilutions, is attributed to increase in the ionic mobilities of ions due decrease in inter-ionic attraction. As dilution approaches unity, the member of ions becomes maximum and hence Λ as well as Λ_m approach their respective maximum value. In the case of strong electrolyte, however, the maximum value of Λ or Λ_m is attained due to the maximum ionic mobilities of the ions since at infinite dilution the dissociation of strong electrolyte is complete and inter-ionic attraction cases to exist completely.

The decrease in K may also be explained in the following way. Upon dilution the number of ions, in the case of weak electrolyte, increase but volume of solution also increases. The increase of volume is in greater proportion than the increase of number of ions resulting into decrease in number of ions per c.c. solution. The specific conductivity being the conductivity of 1 c.c. solution, should obviously decrease.

The variation of molar conductance of a strong electrolyte with concentration is theoretically give by Debye-Hückel-Onsager equation

$$\Lambda_m = \Lambda_m^0 - (A + B \Lambda_m^0) \sqrt{C}$$

Where A and B are the Debye-Hückel constants depending upon nature of the solvent and temperature and C is the molar concentration of solution.



Arrhenius Theory of Electrolytic Dissociation for weak Electrolytes

According to the Arrhenius theory of electrolytic dissociation, there exists an equilibrium between the undissociated molecule AB and the ions A^+ and B^- which result from the dissociation of the molecule. Thus,



This equilibrium is characterized by the equilibrium constant, defined as

$$K = \frac{[A^+][B^-]}{[AB]}$$

If α is the degree of dissociation and c is the initial concentration of the weak electrolyte AB, then concentrations of various species are :

$$\begin{aligned} [A^+] &= [B^-] = c\alpha \\ [AB] &= c(1 - \alpha) \end{aligned}$$

$$\text{Thus } K = \frac{(c\alpha)(c\alpha)}{c(1 - \alpha)} = \frac{c\alpha^2}{1 - \alpha}$$

Since $\alpha \ll 1$, we have $K = c\alpha^2$ or $\alpha = \sqrt{K/c}$.

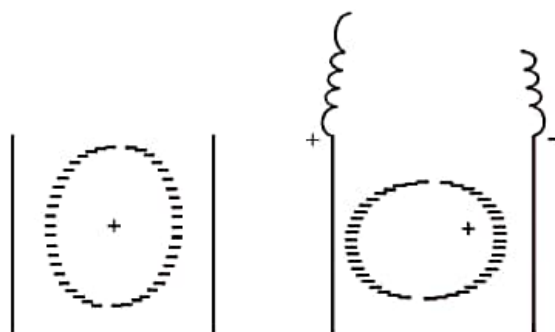
The expression $\alpha = \sqrt{K/c}$ is known as the Ostwald dilution law, according to which the degree of dissociation increases as c decreases. As α is increased, the concentration of the ion A^+ and B^- are also increased. Thus, the increase of conductance for a weak electrolyte is primarily due to the increase in the number of ions on dilution.

Debye-Huckel-Onsager Theory Ionic Atmosphere for strong electrolytes

The conductance data of many substances did not conform to Ostwald dilution law. These substances are strong electrolytes which are known to be completely ionized in solution. The variation of molar conductivity of a dilute solution of a strong electrolyte on dilution is explained in the basis of Debye-Huckel-Onsager theory. According to this theory, each ion in solution is surrounded by an ionic atmosphere consisting of other ions whose net average charge is opposite to that of the central ion. This ionic atmosphere is spherical and symmetrical in nature in the absence of any disturbing factor such as the application of potential across the two electrodes immersed in the solution during the conductance measurements. However, when the potential is applied, the ions start moving towards the respective electrodes and as a result the ionic atmosphere is distorted which results in a decrease in speed of the ions. Debye and Huckel showed that these effects are due to two factors, namely, (a) relation of ionic atmosphere due to an applied potential or symmetry effect and (b) the electrophoretic effect.

Asymmetry Effect

This arises from the fact that any central ion and its atmosphere are oppositely charged, i.e., when the central ion is positively charged, the atmosphere is negative, and vice versa. Because of this, the central ion and the atmosphere tend to move in opposite directions as the potential is applied across the electrodes. Thus, a central positive ion will tend to move towards the cathode while its ionic atmosphere will tend towards the anode. This results in the distortion of spherical and symmetrical nature of the ionic atmosphere as shown in figure. Consequently, the force exerted by the atmosphere on the central ion is no longer uniform in all directions : it is greater behind the ion than in front of it. Thus, the central ion experiences a retarding force opposite to the direction of its motion with the result that its speed is lowered.



Electrophoretic Effect

Ions in solution are generally solvated and when these move, they carry with them the associated solvent molecules. Since cations and anions move in the opposite directions, it is obvious that any particular ion, say the central ion, does not move through a stationary medium but through a medium in which solvent molecules carried by the ions of the atmosphere move in the opposite direction. Similarly, the ion involved in the ionic atmosphere move in a medium of opposite moving solvent molecules carried by the central ion. Thus, both type of ions, while moving in solution do not travel through a stationary medium but through a medium which moves in the opposite direction. These counter-currents make it more difficult for the ion to move through the solution and thus slow down its motion. This is known as the electrophoretic effect.

Onsager expression for strong electrolytes

$$\Lambda_m = \Lambda_m^\infty - (A\Lambda_m^\infty + B)c^{1/2}$$

The first term $A\Lambda_m^\infty\sqrt{c}$ is the decrease in molar conductivity due to the asymmetric effect.

The second term $B\sqrt{c}$ is the decrease in molar conductivity due to the electrophoretic effect.

Kohlrausch's Law of Independent Migration of Ions

At very low concentrations, the molar conductivity of a strong electrolyte tends to reach a limiting value.

This value of molar conductivity is called the molar conductivity at infinite dilution (Λ_m^∞). At such high dilutions, the interionic attractions become negligible and each ion migrates independent of the other ions. These observations were used by Kohlrausch to postulate a famous law called Kohlrausch's law of independent ion migration. The Kohlrausch's law in terms of molar conductivity is stated as follows: "At infinite dilution, the molar conductivity of an electrolyte can be expressed as the sum of contributions from its individual ions."

$$\Lambda_m^\infty = \nu_+\lambda_+^\infty + \nu_-\lambda_-^\infty$$

where ν_+ and ν_- are the number of cations and anions per formula unit of electrolyte respectively and λ_+^∞ and λ_-^∞ are the molar conductivities of the cation and anion at infinite dilution respectively.

Application of Kohlrausch's Law**(i) Determination of λ_m^0 of a weak electrolyte**

In order to calculate Λ_m^0 of a weak electrolyte say CH_3COOH , we determine experimentally Λ_m^0 values of the following three strong electrolysis:

- A strong electrolyte containing same cation as in the last electrolyte, say HCl
- A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa
- A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl

of CH_3COOH is the given as

$$(\text{CH}_3\text{COOH}) = (\text{HCl}) + (\text{CH}_3\text{COONa}) - (\text{NaCl})$$

Proof:

$$(\text{HCl}) = \dots \text{I}$$

$$(\text{CH}_3\text{COONa}) = \dots \text{II}$$

$$(\text{NaCl}) = \dots \text{III}$$

Adding equation (I) and equation (II) and subtracting (III) from them

$$\Lambda_{(\text{HCl})}^0 + \Lambda_{(\text{CH}_3\text{COONa})}^0 - \Lambda_{(\text{NaCl})}^0 = \lambda_{\text{H}^+}^0 + \lambda_{(\text{CH}_3\text{COO}^-)}^0 = \Lambda_{0(\text{CH}_3\text{COOH})}$$

(ii) **Determination of degree of dissociation (α)**

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$$

(iii) **Determination of solubility of sparingly soluble salt**

$$S = \frac{K \times 1000}{\Lambda_m^0}$$

S is solubility of sparingly soluble salt.

