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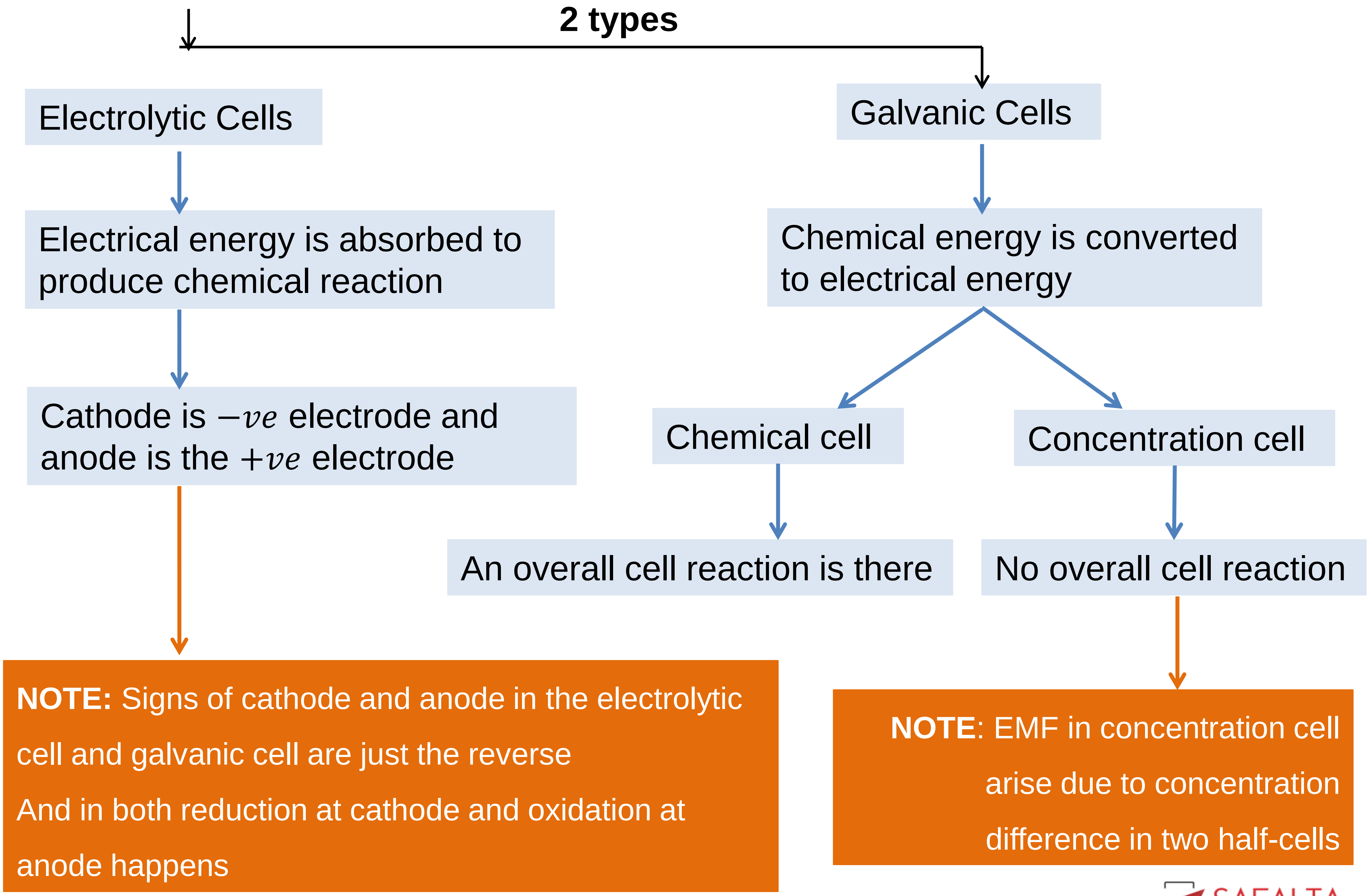
Electrochemical Cells



2 types

Electrolytic Cells

Electrical energy is absorbed to produce chemical reaction

Cathode is $-ve$ electrode and anode is the $+ve$ electrode

NOTE: Signs of cathode and anode in the electrolytic cell and galvanic cell are just the reverse

And in both reduction at cathode and oxidation at anode happens

Galvanic Cells

Chemical energy is converted to electrical energy

Chemical cell

An overall cell reaction is there

Concentration cell

No overall cell reaction

NOTE: EMF in concentration cell arise due to concentration difference in two half-cells

GALVANIC CELLS

The device in which chemical energy is converted into electrical energy is called galvanic cell or electrochemical cell or voltaic cell. In a galvanic cell, a redox reaction is carried out in an indirect manner and the decrease in free energy during the chemical process appears as electrical energy. An indirect redox reaction is such that reduction and oxidation processes are carried out in separate vessels. Let us consider the Zn-$CuSO_4$ reaction as the basis of the cell reaction.

A zinc strip is dipped in the $ZnSO_4$ solution and a copper strip is dipped in the $CuSO_4$ solution taken in separate beakers. The two metallic strips which act as electrodes are connected by the conducting wires through a voltmeter. The two solutions are joined by an inverted U-tube known as salt bridge. The U-tube is filled with the solution of some electrolyte such as KCl, KNO_3 or NH_4Cl to which gelatin or agar-agar has been added convert it into semisolid paste.

An overall cell reaction is there

Representation of Chemical Cell

For example: $Zn \rightleftharpoons Zn^{2+} + 2e^-$; (Oxidation) At anode

$Cu^{2+} + 2e^- \rightleftharpoons Cu$; (Reduction) At cathode

It is represented as $Zn \quad (aq)|ZnSO_4||CuSO_4|Cu \quad (aq)$

Electrode at which reduction takes place is written on right side

Double vertical lines represent separation of two half cells

Electrode at which oxidation happens is written on left side

The electrical work done in moving a charge through conductor

Work Done by a Galvanic Cell

Electrical work (W) $=$ charge (q) $\times$ potential difference (V)

(joules) (coulombs) (volts)

When **96500** Coulombs OR **1 Faraday (F)** of charge is moved from one electrode to another.

$$\mathbf{W = F \times V}$$

NOTE: Electrical work is usually expressed in energy units of watts times time i.e. $1\,J = 1\,W.s$

Watt is unit of **electrical Power** i.e. rate of energy expenditure

Maxi $W = q.V$ ***ne by cell***

Note that W_{max} is when V is maximum

$$\boldsymbol{W_{max} = -n.F.Ecell}$$

n equals the number of electrons in either half–cell reaction

Note that if number of electrons are different in the half-cells, then their LCM is taken to get n

$$A^{3+} + e^- \rightarrow A^{2+}, \qquad E_1{}^\circ = +0.77\ V$$

$$A^{2+} + 2e^- \rightarrow A, \qquad E_2{}^\circ = -0.44\ V$$

$$\therefore \boldsymbol{E^\circ(A^{3+} + 3e^-} \rightarrow A) \neq \boldsymbol{(0.77 - 0.44)V}$$

Note that Potentials are not thermodynamic functions and may not be added directly

Free energy change (ΔG°)$= -nFE^\circ$

Note that ΔG° is thermodynamic function and can be added

$$\therefore\ \Delta G^\circ = \Delta G_1{}^\circ + \Delta G_2{}^\circ$$

$$\Rightarrow \frac{-3F}{E^\circ} = \frac{-F}{E_1{}^\circ} - \frac{2F}{E_2{}^\circ}$$