(iv) **Determination of ionic product of water**

$$[\text{H}^+] = [\text{OH}^-] = \frac{K \times 1000}{\Lambda_m^0} \quad K_w = [\text{H}^+]^2 \quad K_w = \text{ionic product of water}$$

TRANSPORT NUMBER

According to Faraday's first law of electrolysis, the number of ions discharged at an electrode is proportional to the total quantity passed through the solution, hence it follows that

Total quantity of electricity that passes through the solution } $\propto$ sum of the mobilities of the ions

The quantity of electricity carried by particular ions } $\propto$ the mobilities of that particular ion

The fraction of the total current carried by each ion is called **transport number**. Thus, if u_+ is the mobility of cation and u_- that of the anion, then

$$\text{Transport number of the cation, } t_+ = \frac{\text{Current carried by the cation}}{\text{Total current}} = \frac{u_+}{u_+ + u_-}$$

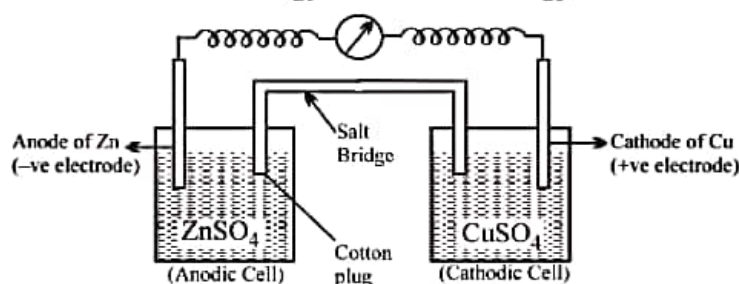
Similarly, transport number of the anion, $t_- = u_- / (u_+ + u_-)$

Further, since $t_+ + t_- = 1$, it follows that if the transport number of one of the ions is known, that of the other can be easily calculated.

$$u_+ = \frac{\lambda_+}{z_+ F}$$

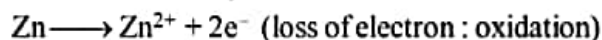
GALVANIC CELL

This cell converts chemical energy into electrical energy.



Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as *voltaic cell*. It may be represented as shown in Fig. Zinc rod immersed in ZnSO_4 behaves as anode and copper rod immersed in CuSO_4 behaves as cathode.

Oxidation takes place at anode:



Reduction takes place at cathode:



Over all process:



In galvanic cell like Daniell cell; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and become deposited at cathode.

SALT BRIDGE

Two electrolyte solutions in galvanic cells are separated using salt bridge as represented in the Fig. salt bridge is a device to minimize or eliminate the liquid junction potential. Saturated solution of salt like KCl, KNO_3 , NH_4Cl and NH_4NO_3 etc. in agar-agar gel is used in salt bridge. Salt bridge contains high concentration of ions viz. K^+ and NO_3^- at the junction with electrolyte solution. Thus, salt bridge carries whole of the current across the boundary; more over the K^+ and NO_3^- ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions minimize the liquid junction potential & completes the electrical circuit & permits the ions to migrate.

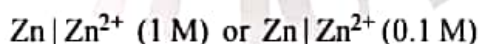
REPRESENTATION OF AN ELECTROCHEMICAL CELL (GALVANIC CELL)

The following universally accepted conventions are followed in representing an electrochemical cell:

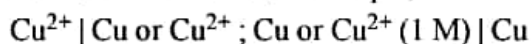
- (i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.
- (ii) A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example $\text{Zn} | \text{Zn}^{2+}$ or $\text{Zn} ; \text{Zn}^{2+}$

The molar concentration or activity of the solution is written in brackets after the formula of the ion.

For example



- (iii) The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,



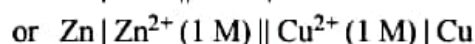
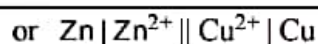
- (iv) The salts bridge which separates the two half-cells is indicated by two parallel vertical lines.
- (v) Sometimes negative and positive signs are also put on the electrodes.

The Daniel cell can be represented as :



Anode Salt bridge Cathode

Oxidation half-cell Reduction half-cell



ELECTROCHEMICAL SERIES

By measuring the potentials of various electrodes versus standard hydrogen electrode (SHE), a series of standard electrode potentials has been established. When the electrodes metals and non-metals) in contact with their ions are arranged on the basis of the values of their standard reduction potential or standard oxidation potential, the resulting series is called the electrochemical or electromotive or active series of the elements

Standard Aqueous Electrode Potentials at 25°C

'The Electrochemical Series'

Element	Electrode Reaction	Standard Electrode Reduction Potential E° , volt
Li	$\text{Li}^+ + e^- = \text{Li}$	-3.05
K	$\text{K}^+ + e^- = \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2e^- = \text{Ca}$	-2.87
Na	$\text{Na}^+ + e^- = \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2e^- = \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3e^- = \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2e^- = \text{Zn}$	-0.7628
Cr	$\text{Cr}^{3+} + 3e^- = \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2e^- = \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2e^- = \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2e^- = \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2e^- = \text{Sn}$	-0.14
H_2	$2\text{H}^+ + 2e^- = \text{H}_2$	0.00
Cu	$\text{Cu}^{2+} + 2e^- = \text{Cu}$	0.337
I_2	$\text{I}_2 + 2e^- = 2\text{I}^-$	0.535
Ag	$\text{Ag}^+ + e^- = \text{Ag}$	0.799
Hg	$\text{Hg}^{2+} + 2e^- = \text{Hg}$	0.885
Br_2	$\text{Br}_2 + 2e^- = 2\text{Br}^-$	1.08
Cl_2	$\text{Cl}_2 + 2e^- = 2\text{Cl}^-$	1.36
Au	$\text{Au}^{3+} + 3e^- = \text{Au}$	1.50
F_2	$\text{F}_2 + 2e^- = 2\text{F}^-$	2.87

Increasing tendency to accept electrons
Increasing strength as oxidising agent

Increasing strength as reducing agent
Increasing tendency to lose electron

APPLICATION OF ELECTROCHEMICAL SERIES

- (i) **Reactivity of metals :** The activity of the metal depends on its tendency to lose electron or electrons, i.e., tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electrons and is converted into cation. Such a metal is said to be chemically active.

The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

- (a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substance which accept electrons.
- (b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.
- (c) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

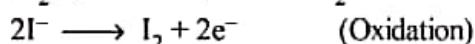
- (ii) **Electropositive character of metals :** the electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups :

- (a) **Strongly electropositive metals :** Metals having standard reduction potential near about 2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.
- (b) **Moderately electropositive metals.** Metals having values of reduction potential between 0.0 and about -2.0 volt are moderately electropositive. Al, Zn, Fe, Ni, Co, etc., belong to this group.
- (c) **Weakly electropositive metals :** The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. Cu, Hg, Ag, etc., belong to this group.

- (iii) **Displacement reactions :**

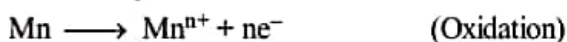
- (a) **To predict whether a given metal will displace another, from its salt solution :** A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., the metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

- (b) **Displacement of one non-metals from its salt solution by another non metal :** A nonmetal higher in the series (towards bottom side), i.e., having high value of reduction potential will displace another non metal with lower reduction potential i.e., occupying position above in the series. The nonmetal's which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the nonmetal having low value of reduction potential. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.



[The activity or electronegative character or oxidising nature of the nonmetal increases as the value of reduction potential increases.]

- (c) **Displacement of hydrogen from dilute acids by metals :** The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.



The metal having negative values of reduction potential possess the property of losing electron or electrons.

Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.

The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

- (d) **Displacement of hydrogen from water :** Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series.

Alkali and alkaline earth metals liberate hydrogen from cold water but Mg, Zn and Fe liberate hydrogen from hot water or steam.

- (iv) **Reducing power of metals :** Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. Thus, reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases as the standard reduction potential becomes more and more negative.

Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron.

Element	Na	Zn	Fe
Reduction	-2.71	-0.78	-0.44

→

Reducing nature decreases

Alkali and alkaline earth metals are strong reducing decreases.

- (v) **Oxidising nature of nonmetals :** Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. Thus, oxidising nature increases from top to bottom in the electrochemical series. The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

F_2 (Fluorine) is a stronger oxidant than Cl_2 , Br_2 and I_2 .

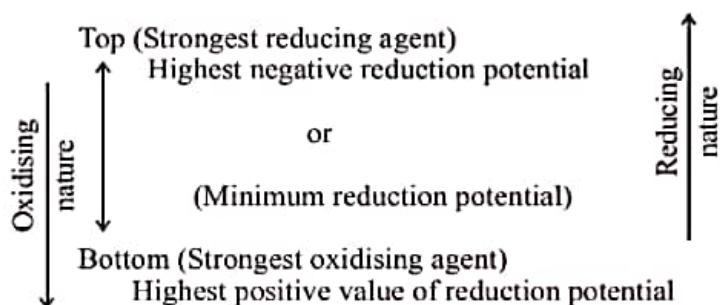
Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2 .

Element	I_2	Br_2	Cl_2	F_2
Reduction potential	+0.53	+1.06	+1.36	+2.85

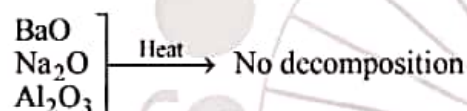
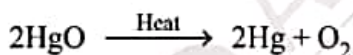
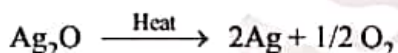
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Oxidising nature increases

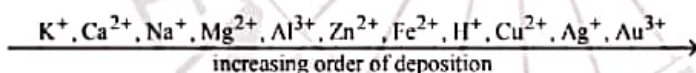
Thus, in electrochemical series



- (vi) **Thermal stability of metallic oxides :** The thermal stability of the metal oxide depends on its electropositive nature. As the electropositivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction potential are not stable towards heat. The metals which come below copper form unstable oxides, i.e. these are decomposed on heating.

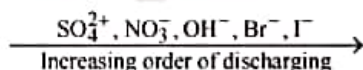


- (vii) **Product of electrolysis :** In case two or more type of positive and negative ions are present in solution, during electrolysis certain ions are discharged or liberated at the electrode in preference to others. In general, in such competition the ions which is stronger oxidising agent (high value of standard reduction potential) is discharged first at the cathode. The increasing order of deposition of few cations is :



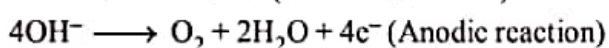
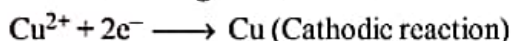
Similarly, the anion which is stronger reducing agent (low value of standard reduction potential) is liberated first at the anode.

The increasing order of discharge of few anion is :



Thus, when an aqueous solution of NaCl containing Na^+ , Cl^- , H^+ and OH^- ions is electrolysed, H^+ ions are discharged at cathode and Cl^- ions at the anode, i.e., H_2 is liberated at cathode and chlorine at anode.

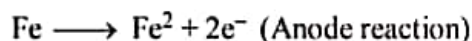
When an aqueous solution of CuSO_4 containing Cu^{2+} , SO_4^{2-} , H^+ and OH^- ions is electrolysed, Cu^{2+} ions are discharged at cathode and OH^- ions at the anode.



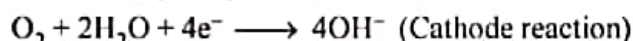
Cu is deposited on cathode while O_2 is liberated at anode.

- (viii) **Corrosion of metals :** Corrosion is defined as the deterioration of a substance because of its reaction with its environment. This is also defined as the process by which metals have the tendency to go back to their combined state, *i.e.*, reverse of extraction of metals.

Ordinary corrosion is a redox reaction by which metals are oxidised by oxygen in presence of moisture. Oxidation of metals occurs more readily at points of strain. Thus, a steel nail first corrodes at the tip and head. The end of a steel nail acts as an anode where iron is oxidised to Fe^{2+} ions.



The electrons flow along the nail to areas containing impurities which act as cathodes where oxygen is reduced to hydroxyl ions.



REVERSIBLE AND IRREVERSIBLE CELLS

In dealing with the energy relations of cells, thermodynamic principles find extensive applications. However, the use of these principles is subject to one important restriction, namely, that the system to which they are applied be reversible in thermodynamic sense. This requires that :

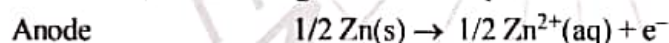
- (1) the driving and opposing forces be infinitesimally different from each other, and
- (2) it should be possible to reverse any change taking place by applying a force infinitesimally greater than the acting one.

A cell satisfying the above two requirements constitutes a reversible cell. The potential difference of the cell can be substituted into the relevant thermodynamic relations and hence the value of thermodynamic properties such as free energy change, entropy change and enthalpy change of the cell reaction can be determined. When the above conditions are not satisfied, the cell is said to be irreversible, and thermodynamic relations do not apply.

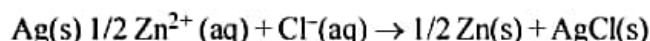
The difference between reversible and irreversible cells may be illustrated with the following two examples.

An example of Reversible Cell

Consider a cell composed of Zn and Ag-AgCl electrodes into an aqueous solution of zinc chloride. As seen earlier, the following reactions take place on connecting externally.



The above process continues as long as the external opposing potential is infinitesimally smaller than that of the cell. However, if the opposing potential becomes slightly larger than that of the cell, the direction of current flow is reversed, and so is the cell reaction. Now zinc ions are converted to zinc at one electrode, silver chloride is formed from silver and chloride ions at the other, and the overall cell reaction becomes



Thus, it is obvious that the second condition of irreversibility mentioned above is satisfied. The first condition can be satisfied by drawing from or passing through the cell a very minute current. Hence, the cell is reversible.

STANDARD ELECTRODE POTENTIAL

The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25°C (298 K) is called standard electrode potential.

Standard reduction potential = $-(\text{Standard oxidation potential})$
 or Standard oxidation potential = $-(\text{Standard reduction potential})$

CONCEPT OF ELECTROMOTIVE FORCE (EMF) OF A CELL

Electron flows from anode to cathode in external circuit due to a pushing effect called electromotive force (e.m.f.). E.m.f. is some times called as *cell potential*. Unit of e.m.f. of cell is volt.

EMF of cell may be calculated as :

$E_{\text{cell}} = \text{reduction potential of cathode} - \text{Reduction potential of anode}$

Similarly, standard e.m.f. of the cell (E°) may be calculated as

$E^\circ_{\text{cell}} = \text{Standard reduction potential of cathode} - \text{Standard reduction potential of anode}$

SIGN CONVENTION OF EMF

EMF of cell should be positive other wise it will not be feasible in the given direction .

$\text{Zn} | \text{ZnSO}_4 || \text{CuSO}_4 | \text{Cu} \quad E = +1.10 \text{ volt (Feasible)}$

$\text{Cu} | \text{CuSO}_4 || \text{ZnSO}_4 | \text{Zn} \quad E = -1.10 \text{ volt (Not Feasible)}$

Nernst Equation

- For a single electrode involving the reduction process, $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}$, the nernst equation is

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[\text{M}]}{[\text{M}^{n+}]} \quad \text{or} \quad E = E^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[\text{M}]}{[\text{M}^{n+}]}$$

$$\text{or} \quad E = E^\circ - \frac{0.059}{n} \log \frac{[\text{M}]}{[\text{M}^{n+}]}$$

- For an electrochemical cell having net reaction :

$x\text{A} + y\text{B} \xrightarrow{n\text{e}^-} \text{IC} + m\text{D}$, the EMF can be calculated as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{C}]^l [\text{D}]^m}{[\text{A}]^x [\text{B}]^y}$$

- In using the above equation, the following facts should be kept in mind.
 - Concentration or activity of solids is taken to be UNITY.
 - Concentration of activity of gases is expressed in terms of their partially pressures.
 - n , the number of electrons transferred should be calculated from the balanced net reaction.

Note :

- Relationship between free energy change and cell potential can be written as

$$\Delta G = -nF E_{\text{cell}}$$

For standard state condition

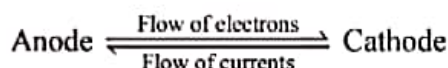
$$\Delta G^\circ = -nF E^\circ_{\text{cell}}$$

- Equilibrium constant of net cell reaction is related to the standard EMF as

$$E^\circ_{\text{cell}} = \frac{0.059}{n} \log K.$$

EMF OF GALVANIC CELL

Every galvanic or voltaic cell is made up of two half-cells, the oxidation half-cell (anode) and the reduction half-cell (cathode). The potential of these half-cells are always different. On account of this difference in electrode potentials, the electric current moves from the electrode at higher potential to the electrode at lower potential, *i.e.* from cathode to anode. The direction of the flow of electrons is from anode to cathode.



The difference in potential of the two half-cells is known as the electromotive force (emf) of the cell or cell potential.

PREDICTION AND FEASIBILITY OF SPONTANEITY OF A CELL REACTION

Work done by the cell = nFE ;

It is equivalent to decrease in free energy

$$\Delta G = -nFE$$

Under standard state

$$\Delta G^0 = -nFE^0 \quad (i)$$

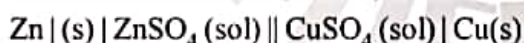
- (i) From thermodynamics we know, ΔG = negative for spontaneous process. Thus from eq.(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.
- (ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.
- (iii) When $G = 0$, $E = 0$ and the cell will attain the equilibrium.