Half Cell Potential

Tendency to lose electrons i.e. get oxidized is called **Oxidation Potential**

Tendency to gain electrons i.e. get reduced is called **Reduction Potential**

Note that since any half-cell reaction can be written as reversible process

For a single cell: $E_{ox} = -E_{red}$

Example: For electrode $Cu/CuSO_4(1M)$

$$E_{red}\ i.e.\ E°_{Cu^{2+},Cu} = +0.34V$$

$$\therefore E_{ox}\ i.e.\ E°_{Cu,Cu^{2+}} = -0.34V$$

Note that half-cell potentials are generally taken in **reduction terms**

Note that Half-Cell potentials cannot be directly determined as there is no way of isolating a single half-cell reaction

Electrode potential (E) is determined by coupling it with a standard hydrogen electrode

E of a standard hydrogen electrode ($\boldsymbol{SHE}$) is assumed as $0\,V$ at $\mathbf{25}$℃

SHE is Represented as $P_t, H_2(1atm), HCL$ $([H^+] = 1M)$

When a half-cell reaction involves reduction → Er_{ed} is positive

Example: $M^{n+} + ne^{-} \rightarrow M, \quad Ered$

When a half-cell reaction involves oxidation → $Eoxd$ is negative

Example: $M \rightarrow M^{0+} + ne^{-}$ $\quad E_{oxd}$

Note that $E_{red} + E_{oxd} = 0$, for the same metal M in example above

Standard Electrode Potential ($E°$)

For Half Cell: $M|M^{n+}(aq)$

$$\boldsymbol{M \rightleftharpoons M^{n+} + ne^-}$$

If $[M^{n+}] = 1M$ at 25℃ → Potential of half cell is termed $E°$

Example:

$$2X^+ + 2e^- \rightleftharpoons X_2, \qquad E°$$

$$X^+ + e^- \rightleftharpoons \frac{1}{2}X_2, \qquad E°$$

Note that $E°$ is an intensive property;
it is same whichever way the reaction is
written as shown in example

When $E°_{\text{red}}$ values of different half cells are arranged **in decreasing order**

Electrochemical Series (IUPAC Convention)

This arrangement of $E°$ is known as **electrochemical series**

Example:

$$\boldsymbol{F^2|F^- > Hg^{2+}|Hg > Fe^{3+}|Fe^{2+} > Sn^{4+}|Sn^{2+} > Cu^{2+}|Cu^+ > Sn^{2+}|Sn > Ni^{2+}|Ni > Zn^{2+}|Zn}$$

Note that higher the $E°_{red}$ for an electrode, more will be its tendency to get reduced

Since Galvanic Cells are formed by coupling two half cells

$\boldsymbol{E^\circ}_{\boldsymbol{Cell}} =$ reduction potential of right hand electrode $(R.H.E)$

$-$ reduction potential of Left hand electrode $(L.H.E)$

Example: $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$

$\mathrm{L.H.E}$ $\qquad\qquad$ $\mathrm{R.H.E}$

Given: $E_{Zn^{2+},Zn} = -0.76V$ and $E_{Cu^{2+},Cu} = 0.34V$ (Reduction Potentials)

$$E^\circ_{Cell} = (0.34)V - (-0.76)V = 1.1V$$

Note that for a given half cell, potential may be in $-ve$ or $+ve$ sign, but the EMF of cell should always be positive

No resultant chemical reaction,

But **EMF** arises due to concentration difference between half cells

$$(C_2 - C_1 = \Delta C)$$

$$E_{Cell} = \frac{2.303RT}{n.F} log \frac{C_2}{C_1}$$

Note that: There is no $E°_{Cell}$ as $E°$ of two half cells are same AND get cancelled

n is the number of electrons exchanged, in oxidation and reduction processes

Relates the EMF of Cell AND concentrations of species involved

For the general cell reaction: $aA + bB \rightleftharpoons cC + dD$

$$E_{cell} = E° - \frac{2.303R.T}{nF} log\left(\frac{[C]^c.[D]^d}{[A]^a.[B]^b}\right)$$

→ **Note that:** It is Valid for Complete cell or even a half-cell

$E°$ = standard emf of cell (or half cell)

n = number of electrons involved in the reaction

Note that: $\left(\frac{[C]^c.[D]^d}{[A]^c.[B]^b}\right) =$ Q (reaction Quotient)

Equilibrium Constant and Standard Free Energy Change

For a cell reaction: $aA + bB \rightleftharpoons cC + dD$

At equilibrium

$$\left(\frac{[C]^c.[D]^d}{[A]^a.[B]^b}\right) = \boldsymbol{K} \text{ (equilibrium constant)}$$

$$E_{cell} = 0$$

From Nernst Equation

$$\boldsymbol{E^\circ = \frac{2.303RT}{n.F} logK}$$

Note that $\Delta G^\circ = -nFE^\circ$

$$\boldsymbol{\Delta G^\circ = -2.303R.T.logK}$$

Note that knowing $\boldsymbol{E^\circ}$, we can calculate $\boldsymbol{K}$ and $\Delta \boldsymbol{G^\circ}$

Feasibility of Cell Reactions

$$\Delta G^\circ = -2.303R.T.logK$$

Note that reaction is spontaneous only if $\Delta G^\circ < 0$

Spontaneity of forward reaction	ΔG°	K	E_{cell}
Spontaneous	$-ve$	> 1	$+ve$
At equilibrium	0	1	0
Non spontaneous	$+ve$	< 1	$-ve$

Note that this is steady state condition

Temperature Coefficient of Cell

Note that E varies with temperature

$$\left(\frac{\partial E}{\partial T}\right)_P$$

- Known as **temperature coefficient**
- $= 0 \Rightarrow$ no cooling/ heating of cell during its working
- $> 0 \Rightarrow$ cooling of cell during working
- $< 0 \Rightarrow$ heating of cell during working

d ΔS for a cell

$$\Delta S = n.F\left(\frac{\partial E}{\partial T}\right)_P$$

$\left(\frac{\partial E}{\partial T}\right)_P$ is temperature coefficient

$$\Delta H = T\Delta S + \Delta G$$

$$= n.F\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right]$$

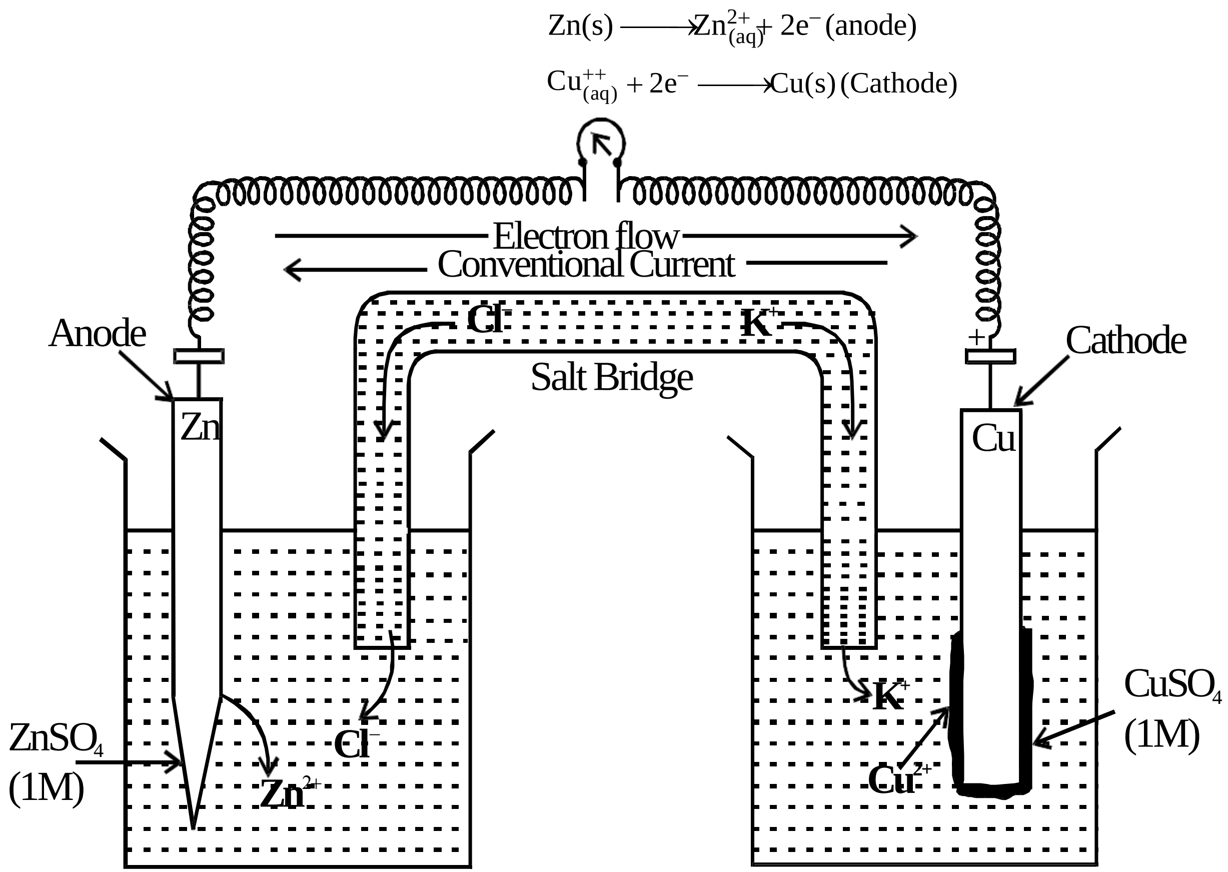


Fig. *Electrochemical cell*

Function of Salt Bridge

In the electrochemical cell a salt bridge serves two very important functions :

(i) It allows the flows of current by completing the circuit.

(ii) It maintains electrical neutrality.

Representation of Galvanic Cell

Galvanic cell is a combination of two half cells, namely; oxidation half cell and reduction half cell. If M represents the symbol of the element and M^{n+} represents its cation (i.e. its oxidation state) in solution, then

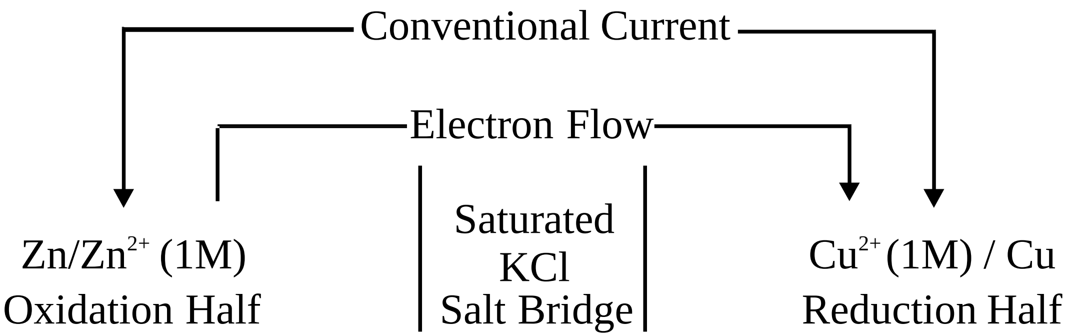
Oxidation half cell is represented as $M/M^{n+}(C)$

Reduction half cell is represented as $M^{n+}(C)/M$.

In both the notations C refers to the molar concentration of the ions in solution. Conventionally, a cell is represented by writing the cathode on the right hand side and anode on the left hand side. The two vertical lines are put between the two half cells which indicate salt bridge. Some times the formula of the electrolyte used in the salt bridge is also written below the vertical lines.

For example, zinc-copper sulphates cell is represented as follows :

$$\mathrm{Zn}|\,\mathrm{Zn}^{2+}_{(aq)}(1M)|\,\mathrm{standardnet}|\mathrm{Cu}^{2+}(aq)(1M)|\,\mathrm{Cu}$$



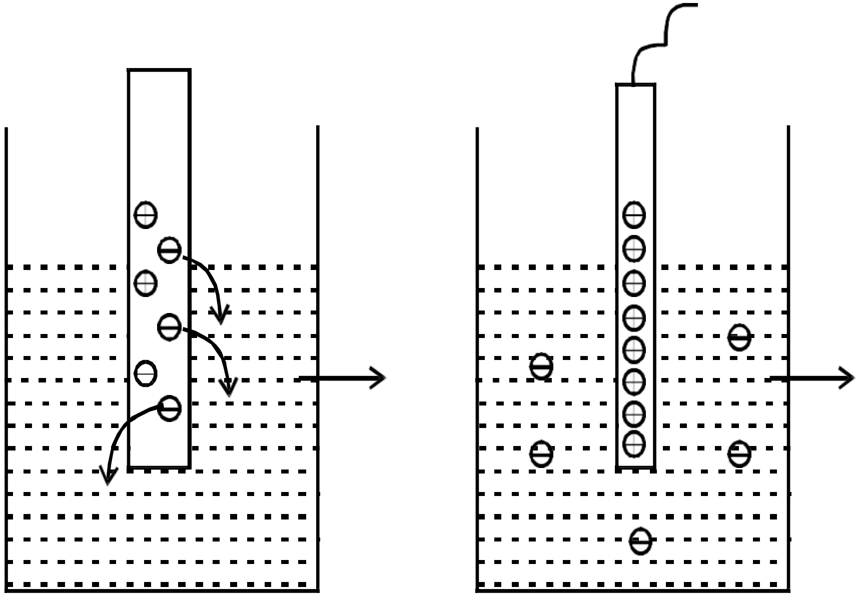
Key point : Remember LOAN, means left side oxidation occurs, anode is negatively charged.

ELECTRODE POTENTIAL

The potential difference between electrode and the electrolyte is called electrode potential. There are two types of electrode potentials.

(a) Oxidation potentials

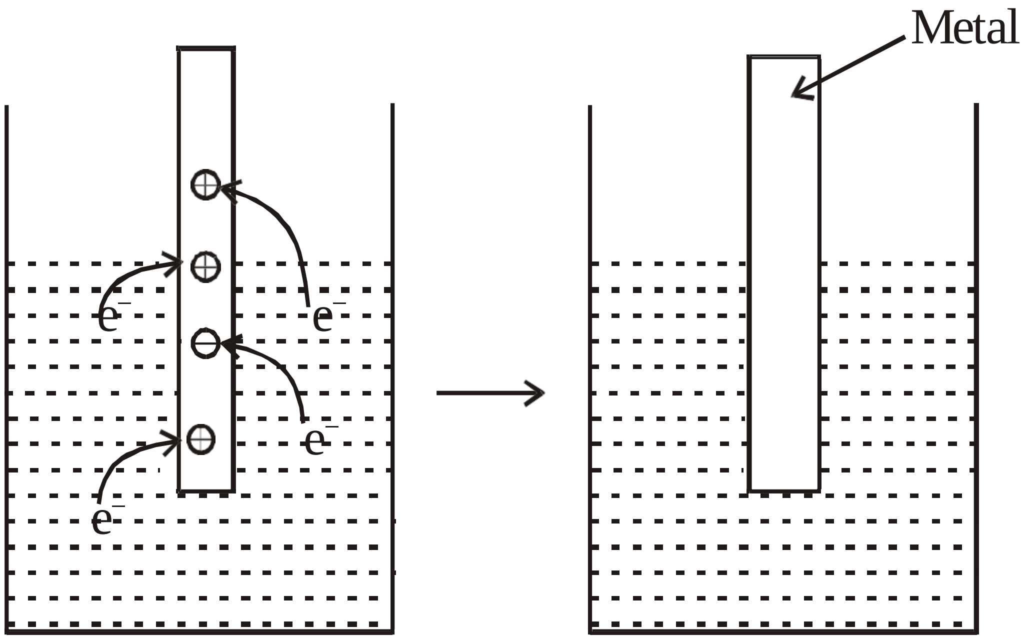
When metal atom as the strip may lose n electron and move to the solution as M^{n+} ion, metal is oxidised and the potential develop between metal and its solution is called oxidation electrode potential.