Reactions	ΔG	E
Spontaneous	(-)	(+)
Non- spontaneous	(+)	(-)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data.

Substituting the value of E^0 (*i.e.*, standard reduction potential of cathode- standard reduction potential of anode) in eq. (i) we may get ΔG^0 .

Let us see whether the cell (Daniell) is feasible or not; *i.e.* whether Zinc will displace copper or not.



$$E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ volt} ; E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34 \text{ volt}$$

$$E_{\text{cell}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

$$= 0.34 - (-0.76) = +1.10 \text{ volt}$$

Since $E^0 = +ve$, hence the cell will be feasible and zinc will displace copper from its salt solution. In other words zinc will reduce copper.

THERMODYNAMIC TREATMENT OF NERNST EQUATION

Determination of equilibrium constant : We know, that

$$E = E^0 - \frac{0.0591}{n} \log Q \quad \dots (i)$$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0$

$\therefore$ From Eq. (i), we have

$$0 = E^0 - \frac{0.0591}{n} \log K_{eq} \quad \text{or} \quad K_{eq} = \text{anti log} \left[\frac{nE^0}{0.0591} \right]$$

Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E , then

$$-\Delta G = nFE \quad (i)$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad (ii)$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[\frac{\partial (-nFE)}{\partial T} \right]_p = \Delta H - nFT \left[\frac{\partial E}{\partial T} \right]_p$$

$$\therefore \Delta H = -nFE + nFT \left[\frac{\partial E}{\partial T} \right]_p$$

Entropy change inside the cell : We know that $G = H - TS$ or $\Delta G = \Delta H - T\Delta S$... (i)

where ΔG = Free energy change ; ΔH = Enthalpy change and ΔS = entropy change.

According to Gibbs Helmholtz equation,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \dots (ii)$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T \left[\frac{\partial \Delta G}{\partial T} \right]_p \quad \text{or} \quad \Delta S = - \left[\frac{\partial \Delta G}{\partial T} \right]_p$$

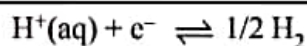
$$\text{or} \quad \Delta S = nF \left[\frac{\partial E}{\partial T} \right]_p$$

where $\left[\frac{\partial E}{\partial T} \right]_p$ is called temperature coefficient of cell e.m.f.

DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL

Gas-Ion Half Cell

In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this half cell, purified H_2 gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.



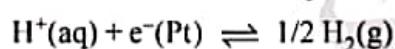
$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^0 - \frac{0.0591}{1} \log \frac{(\text{pH}_2)^{1/2}}{[\text{H}^+]}$$

Hydrogen gas Hydrogen ion Half cell

One of the most important gas-ion half-cell is the hydrogen gas-hydrogen ion half-cell (also commonly known as hydrogen electrode). In this half-cell, purified hydrogen gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.

Expression of Reduction Potential (Nernst Equation)

The expression of $E_{\text{half-cell}}$ can be derived by considering the reversible reduction reaction that occurs at the electrode. For the present case, we have



$$E_{\text{H}^+/\text{H}_2|\text{Pt}} = E_{\text{H}^+/\text{H}_2|\text{Pt}}^0 - \frac{RT}{F} \ln \frac{(f_{\text{H}_2(\text{g})}/f^\circ)^{1/2}}{a_{\text{H}^+}}$$

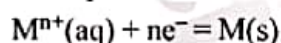
Equation of the above type is known as the *Nernst equation*.

METAL-METAL ION HALF-CELL

Metal-metal ion half-cell consists of a bar of metal M in contact with a solution containing M^{n+} ions. Examples include zinc-zinc ion, copper-cupric ion, silver-silver ion and gold-auric ion half-cells.

Expression of Reduction Potential

The equilibrium reaction at the electrode is



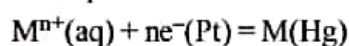
$$E_{\text{M}^{n+}|\text{M}} = E_{\text{M}^{n+}|\text{M}}^0 - \frac{RT}{nF} \ln \frac{1}{a_{\text{M}^{n+}}}$$

METAL AMALGAM-METAL ION HALF CELL

In this electrode, metal amalgam is placed in contact with a solution containing metal ion. Electrical contact is made by a platinum wire dipping into the amalgam pool.

Expression of Reduction Potential

The equilibrium reaction at the electrode is



$$\begin{aligned} E_{\text{M}^{n+}|\text{M}(\text{Hg})|\text{Pt}} &= E_{\text{M}^{n+}|\text{M}|\text{Pt}}^0 - \frac{RT}{nF} \ln a_{\text{M}(\text{Hg})} - \frac{RT}{nF} \ln \frac{1}{a_{\text{M}^{n+}}} \\ &= E_{\text{M}^{n+}|\text{M}(\text{Hg})|\text{Pt}}^0 - \frac{RT}{nF} \ln \frac{1}{a_{\text{M}^{n+}}} \end{aligned}$$

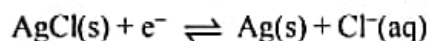
where $E_{M^{n+}|M(Hg)|Pt}^{\circ}$ is the standard potential of the given metal amalgam. Its value may be determined by using a solution of known activity of M^{n+} .

METAL-INSOLUBLE SALT-ANION HALF-CELL

In this half-cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. Three such half-cell are described below.

Silver-Silver chloride chloride half-cell

This half cell is represented as $Cl^{-}|AgCl|Ag$. The equilibrium reaction that occurs at the electrode is

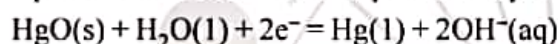


Expression of Reduction Potential

$$E_{Cl^{-}|AgCl|Ag}^{\circ} = E_{Cl^{-}|AgCl|Ag}^{\circ} - \frac{RT}{F} \ln a_{Cl^{-}}$$

Mercury-mercuric oxide-hydroxide ion half-cell

In this half-cell, a pool mercury is covered with a paste of solid HgO and a solution of a base. This equilibrium reaction that takes place at the platinum electrode is

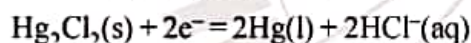


Expression of Reduction Potential

$$E_{OH^{-}|HgO|Hg}^{\circ} = E_{OH^{-}|HgO|Hg}^{\circ} - \frac{RT}{F} \ln a_{OH^{-}}$$

Mercury-mercurous chloride-chloride ion half cell

This half-cell is known as calomel half-cell. The equilibrium reaction is



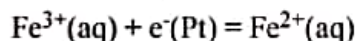
Its Nernst equation is

$$E_{Cl^{-}|Hg_2Cl_2|Hg}^{\circ} = E_{Cl^{-}|Hg_2Cl_2|Hg}^{\circ} - \frac{RT}{F} \ln a_{Cl^{-}}$$

OXIDATION REDUCTION HALF-CELL

An oxidation reduction half-cell has an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same elements in different states of oxidation.

Ferric-ferrous half-cell

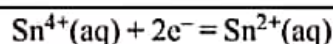


The Nernst equation is

$$E_{Fe^{3+}, Fe^{2+}|Pt} = E_{Fe^{3+}, Fe^{2+}|Pt}^{\circ} - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}$$

Stannic-Stannous Half-cell

Another example is stannic-stannous half-cell where the reduction reaction to be considered is



and the Nernst equation is

$$E_{\text{Sn}^{4+}, \text{Sn}^{2+}|\text{Pt}} = E_{\text{Sn}^{4+}, \text{Sn}^{2+}|\text{Pt}}^{\circ} - \frac{RT}{2F} \ln \frac{a_{\text{Sn}^{2+}}}{a_{\text{Sn}^{4+}}}$$

Reference half-cell

If E_L is arbitrarily assigned some value, then the value of E_R can be determined using the expression

$$E_R = E_{\text{cell}} + E_L$$

In the study of electrochemical cell, the *hydrogen-hydrogen ion half-cell* has been adopted as the reference half-cell and its standard potential has been assigned the value zero at all temperatures. By standard potential of hydrogen-hydrogen ion half-cell, we mean that the hydrogen ion and hydrogen gas involved in half-cell.

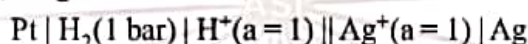


are present in their standard states of unit activity and unit fugacity (taken as 1 bar pressure), respectively.

$$\begin{aligned} E_R &= E_{\text{cell}} + 0 \\ &= E_{\text{cell}} \end{aligned}$$

Illustrations

To illustrate the procedure, we cite below two typical examples of silver-silver ion and zinc-zinc ion half-cells. If the silver-silver ion half-cell is coupled with the standard hydrogen-hydrogen ion half-cell (to be kept on left side), we get a cell



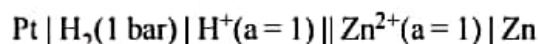
The emf of the cell is given by

$$E_{\text{cell}}^{\circ} = E_{\text{Ag}^+|\text{Ag}}^{\circ} - E_{\text{H}^+|\text{H}_2|\text{Pt}}^{\circ}$$

and its value as determined experimentally is found to be 0.799 V. Hence

$$\begin{aligned} E_{\text{Ag}^+|\text{Ag}}^{\circ} &= E_{\text{cell}}^{\circ} + E_{\text{H}^+|\text{H}_2|\text{Pt}}^{\circ} \\ &= E_{\text{cell}}^{\circ} = 0.799 \text{ V} \end{aligned}$$

Taking the example of zinc-zinc ion half-cell, we have



Its emf as determined experimentally is found to be -0.763 V. Hence

$$\begin{aligned} E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} &= E_{\text{cell}}^{\circ} + E_{\text{H}^+|\text{H}_2|\text{Pt}}^{\circ} \\ &= E_{\text{cell}}^{\circ} = -0.763 \end{aligned}$$

INFLUENCE OF IONIC ACTIVITY ON REDUCTION POTENTIAL

The reduction potential for the reaction



as given by the Nernst equation is

$$E_1 = E_{M^{n+}|M}^{\circ} - \frac{RT}{nF} \ln \left(\frac{1}{a_{M^{n+}}} \right)$$

It follows that the reduction potential $E_{M^{n+}|M}^{\circ}$ depends on the activity of M^{n+} ; it increases as the activity of M^{n+} is decreased to one-tenth of its original activity, then the reduction potential becomes

$$E_2 = E_{M^{n+}|M}^{\circ} - \frac{RT}{nF} \ln \left(\frac{1}{0.1 a_{M^{n+}}} \right)$$

The resulting change in potential is given by

$$\begin{aligned} E_2 - E_1 &= -\frac{RT}{nF} \ln \left(\frac{1}{0.1 a_{M^{n+}}} \right) + \frac{RT}{nF} \ln \left(\frac{1}{a_{M^{n+}}} \right) \\ &= -\frac{RT}{nF} \ln 10 = -\frac{2.303 RT}{nF} \end{aligned}$$

At 298 K, we have

$$E_2 - E_1 = -\frac{(0.0592 \text{ V})}{n}$$

Thus every ten-fold decrease in the activity of cation produces a decrease of $(0.0592/n)$ volt of the reduction potential, where n is the valence of the cation. For univalent cations n is 1, and hence reduction potential decreases by a factor of 0.0592 V. For bivalent cations n is 2, and hence reduction potential decreases by a factor of $(0.0592/2)$ V, i.e. 0.0296 V. The magnitude of reduction potential will change by the same factor $(= 0.0592/n \text{ volt})$ for every ten-fold change in the activity of cation. For a hundred-fold change in the activity; the change of potential will be $2 \times 0.0592/n$ volt and for a thousand-fold change in activity, the potential will change by a factor of $3 \times 0.0592/n$ volt.

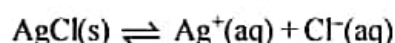
Relation between metal-metal ion half-cell and the corresponding metal-insoluble salt-anion half-cell

Consider a silver electrode dipped into a solution of silver nitrate. The potential of the electrode as given by the Nernst equation is

$$E_{Ag^+|Ag} = E_{Ag^+|Ag}^{\circ} - \frac{RT}{F} \ln \left(\frac{1}{a_{Ag^+}} \right) \quad \dots(i)$$

with $E_{Ag^+|Ag}^{\circ} = 0.799 \text{ V}$

If now NaCl is added, the following equilibrium will be established :



with its solubility product K_{sp} as

$$K_{sp} = (a_{Ag^+})(a_{Cl^-})$$

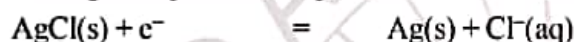
Multiplying and dividing the term within parantheses in eq. (i) by a_{Cl^-} , we get

$$E_{Ag^+/Ag} = E_{Ag^+/Ag}^{\circ} - \frac{RT}{F} \ln \left(\frac{a_{Cl^-}}{a_{Ag^+} a_{Cl^-}} \right)$$

$$E_{Ag^+/Ag}^{\circ} = E_{Ag^+/Ag}^{\circ} - \frac{RT}{F} \ln \left(\frac{a_{Cl^-}}{K_{sp}^{\circ}(AgCl)} \right)$$

$$\text{or } E_{Ag^+/Ag} = \left(E_{Ag^+/Ag}^{\circ} + \frac{RT}{F} \ln K_{sp}(AgCl) \right) - \frac{RT}{F} \ln a_{Cl^-}$$

Now the electrode can also be treated as $Ag | AgCl | Cl^-$ since part of $AgCl$ will deposit on solid Ag . Writing the equilibrium expression for this electrode, we have



The corresponding Nernst equation gives

$$E_{Cl^-|AgCl|Ag} = E_{Cl^-|AgCl|Ag}^{\circ} - \frac{RT}{F} \ln a_{Cl^-}$$

Above equation must be identical and hence on comparing these two equations, we get

$$E_{Cl^-|AgCl|Ag}^{\circ} = E_{Ag^+/Ag}^{\circ} + \frac{RT}{F} \ln K_{sp}(AgCl)$$

$$\text{or } E_{Cl^-|AgCl|Ag}^{\circ} = E_{Ag^+/Ag}^{\circ} - \frac{2.303 RT}{F} pK_{sp}(AgCl)$$

$$\text{where } pK_{sp}(AgCl) = -\log K_{sp}(AgCl)$$

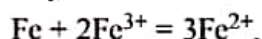
Cell reaction and its relation with cell potential

$$\Delta G = -nF(E_R - E_L) = -nFE_{\text{cell}}$$

we consider the various ways in which the following three half-cell reactions



may be combined to form a cell with the following overall cell reaction.

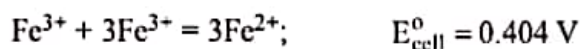


Combination of Equations

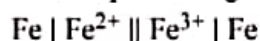




with the overall reaction



The cell producing this reaction would be



REFERENCE HALF CELLS

Common examples of reference half-cell

The most common type of reference half-cell has the following form :

saturated solution of sparingly soluble salt of metal + addition strongly ionized salt with a common anion | Metal

Examples include :

(1) Calomel half-cell : $\text{KCl(aq)} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}$

(2) Silver-silver chloride half-cell : $\text{KCl(aq)} | \text{AgCl(s)} | \text{Ag}$

(3) Mercury-mercurous sulphate half-cell : $\text{K}_2\text{SO}_4(\text{aq}) | \text{Hg}_2\text{SO}_4(\text{s}) | \text{Hg}$

Calomel half-cell

The half-cell reaction is



and the Nernst equation has the form

$$E_{\text{Cl}^-|\text{Hg}_2\text{Cl}_2|\text{Hg}} = E_{\text{Cl}^-|\text{Hg}_2\text{Cl}_2|\text{Hg}}^{\circ} - \frac{RT}{F} \ln (a_{\text{Cl}^-})$$

with $E_{\text{Cl}^-|\text{Hg}_2\text{Cl}_2|\text{Hg}}^{\circ} = 0.2676 \text{ V}$

Thus, the calomel half-cell functions as the reversible chloride electrode.

Silver-Silver chloride Half-cell

The half-cell reaction is



Hence the half cell potential is given by

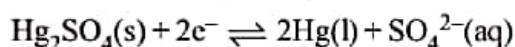
$$E_{\text{Cl}^-|\text{AgCl}|\text{Ag}} = E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^{\circ} - \frac{RT}{F} \ln (a_{\text{Cl}^-})$$

with $E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^{\circ} = 0.222 \text{ V}$

This half-cell cannot be used in a solution which contains HNO_3 , I^- and CN^- ions.