(b) Reduction potential

The metal ion M^{n+} may colloid with the strip, gain ‘n’ electrons and get converted into metal atom. The potential develop between metal and solution is now called reduction electrode potential.

$M^{n+} + ne^- \longrightarrow M(s)$ (Reduction)



EMF OF THE CELL

The difference in the electrode potentials of the two electrodes of the cell is termed as electromotive force (abbreviated as EMF) or cell voltage. Mathematically

$$\text{EMF} = E_{\text{Red}}(\text{Cathode}) - E_{\text{Red}}(\text{Anode}) \text{ or simply as EMF}$$

$$= E_{\text{Cathode}} - E_{\text{Anode}}$$

Since in the representation of a cell, the cathode is written on right hand side and the anode on left side, Thus, EMF of a cell is also written as :

$$\text{EMF} = E_{\text{right}} - E_{\text{Left}}$$

EMF of the cell may be defined as the potential difference between the two terminals of the cell when either no or very little current is drawn from it. It is measured with the help of potentiometer or vacuum tube voltmeter.

Standard Electrode Potentials

Its electrode potential at 298 K and 1M concentration of electrolyte is called standard electrode potential.

Standard Hydrogen Electrode (SHE)

Standard hydrogen electrode consists of a platinum wire sealed into a glass tube and carrying a platinum foil at one end. The platinum foil is coated with finely divided platinum. The electrode is placed in beaker containing an aqueous solution of some acid having one molar concentration of H^+ ions. Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at a temperature of 298 K. The oxidation or reduction in the SHE takes place at platinum foil.

$$Pt(s), H_2(aq)\ (1\ bar)\ |\ H_+(aq)\ (+M)\ \text{or}$$

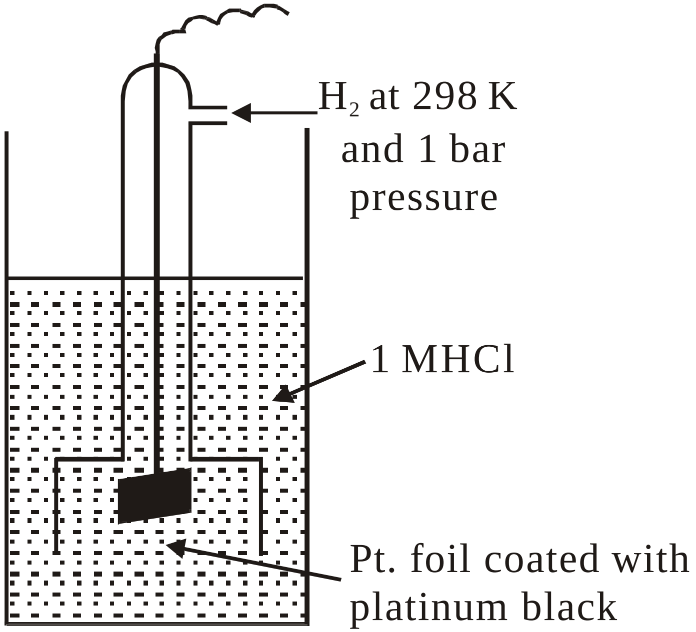
$$M^+(aq)\ (1M)\ |\ \frac{1}{2}H_2\ (1\ bar), Pt(s)$$

If SHE acts as anode then oxidation will take place at it as

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

If SHE acts as cathode then reduction will take place at it as

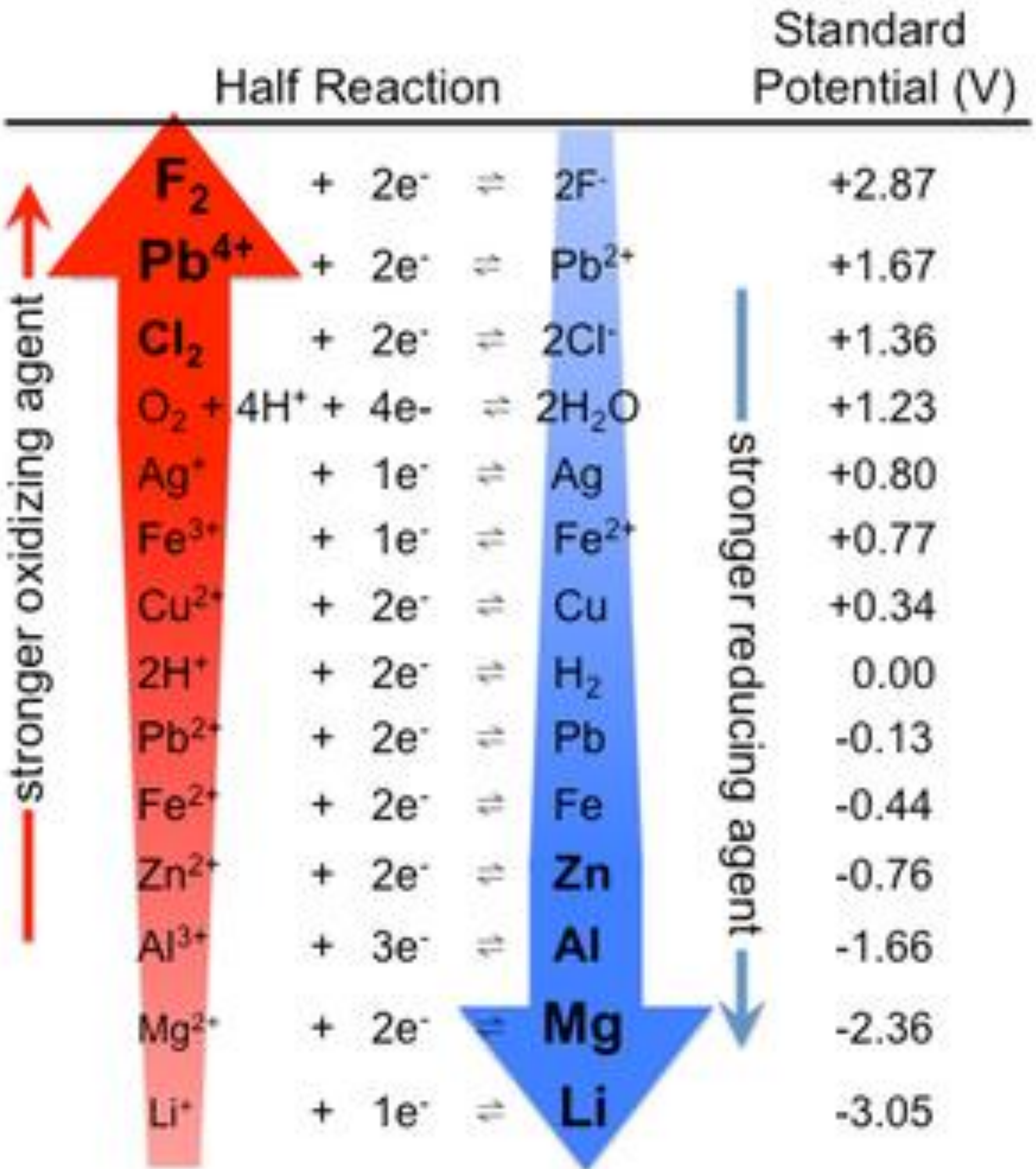
$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$



The electrode potential of other electrodes are determined by coupling them with SHE. The electrode potential of an electrode determined relative to the standard hydrogen electrode under standard conditions is called standard electrode potential. It is represented as E°. The standard conditions are 1M concentration of ions at 298 K temperature and 1 bar pressure.