Mercury-Mercurous sulphate half-cell

The half-cell set up is very similar to that of calomel half-cell. the cell-reaction is



Hence the half-cell potential is given by

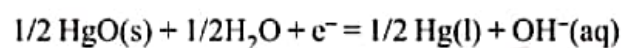
$$E_{\text{SO}_4^{2-}|\text{Hg}_2\text{SO}_4|\text{Hg}} = E_{\text{SO}_4^{2-}|\text{Hg}_2\text{SO}_4|\text{Hg}}^0 - \frac{RT}{2F} \ln (a_{\text{SO}_4^{2-}})$$

with $E_{\text{SO}_4^{2-}|\text{Hg}_2\text{SO}_4|\text{Hg}}^0 = 0.6151 \text{ V}$

This half-cell potential depends upon the activity of SO_4^{2-} ions.

Mercury-mercuric oxide half-cell

The half-cell reaction is



and thus the Nernst equation has the form

$$E_{\text{OH}^+|\text{HgO}|\text{Hg}} = E_{\text{OH}^+|\text{HgO}|\text{Hg}}^0 - \frac{RT}{F} \ln (a_{\text{OH}^-})$$

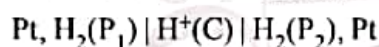
CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

(i) Electrode concentration cell

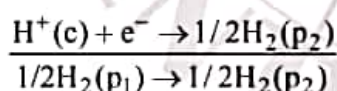
(ii) Electrolyte concentration cell

Electrode Gas concentration cell :



Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell process : $1/2 \text{ H}_2(\text{p}_1) \rightarrow \text{H}^+(\text{c}) + e^-$ (Anode process)

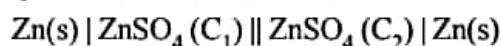


$$\therefore E = -\frac{2.303RT}{F} \log \left[\frac{\text{p}_2}{\text{p}_1} \right]^{1/2}$$

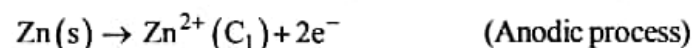
$$\text{or } E = -\left[\frac{2.303 RT}{2F} \right] \log \left[\frac{\text{p}_2}{\text{p}_1} \right], \text{ At } 25^\circ\text{C}, E = \frac{0.059}{2F} \log \left[\frac{\text{p}_1}{\text{p}_2} \right]$$

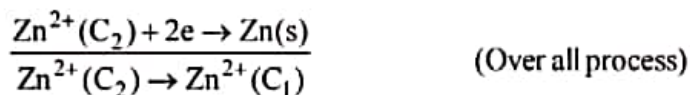
For spontaneity of such cell reaction, $\text{p}_1 > \text{p}_2$

Electrolyte concentration cells:



In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,





∴ From Nernst equation, we have

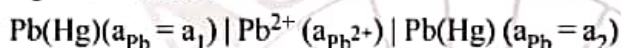
$$E = 0 - \frac{2.303RT}{2F} \log \left[\frac{\text{C}_1}{\text{C}_2} \right] \quad \text{or} \quad E = \frac{2.303RT}{2F} \log \left[\frac{\text{C}_2}{\text{C}_1} \right]$$

For spontaneity of such cell reaction, $\text{C}_2 > \text{C}_1$

CONCENTRATION CELLS WITHOUT LIQUID JUNCTION POTENTIAL

Concentration cells are made up of two half-cells which are similar chemically but differ in the activity of some common component. The common component may be the electrode or the electrolytic solution. The emf of the cell is due to the difference of activity of the common component. We describe below three categories of concentration cells without liquid junction.

Cells with Amalgam Electrodes

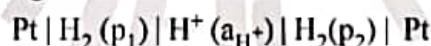


Electrode	Reduction reaction	Reduction Potential
Right	$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb(Hg)}(a_2)$	$E_R = E^\circ - \frac{RT}{2F} \ln \frac{a_2}{a_{\text{Pb}^{2+}}} \quad \dots(\text{i})$
Left	$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb(Hg)}(a_1)$	$E_L = E^\circ - \frac{RT}{2F} \ln \frac{a_1}{a_{\text{Pb}^{2+}}} \quad \dots(\text{ii})$

Subtracting Eq. (ii) from eq. (i), we get

$$\begin{array}{l} \text{Pb(Hg)}(a_1) = \text{Pb(Hg)}(a_2) \\ \text{and } E_{\text{cell}} = \frac{RT}{2F} \ln \frac{a_1}{a_2} \end{array}$$

Cells with gas electrodes operating at different Pressures



We have

Electrode	Reduction reaction	Reduction potential
Right	$2\text{H}^+ + 2\text{e}^- = \text{H}_2(p_2)$	$E_R = -\frac{RT}{2F} \ln \frac{(p_2/p^\circ)}{a_{\text{H}^+}^2} \quad \dots(\text{i})$
Left	$2\text{H}^+ + 2\text{e}^- = \text{H}_2(p_1)$	$E_L = -\frac{RT}{2F} \ln \frac{(p_1/p^\circ)}{a_{\text{H}^+}^2} \quad \dots(\text{ii})$

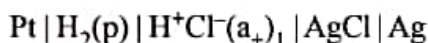
Subtracting Eq. (ii) from eq. (i), we get

$$H_2(p_1) = H_2(p_2)$$

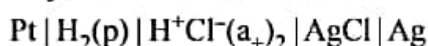
and $E_{\text{cell}} = \frac{RT}{2F} \ln \frac{p_1}{p_2}$

Cells with different Electrolytic Activities

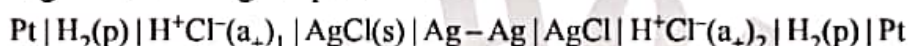
This type of cells can be formed by making a composite cell out of two cells differing only in the activity of the electrolytic solution. For example, the cell



may be combined with a cell



to give the following composite cell.



$$E_{\text{cell}} = E_L + E_R$$

$$= (E_{Cl^- | AgCl | Ag} - E_{H^+ | H_2 | Pt})_L + (E_{H^+ | H_2 | Pt} - E_{Cl^- | AgCl | Ag})_R$$

Writing the Nernst equation for each potential, we obtain

$$E_{\text{cell}} = \left[E_{Cl^- | AgCl | Ag}^{\circ} - \frac{RT}{F} \ln (a_{Cl^-})_1 + \frac{RT}{F} \ln \frac{(p/p^{\circ})^{1/2}}{(a_{H^+})_1} \right]$$

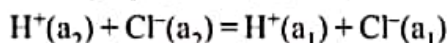
$$+ \left[-\frac{RT}{F} \ln \frac{(p/p^{\circ})^{1/2}}{(a_{H^+})_2} - E_{Cl^- | AgCl | Ag}^{\circ} + \frac{RT}{F} \ln (a_{Cl^-})_2 \right]$$

or $E_{\text{cell}} = \frac{RT}{F} \ln \frac{(a_{H^+})_2 (a_{Cl^-})_2}{(a_{H^+})_1 (a_{Cl^-})_1} = \frac{2RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$

The net cell reaction is obtained by adding the individual cell reactions. Thus, we have

Cell	Cell reaction
Right	$AgCl + 1/2 H_2 = Ag + H^+(a_1) + Cl^-(a_1) \dots (i)$
Left	$Ag + H^+(a_2) + Cl^-(a_2) = AgCl + 1/2 H_2 \dots (ii)$

Adding eqs. (i) and (ii), we get



Note that the emf of the cell may be derived directly from the cell reaction.

If one faraday of electricity is withdrawn from the cell, the net result that is produced is the transfer of 1 mol of each of hydrogen and chloride ions from the right-side cell to the left-side cell. A cell of this type is called a *concentration cell without transference*. The operation of cell is not accompanied by the direct transfer of electrolyte from one solution to the other.

CONCENTRATION CELL WITH LIQUID JUNCTION POTENTIAL

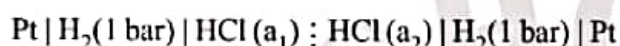
Development of Liquid Junction Potential

In a cell if two electrolytic solutions of different concentration are in contact with each other, a potential difference develops across the boundary of the two solutions. This potential difference is called the *liquid junction potential* or the *diffusion potential*. It arises because of the difference in the rates of diffusion of positive and negative ions from more concentrated solution to less concentrated solution. The rate of diffusion of an ion is determined by its transference number. To illustrate how the liquid junction potential arises.

CELL IN WHICH ELECTRODES ARE REVERSIBLE WITH RESPECT TO CATION

A Typical Example

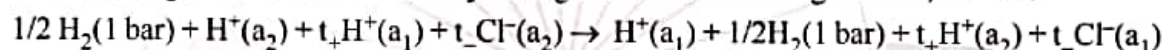
Consider the cell



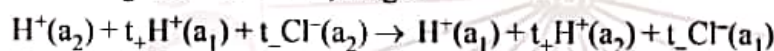
Working of the cell

- (i) Electrode reaction at anode $\frac{1}{2} \text{H}_2(1 \text{ bar}) \rightarrow \text{H}^+(a_1) + e^-$
- (ii) Electrode reaction at cathode $\text{H}^+(a_2) + e^- \rightarrow \frac{1}{2} \text{H}_2(1 \text{ bar})$
- (iii) Transfer of t_+ mole of H^+ from left to right $t_+ \text{H}^+(a_1) \rightarrow t_+ \text{H}^+(a_2)$
- (iv) Transfer of t_- mole of Cl^- from right to left $t_- \text{Cl}^-(a_2) \rightarrow t_- \text{Cl}^-(a_1)$

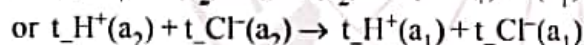
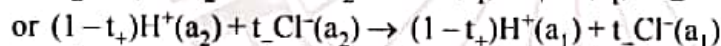
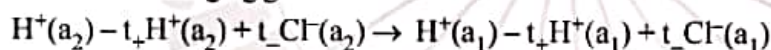
The net change in the cell is obtained by adding the above four changes. Thus, we have



Cancelling the common term, we get



which on rearranging gives



Thus, the net cell reaction is to transfer t_- mole of HCl from the solution of activity a_2 to that of activity a_1 .

Free-energy of cell Reaction

The total free energy change of the net cell reaction is

$$= t_- RT \ln \left\{ \frac{(a_1)_{\text{H}^+} (a_1)_{\text{Cl}^-}}{(a_2)_{\text{H}^+} (a_2)_{\text{Cl}^-}} \right\}$$

$$= 2t_- RT \ln \frac{(a_{\pm})_{\text{HCl}}}{(a_{\pm})_{\text{HCl}}}$$

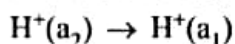
$$E_{\text{cell(wlj)}} = -2t_- \frac{RT}{F} \ln \frac{(a_{\pm})_{\text{HCl}}}{(a_{\pm})_{\text{HCl}}}$$

Cell without liquid Junction Potential

Electrode reaction at anode $1/2 \text{H}_2(1 \text{ bar}) \rightarrow \text{H}^+(\text{a}_1) + \text{e}^-$

Electrode reaction at cathode $\text{H}^+(\text{a}_2) + \text{e}^- \rightarrow 1/2 \text{H}_2(1 \text{ bar})$

The net cell reaction is



and the cell potential is

$$E_{\text{cell(wlj)}} = -\frac{RT}{F} \ln \frac{(\text{a}_1)_{\text{H}^+}}{(\text{a}_2)_{\text{H}^+}} = -\frac{RT}{F} \ln \frac{(\text{a}_{\pm 1})_{\text{HCl}}}{(\text{a}_{\pm 2})_{\text{HCl}}}$$

where a_{H^+} has been replaced by the mean ionic activity $\text{a}_{\pm}$.

Expression of liquid junction potential

$$\begin{aligned} E_{\text{lj}} &= E_{\text{cell(wlj)}} - E_{\text{cell(wolj)}} \\ &= -2t_- \frac{RT}{F} \ln \frac{(\text{a}_{\pm 1})_{\text{HCl}}}{(\text{a}_{\pm 2})_{\text{HCl}}} + \frac{RT}{F} \ln \frac{(\text{a}_{\pm 1})_{\text{HCl}}}{(\text{a}_{\pm 2})_{\text{HCl}}} \\ &= (1 - 2t_-) \frac{RT}{F} \ln \frac{(\text{a}_{\pm 1})_{\text{HCl}}}{(\text{a}_{\pm 2})_{\text{HCl}}} \end{aligned}$$

Since $t_+ + t_- = 1$, equation above may be written as

$$E_{\text{lj}} = (t_+ - t_-) \frac{RT}{F} \ln \frac{(\text{a}_{\pm 1})_{\text{HCl}}}{(\text{a}_{\pm 2})_{\text{HCl}}}$$

Comparing Eqs we get

$$E_{\text{cell(wlj)}} = 2t_- E_{\text{cell(wolj)}}$$

If the cell without liquid junction is to function spontaneously, we must have

$$(\text{a}_{\pm 2})_{\text{HCl}} > (\text{a}_{\pm 1})_{\text{HCl}}$$

Comment on liquid junction potential

In a cell with $(\text{a}_{\pm 2})_{\text{HCl}} > (\text{a}_{\pm 1})_{\text{HCl}}$, we will have

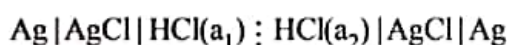
$$\begin{aligned} E_{\text{lj}} &\text{ positive} && \text{if } t_- > t_+ \\ E_{\text{lj}} &\text{ negative} && \text{if } t_- < t_+ \\ \text{and } E_{\text{lj}} &\text{ zero} && \text{if } t_- = t_+ \end{aligned}$$

From equation above, we get

$$\begin{aligned} E_{\text{cell(wlj)}} &> E_{\text{cell(wolj)}} && \text{if } t_- > t_+ \\ E_{\text{cell(wlj)}} &< E_{\text{cell(wolj)}} && \text{if } t_- < t_+ \\ \text{and } E_{\text{cell(wlj)}} &= E_{\text{cell(wolj)}} && \text{if } t_- = t_+ \end{aligned}$$

CELL IN WHICH ELECTRODES ARE REVERSIBLE WITH RESPECT TO ANIONS**A typical Example**

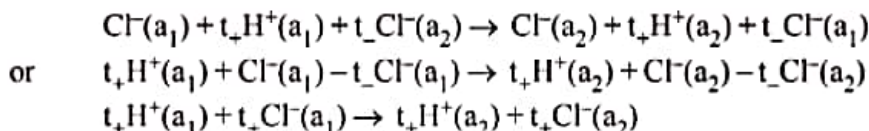
Consider the cell



Working of the cell

- (i) Electrode reaction at anode $\text{Ag(s)} + \text{Cl}^-(a_1) \rightarrow \text{AgCl(s)} + e^-$
 (ii) Electrode reaction at cathode $\text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^-(a_2)$
 (iii) Migration of H^+ ions $t_+ \text{H}^+(a_1) \rightarrow t_+ \text{H}^+(a_2)$
 (iv) Migration of Cl^- ions $t_- \text{Cl}^-(a_2) \rightarrow t_- \text{Cl}^-(a_1)$

The net effect is obtained by adding the above



Thus, the net cell reaction is to transfer t_+ mole of HCl from the solution of activity a_1 to that of activity a_2 .

The free energy change of the net cell reaction is

$$\Delta G = t_+ RT \ln \frac{(a_2)_{\text{H}^+} (a_2)_{\text{Cl}^-}}{(a_1)_{\text{H}^+} (a_1)_{\text{Cl}^-}} = 2t_+ RT \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

$$\text{Hence } E_{\text{cell(wlj)}} = -\frac{\Delta G}{F} = -2t_+ \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

Cell without liquid junction potential

$$\text{The cell potential would be } E_{\text{cell(wolj)}} = -\frac{RT}{F} \ln \frac{(a_2)_{\text{Cl}^-}}{(a_1)_{\text{Cl}^-}} = -\frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

where a_{Cl^-} has been replaced by the mean ionic activity $a_{\pm}$.