Electrochemical Series

We have seen that different metal/metal ion combinations have different values of electrode potentials. The various elements can be arranged in order of increasing or decreasing values of their reduction potentials. The arrangement of various element in the order of increasing values of standard reduction potentials is called electrochemical series. The electrochemical series, also called activity series consisting of some electrodes along with their respective reduction reactions as given below :-



Half Reaction	Standard Potential (V)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

Table: *Standard Electrode Potential*

Element	Electrode Reaction	E°$_{red}$ (volts)
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	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2$	+1.97
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	$Cr_2O_4^{2-} + 14H^+ + e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33
Cl_2	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-$	+1.36
Au	$Au^{3+}(aq) + 3e^-$ (aq)	+1.42
$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 12H_2$	$\longrightarrow Au(s)$	+1.51
F_2	$F_2(g) + 2e^-$ $O(l)$ $\longrightarrow 2F^-(aq)$	+2.87

Applications of Electrochemical Series

1. Relative oxidising and reducing powers of various substances
2. Calculation of standard EMF of the cell (E°_{cell})
3. Predicting feasibility of redox reaction
4. Predicting the capability of metal to displace H_2 gas from acid.

Solved Examples:

Q.1. Which of the following electrolyte can be used in a salt bridge in a cell ?

(1) KCl (2) K_2SO_4 (3) KNO_3 (4) All of these

Ans.(4) In all the cases, ionic mobility of cations and anions are same.

Q.2. The half cell potentials were determined as

$Co^{2+} + 2e^- \longrightarrow Co$ $E^\circ = -0.277\ V$

$Cr^{3+} + 3e^- \longrightarrow Cr$ $E^\circ = -0.744\ V$

of the following which one is the strongest oxidant

(1) Co (2) Co^{2+} (3) Cr (4) Cr^{3+}

Ans.(2) Reduction potential of Co^{2+} is more, so it is stronger oxidant

Q.3. A gas x at 1 atm is bubbled through the solution containing 1m y^- and 1m z^- at 25°C. If reduction potential $x < y < z$ then

(1) y will oxidize x and not z	(2)y will oxidize z and not x
(3) y will oxidasic z and x	(4)y will reduce x and z

Ans.(1) Because reduction potential of ‘y’ lies in between ‘x’ and ‘z’ and it is more than *x* but lesser than *z*.

Nernst Equation for Electrode Potential

The quantitative relationship between the concentration of ions and electrode potentials is given by Nernst equation. For a general electrode reaction:

Nernst equation can be written as

$$E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} + \frac{RT}{nF} \text{In} \frac{[M^{n+}]}{[M]}$$

$$E_{M^{n+}/M} = E^0_{(M^{n+}/M)} + \frac{2.303RT}{nF} \log \frac{[M^{n+}]}{[M]} \quad \ldots (1)$$

where $E_{M^{n+}/M}$ = Electrode potential

$E^0_{M^{n+}/M}$ = Standard electrode potential with reference to SHE when concentration of M^{n+} is 1 mol L^{-1} and temperature is 298 K.

Substituting these values in equation (1) we get

$$E_{M^{n+}/M} = E^0_{(M^{n+}/M)} + \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[M^{n+}]}{[M]} = E^0_{(M^{n+}/M)} + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M]}$$

In general, for any electrode,

$$E_{red} = E^0_{red} + \frac{0.0591}{n}\log\frac{[\text{Oxidisedstate}]}{[\text{Reducedstate}]}$$

The concentration of solids, i.e., [solid] is taken to be unity while concentration of gases is expessed in terms of their respectively partial pressures.

Calculation of Cell Potential using Nernst Equation

1. $Zn/Zn^{2+}(aq)||Cu^{2+}(aq)/Cu$

Cell potential = $E_{cathode} - E_{anode}$

Using Nernst equation for copper electrode $E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} + \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Cu]}$

Similarly, for zinc electrode

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} + \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Zn]}$$

Cell Potential $= E^0_{Cu^{2+}/Cu} + \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Cu]} - E^0_{Zn^{2+}/Zn} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Zn]}$

$$= E^0_{Cu^{2+}/Cu} - E^0_{zn^{2+}/Zn} + \frac{0.0591}{2}\log\frac{[Cu^{2+}][Zn]}{[Cu]\left[Zn^{2+}\right]}$$

Since concentration of solids is taken to be unity $\therefore$ $[Zn] = [Cu] = 1$

Cell potential = $E^0_{Cell} + \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$

In general, for a redox cell reaction involving the transference of n electrons

$$aA + bB \longrightarrow cC + dD$$

$$E_{cell} = E^0_{cell} + \frac{RT}{nF}\ln\frac{[A]^a[B]^b}{[C]^c[D]^d}$$

$$\boxed{E_{cell} = E^0_{cell} + \frac{0.0591}{n}\log\frac{[A]^a[B]^b}{[C]^c[D]^d}}$$

While using equation, the following points must be kept in mind :

(i) Concentration of solids (metals) is taken to be unity.

(ii) Concentration of ionic species are taken in mol L^{-1}.

(iii) Concentration of gases are expressed in terms of their respective partial pressures in bar.

The values of n, a, b, c, d are obtained from the balanced cell reaction. For example, let us consider the cell,

$$Zn/Zn^{2+} \| Ag^+/Ag$$

The balanced cell reaction is

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

Here, n = 2

$$E_{cell} = E^{0}_{cell} + \frac{0.0591}{2}\log\frac{\left[Ag^{+}\right]^{2}[Zn]}{\left[Zn^{2+}\right][Ag]^{2}}$$

[Ag] = [Zn] = 1

Similarly, for the cell,

$Al/Al^{3+}||Ni^{2+}/Ni,$ the cell reaction is

$$2Al\,(s) + 3Ni^{2+}(aq) \longrightarrow 3Ni(s) + 2Al^{3+}(aq)$$

Here n = 6

$$E_{cell} = E^{0}_{cell} + \frac{0.0591}{6}\log\frac{[Ni^{2+}]^{3}[Al]^{2}}{[Al^{3+}][Ni]^{3}}$$

[Ni] = [Al] = 1

NERNST EQUATION AND EQUILIBRIUM CONSTANT

Galvanic cell does not continue working indefinitely and stops working after some time. In fact, as the cell reaction progresses, there is a fall in the concentration of cations around cathode due to reduction and at the same time there is an increase in the concentration of metal cations around anode due to oxidation. Consequently, electrode potential of cathode decreases and that of anode increases with the passage of time. Ultimately, a stage reaches when the potential difference ($E_{cathode} - E_{anode}$)

becomes zero and the flow of electrons stops.

For example :

In a cell, $Zn/Zn^{2+}(aq)||Cu^{2+}(aq)/Cu$, the flow of electrons from zinc to copper stops when $E_{Zn^{2+}/Zn}$ becomes equal to $E_{Cu^{2+}/Cu}$.

In this stage the concentration of Zn^{2+} (aq) and that of Cu^{2+}(aq) will be equilibrium concentration because the cell reaction attains equilibrium.