Expression of liquid Junction potential

$$\begin{aligned} \text{Now since } E_{\text{lj}} &= E_{\text{cell(wlj)}} - E_{\text{cell(wolj)}} \text{ we get} \\ E_{\text{lj}} &= -2t_+ \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}} + \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}} \end{aligned}$$

$$\text{or } E_{\text{lj}} = (1 - 2t_+) \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

$$\text{or } E_{\text{lj}} = (t_- - t_+) \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

$$E_{\text{cell(wlj)}} = 2t_+ E_{\text{cell(wolj)}}$$

If the cell without liquid junction is to function spontaneously, we must have

$$(a_{\pm 1})_{\text{HCl}} > (a_{\pm 2})_{\text{HCl}}$$

Comment on liquid junction potential

In general, the sign and magnitude of the liquid junction potential depends on the transference numbers of involved cations and anions. In a cell with $(a_{\pm 1})_{\text{HCl}} > (a_{\pm 2})_{\text{HCl}}$, we have

$$\begin{aligned} E_{lj} & \text{ positive if } t_+ > t_- \\ E_{lj} & \text{ negative if } t_+ < t_- \\ \text{and } E_{lj} & \text{ zero if } t_+ = t_- \end{aligned}$$

From above equation we get

$$\begin{aligned} E_{\text{cell(wlj)}} & > E_{\text{cell(wolj)}} \text{ if } t_+ > t_- \\ E_{\text{cell(wlj)}} & < E_{\text{cell(wolj)}} \text{ if } t_+ < t_- \\ \text{and } E_{\text{cell(wlj)}} & = E_{\text{cell(wolj)}} \text{ if } t_+ = t_- \end{aligned}$$

Generalization of Results

$$E_{\text{cell(wlj)}} = \pm 2t_{\mp} \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

$$E_{\text{cell(wolj)}} = \pm \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

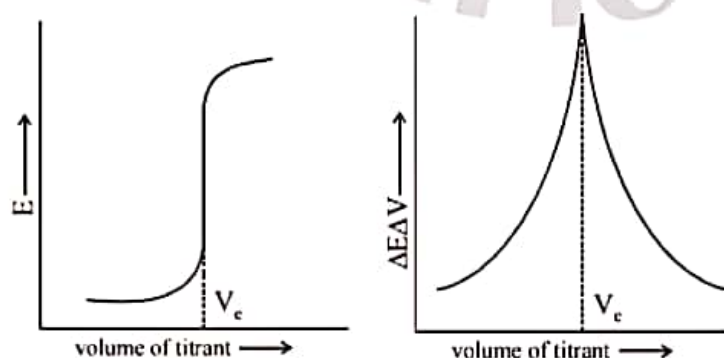
$$E_{\text{cell(wlj)}} = 2t_{\mp} E_{\text{cell(wolj)}}$$

$$E_{lj} = \pm (1 - 2t_{\pm}) \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

$$= (t_- - t_+) \frac{RT}{F} \ln \frac{(a_{\pm 2})_{\text{HCl}}}{(a_{\pm 1})_{\text{HCl}}}$$

POTENTIOMETRIC TITRATIONS**Principle Underlying Potentiometric Titrations**

The equivalence point of titrations can be determined accurately without making use of any visual indicators.

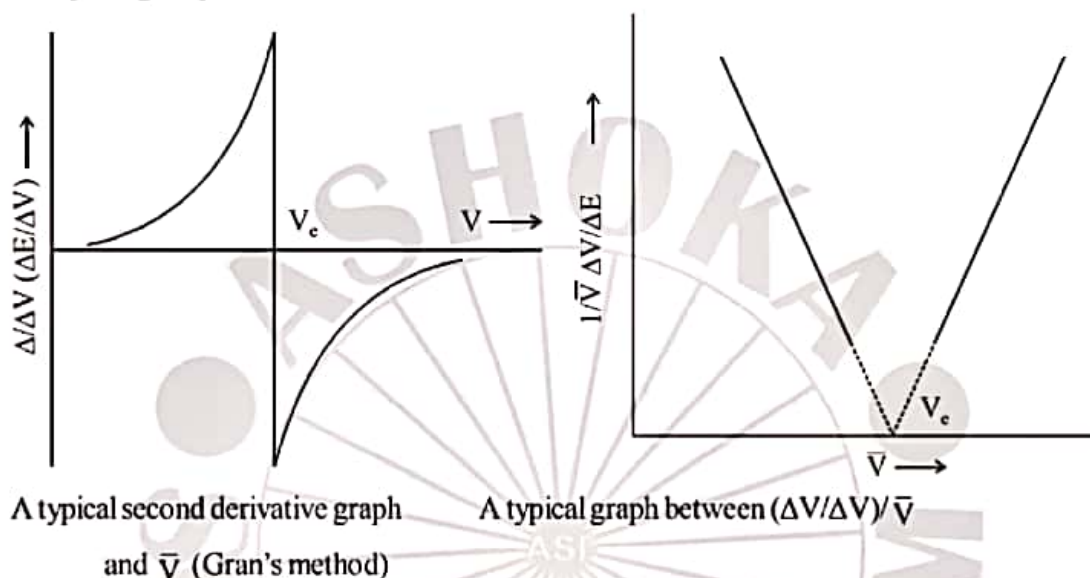
Location of Equivalence Point

A typical potentiometric titration curve A typical first derivative graph

Applicability of Potentiometric Titrations

Potentiometric titrations constitute the most versatile method of electrochemical analysis and practically every analytical determination of both inorganic and organic system carried out with classical method could be performed potentiometrically.

For example, the titration between weak acid and weak base, titrations in coloured solution, titrations in non aqueous media (where indicators cannot be used), and differential determinations of two or more than two substances with different solubility products or with different redox potentials can be carried out by using the potentiometric method.



CONSTRUCTION OF POTENTIOMETRIC TITRATION CURVES

Acid-Base Titrations

In acid-base titrations, the hydrogen-ion concentration varies during the course of titrations. The indicator electrode employed in titration is either the quinhydrone electrode or the glass electrode. The potentials of the electrode is given as follows :

Quinhydrone Electrode

$$E_{Q, QH_2, H^+ | Pt} = E_{Q, QH_2, H^+ | Pt}^0 - \frac{2.303 RT}{F} \text{pH}$$

Glass Electrode

$$E_{\text{glass}} = E_{\text{glass}}^0 + \frac{2.303 RT}{F} \text{pH}$$

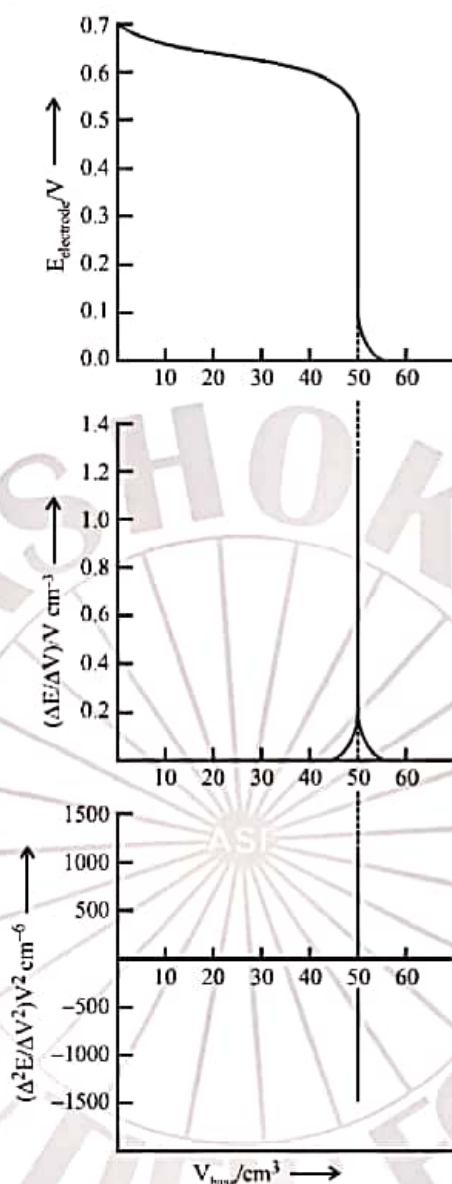
Saturated calomel electrode is almost universally employed as the reference electrode. Thus, the assembly used in potentiometric acid-base titration is

Reference electrode || Indicator electrode

i.e. $Pt | Hg | Hg_2Cl_2 | Cl^- || H^+, Q, QH_2 | Pt$

or $Pt | Hg | Hg_2Cl_2 | Cl^- || H^+ | \text{Glass electrode}$

TITRATION OF HCl VERSUS NaOH



REDOX TITRATIONS

In redox titration, the addition of titrant changes the concentration of reduced and oxidized forms of reactant; the concentration of one of these increases while that of the other decreases. This results into the change in the potential of the electrode which can be determined experimentally or theoretically. The platinum electrode, which is usually employed as the indicator electrode, is dipped into the solution of reactant. The potential of the electrode relative to a reference electrode is measured at different stages of titration and then graphs between E , versus V , $\Delta E/\Delta V$ versus V , etc., are plotted to determine the equivalence point.

PRECIPITATION TITRATIONS

In precipitation titrations, the concentration of reactant decreases as a result of formation of a precipitate with the titrant. If an electrode reversible with the reactant is dipped into the solution, its potential will vary during the course of titration. Hence precipitation titration can be carried out potentiometrically.