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

Considering the concentrations of Zn(s) and Cu(s) to be unity, the equilibrium constant for the above reaction, K_C is given by the expression.

$$K_C = \left[\frac{Zn^{2+}}{Cu^{2+}}\right]$$

Applying the Nernst equation for cell potential

$$E_{cell} = E^0_{cell} + \frac{2.303RT}{nF}\log\left[\frac{Cu^{2+}}{Zn^{2+}}\right]$$

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log\left[\frac{Zn^{2+}}{Cu^{2+}}\right]$$

Since E_{cell} at equilibrium is zero

$$\therefore \qquad 0 = E^0_{cell} - \frac{2.303\,RT}{nF}\log K_c$$

$$\text{or} \qquad E^0_{cell} = \frac{2.303RT}{nF}\log K_C$$

$$\therefore \qquad E^0_{cell} = \frac{2.303 \times 8.314 \times 298}{n \times 96500}\log K_C \qquad \text{or} \qquad E^0_{cell} = \frac{0.0591}{n}\log K_C$$

The value of K_C gives the extent of the cell reaction. For example, the value of K_C for the Zn–$CuSO_4$ cell reaction at 298 K is 2×10^{37}, which shows that the reaction has proceeded almost to completion before attainment of equilibrium conditions.

ELECTROCHEMICAL CELL AND GIBB'S ENERGY

A galvanic cell is a source of electrical energy which can be used for different kinds of work. Unlike heat energy, the electrical energy can be quantitatively converted into work. The electrical work or the electrical energy is equal to the product of EMF of the cell and the electrical charge that flows through the external wire.

W_{Elec} = (EMF) × (Electrical charge flowing through the wire)

If E_{cell} is the EMF of the cell, then $\mathbf{W_{Elec} = nF \times E_{cell}}$ where n is the mole of electron transferred.

In case of electro-chemical cell, the driving force for the cell reaction is provided by decreasing free energy. In other words, the decrease of Gibb's energy $(-\Delta G)$ of cell reaction provides a measure of electrical work $(W_{ele.})$.

Thus $\quad -\Delta G = W_{cell} = nFE_{cell}$

or $\quad \boxed{\Delta G = -nFE_{cell}}$

Standard Gibb's energy change is given as $\boxed{\Delta G^\circ = -nFE^\circ_{cell}}$

For cell reaction to be spontaneous, ΔG must be negative, and for ΔG to be negative, the value of E must be positive.

Relationship between Standard EMF and equilibrium constant

We know that standard free energy change is related to equilibrium constant as

$$\Delta G^\circ = -RT\ In\ K_C$$

also
$$\Delta G^\circ = -nFE^\circ$$

$$\therefore \quad nFE^\circ = RT\ In\ K_C = 2.303RT \log K_C$$

or
$$\boxed{E^\circ = 2.303\frac{RT}{nF}\log K_C}$$

Solved Examples:

Q.1. For a reaction $M \longrightarrow M^{n+} + ne^-$. ***A graph is plotted between reduction potential E and log[M^{n+}].If at 298K the value of slope is 0.0295, then value of n is***

(1) 1 (2) 3 (3) 2 (4) 4

Ans.(3) $E = E^\circ + \frac{0.0591}{n}\log\left[Mn^+\right]$

Slope = $\frac{0.0591}{n} = 0.0295$

n = 2

Q.2. The half reactions for a cell are

$Zn \longrightarrow Zn^{2+} + 2e^-$ E° = 0.76 V

$Fe \longrightarrow Fe^{2+} + 2e^-$ E° = 0.41 V

The ΔG° (in kJ) for the overall reaction

$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$ is

(1) 67.6 kJ (2) –67.6 kJ (3) 33.78 kJ (4) –33.78 kJ

Ans.(2) $E_{cell} = E_R - E_L$

$= -0.41 - (-0.76) = -0.41 + 0.76 = +0.35$

$\Delta G = -nFE^\circ = -2 \times 96500 \times 0.35 = 67.6$ KJ

Q.3. The standard reduction potential of Cu^{2+}/ Cu and Cu^{2+}/Cu^{+} are 0.337 and 0.153 respectively. The standard electrode potential of Cu^{+}/Cu half-cell is

(1) +0.184 V (2) –0.827 V (3) +0.521 V (4) +0.490 V

Ans.(3) $Cu^{2+} \longrightarrow Cu$; $E° = 0.337$

$\Delta G = -2 \times F \times 0.337$

$Cu^{+} \longrightarrow Cu^{2+}$; $E° = -0.153$

$\Delta G = F \times 0.153$

ΔG for $Cu^{+} \longrightarrow Cu$ $= 2.F \times 0.337 + 0.1537 = -0.521\ F$

So, $E° = 0.521$ V

Q.4. The e.m.f of the cell

T1 | $T1^{+}$ (0.001 M) || Cu^{2+} (0.01 M) | Cu is 0.83 V. The emf of this cell could be increased by

(1) Increasing the concentration of $T1^{+}$ ions (2) Increasing the concentration of Cu^{2+} ions

(3) Increasing the concentration of both (4) None of the above

Ans.(2) $Ecell = E° - \frac{0.0591}{n} \log \frac{[Tl^{+}]}{[Cu^{2+}]}$

From given nernst equation it is clear that the Ecell value is directly proportional to $[Cu^{2+}]$

CONCENTRATION CELLS

The galvanic cells in which electrodes are made of same metal but they are immersed in the same electrolytes of different concentrations in two half cells are called concentration cells. The difference in the concentrations of electrolytes in the two half cells, creates potential difference across the two electrodes. The electrode which is placed in electrolyte of larger concentration acts as cathode or + terminal. Whereas electrode which is placed in electrolyte of lower concentration acts as anode or –ve terminal. For example, the copper ion concentration cells has been shown in fig.

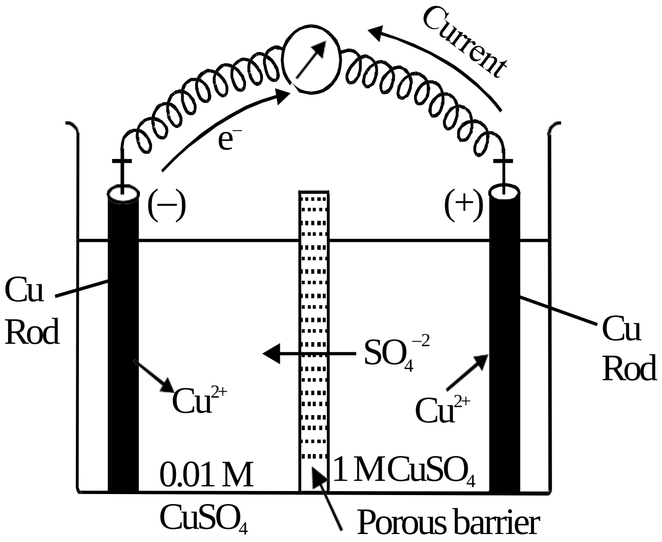


Fig. *Cu^{2+} ion concentration cell*

The cell can be represented as Cu/$CuSO_4$(0.01 M)||$CuSO_4$(1M)/Cu or simply as Cu/Cu^{2+} (0.01M) ||Cu^{2+} (1M)/Cu

Similarly, hydrogen ion concentration cell can be constituted by connecting hydrogen electrodes placed in hydrochloric acid solutions of different concentration. It can be represented as

$$Pt, H_2 (1\ bar)/H^+(0.01\ M) \parallel H^+(1M)/H_2 (1\ bar), Pt$$

E_{cell} of Concentration Cell

Consider the concentration cell of the type $M/M^{n+}C_1 \parallel M^{n+} (C_2)/M$. Since standard electrode potentials of the two electrodes cancel each other, the emf of the cell can be written on the basis of Nernst equation as

$$E_{cell} = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

Evidently, for E_{cell} to be positive $C_2 > C_1$.

Solved Examples:

Q.1. The electrochemical cell is set up as pt, H_2 (1 atm) |HCl(0.1M)||CH_3COOH(0.1M) | H_2 (1 atm) ; pt. The emf of the cell is (Ka = $10^{-5} \times 1.8$)

(1)	0	(2)	Positive
(3)	Negative		(4)Cannot be determined

Ans.(3) $$E_{cell} = 0 - \frac{0.059}{2} \log \frac{[H^+_{HCl}]^2}{[H^+_{CH_3COOH}]^2}$$

as $[H^+_{HCl}] > [H^+_{CH_3COOH}]$

$\log [H^+_{HCl}]/[H^+_{CH_3COOH}] > 1$

$E_{cell} = -ve$

Q.2. A calomel reference electrode is coupled with a half cell p_t H_2 (1 atm) | H^+ to form a cellwhich shows an emf of 0.398 V . If the $E°_{Hg_2Cl_2|Hg}$ = 0.28V. The pH of the solution is

(1) 3 (2) 1 (3) 4 (4) 2

Ans.(4) $E_{cell} = 0.398 - 0.28$

$= 0.118$

$E° = 0.0591 \text{ pH} = 0.118$

$$\text{pH} = \frac{0.118}{0.0591} = 2$$

Q.3. The electrode potential of hydrogen electrode at pH=10 is

(1) 0.51 V (2) –0.59 V (3) 0.00 V (4) 0.059 V

Ans.(2) $-0.0591\ \text{pH} = E_{cell}$

$-0.0591 \times 10 = -0.591\ \text{V}$

First Law of Faraday

$w \propto q$

or

$w \propto I \cdot t$

w is amount of substance discharge at an electrode is weight in grams

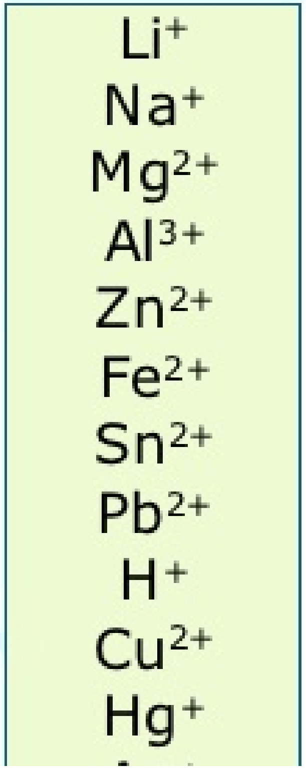
q is quantity of electricity passing through electrolyte in coulombs

$\boldsymbol{w = Z \cdot I \cdot t}$

I is current in ampere

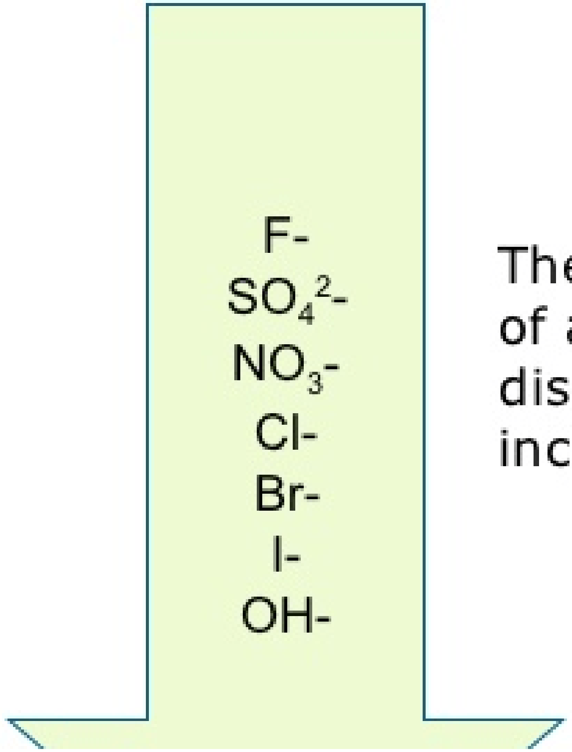
t is time of flow of electricity

Note : Z is constant known as electrochemical equivalent



Li^+
Na^+
Mg^{2+}
Al^{3+}
Zn^{2+}
Fe^{2+}
Sn^{2+}
Pb^{2+}
H^+
Cu^{2+}
Hg^+

The tendency of cation to discharge increases



F^-
SO_4^{2-}
NO_3^-
Cl^-
Br^-
I^-
OH^-

The tendency of anion to discharge increases

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$$\boldsymbol{w = Z \cdot I \cdot t}$$

I is current in ampere

t is time of flow of electricity

Note : Z is constant known as electrochemical equivalent

Second Law of Faraday

$$\boldsymbol{M^{+n} + ne^{-} \rightarrow M}$$

In the reaction n electron deposits $1\ M^{+n}$ ion at electrode

$\therefore$ 1 mole of electron deposits $\frac{1}{n}$moles of M^{+n}

Note that (number of moles × valency) = number of equivalent

And 1 mole of electron = $N_A(6.023 \times 10^{23})$ number of electrons

1 mole of electron deposit 1 equivalent of M^{+n}

Faraday’s second law states that 1 mole of electron / electricity liberates 1 equivalent of matter

Far
Constant (F)

Since, 1 mole of electrons deposit 1 equivalents of matter

Charge of 1 mole electrons $= (6.023 \times 10^{23}) \times (1.6 \times 10^{-19} C)$

$= 96500\ C$

$= 26.8\ \text{ampere} - \text{hour per equivalent}$

$= 1\ \text{Faraday}$

$$\therefore\ \ \mathbf{1}\boldsymbol{F} = \mathbf{96500}\ \boldsymbol{C}$$

Note that second law of Faraday states that 1 Faraday liberates 1 equivalent of matter

Electrochemical equivalent (z)

Number of Equivalent of Substance

Weight in grams of a substance liberated by $1C$ electricity

Electrochemical weight or

gram equivalent weight

Weight in grams liberated by $96500C$ **OR** $1F$

From First law of faraday

$$\boldsymbol{w = z \cdot q}$$

$$\frac{\mathbf{w}}{\mathbf{gram\ equivalent\ weight\ (eq.\,wt.)}} = \frac{\mathbf{z \cdot q}}{\mathbf{eq.\,wt.}}$$

Note that number of equivalents $= \dfrac{z \cdot q}{eq.wt.}$

Electrochemical Equivalent (z) And Equivalent Weight (E)

$$\text{number of equivalents} = \frac{z}{E} \times q$$

$$\boldsymbol{z = \frac{E}{96500}}$$

Note that if number of equivalent $= 1$, then

$$q = 1F = 96500C$$

Note that for 2 substances having equivalent weight E_1 and E_2

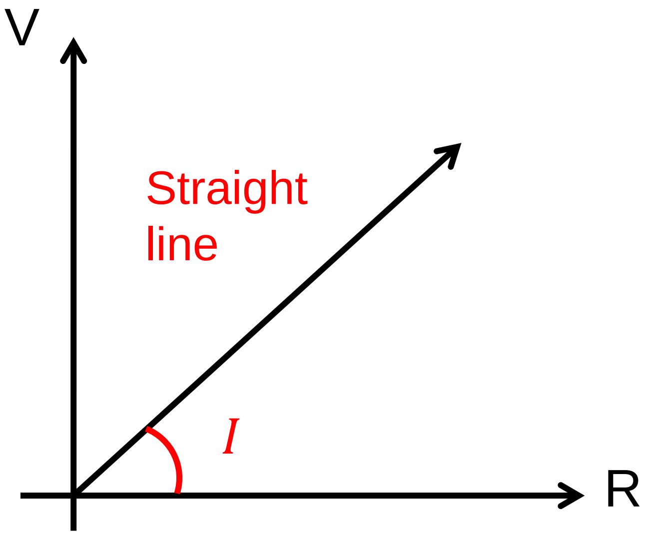
$\frac{E_1}{E_2} = \frac{z_1}{z_2}$ $(And = \frac{w_1}{w_2}$ if same amount of q is passed)

Potential D An
Electrolytic Cell

$V \propto R$

R is resistance across the cell

$\boldsymbol{V = IR}$ → I is current in ampere



Note that this is a statement of ohm’s law

Also if power of cell is W in watts

$$\boxed{W = IR}$$

Electrolytic Conductance

$$\text{conductance} = \frac{1}{\text{resistance}}$$

Depends on

- Number of ions
- Ionic mobility
- Magnitude of charge on ions

Note that passage of current via an electrolyte involves movement of ions carrying an electric charge

Note that Conductance is defined as distance travelled by an ion per second under potential difference of $1\mathrm{V}$ per second

Molar Conductance: conductance due to one mole of an ionic solute

Equivalent conductance: conducting power of all ions produced by one equivalent of electrolyte

Note that to compare the conductance of two solutions equivalent conductance is considered. As one equivalent of different electrolytes involves $1\mathrm{F}$ electrons

Unit of conductance is ohm^{-1} or mho

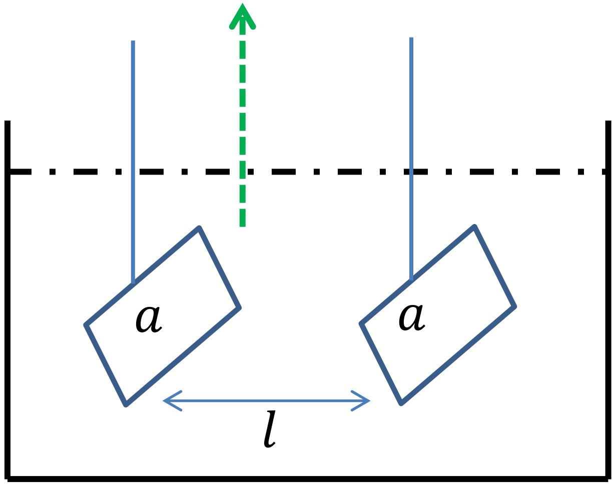
Resistance (R)

Resistance is related to the dimensions of electrolytic cell

$R \propto l$

$R \propto \frac{1}{a}$

Electrolyte is lying between 2 electrodes having area a and separated by l



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

ρ is known as specific resistance

Unit of R is ohm

Note that $\frac{l}{a}$ is termed as cell constant and does not change for a given cell

Specific Conductance (K

$$\boldsymbol{K = \frac{1}{\rho}}$$

$\boldsymbol{\rho}$ is specific resistance

Unit of $\boldsymbol{K}$ is **mho per cm**

And its SI is Siemens (S) → $1\,S = ohm^{-1}$

Since, $R = \rho \frac{l}{a}$

$$\boldsymbol{K} = \frac{1}{\rho} = \frac{1}{R} \times \text{cell constant}$$

Or

$$K = \text{Conductance} \times \text{cell constant}$$

Equivalent Conductance(Λ) And Molar Conductance

$\boldsymbol{\Lambda = K \times \text{volume (in ml)}}$

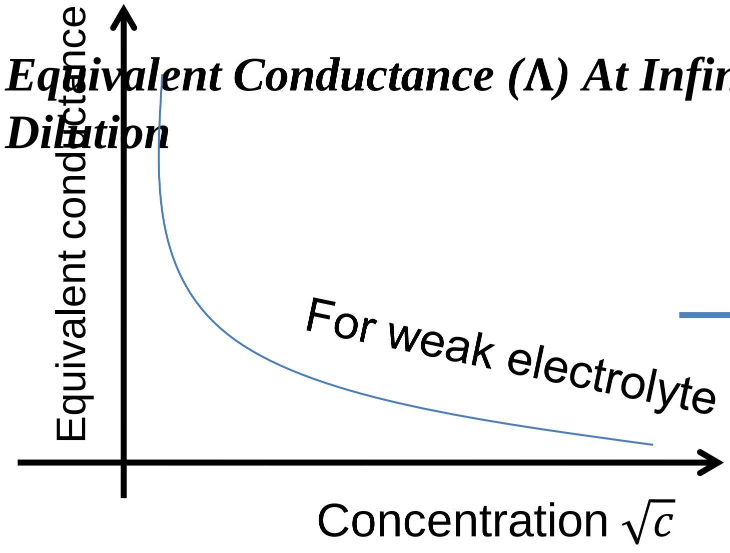
Note : V is the volume that contains 1 equivalents of the electrolyte

$\text{molar conductance} = K \times \text{volume(in ml)}$

Note that : it is the volume that contain 1 mole of electrolyte

Unit of both equivalent and molar conductance is mho cm^2

Equivalent Conductance (Λ) At Infinite Dilution



Assuming its degree of dissociation = α

Note that on dilution concentration will decrease

Λ increases with increase in dilution

But after a limit it becomes constant and does not further increase

$\mathbf{Maximum\ value}\ (\boldsymbol{\Lambda}_{\infty}) = \alpha \boldsymbol{\Lambda}_c$

$\boldsymbol{\Lambda}_c$ is equivalent conductance

Note that above expression can also be used to calculate α for a weak electrolyte

At infinite dilution an ionic specie contributes a fixed value at a given temperature, towards equivalent conductance of electrolyte

Note that : it is independent of other ionic species in combination with it

This contributions are known as **equivalent ionic conductance** at ∞ dilution

$\lambda_c{}^0 \; for\ cation$

$\lambda_a{}^0 \; for\ anion$

$$\therefore \quad \boldsymbol{\Lambda^0} \ (\textbf{of electrolyte at} \infty \textbf{ dilution}) \ = \boldsymbol{\lambda_c{}^0 + \lambda_a{}^0}$$

$$\boldsymbol{U = \frac{\textbf{ionic velocity}}{\textbf{potential gradient}}} \longrightarrow$$

potential gradient is potential difference between the electrodes

Unit of ionic mobility is $cm^2\ volt^{-1}s^{-1}$

Note that ionic mobility is the distance travelled by an ion under a potential gradient

Relation Between λ And U

$$\lambda \propto U$$

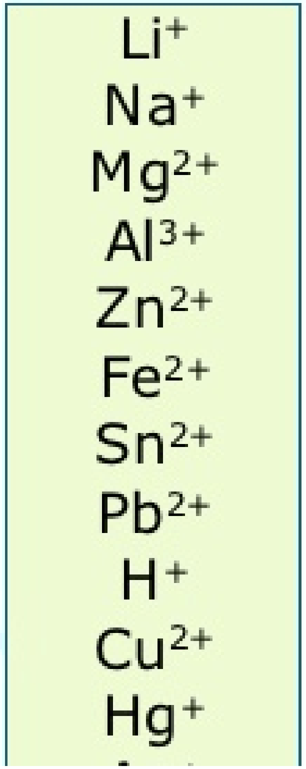
Or $\boldsymbol{\lambda = kU}$ → Where $k = 96500\ C$

$= 1F$

For cation : $\lambda_c{}^0 = kU_c{}^0$

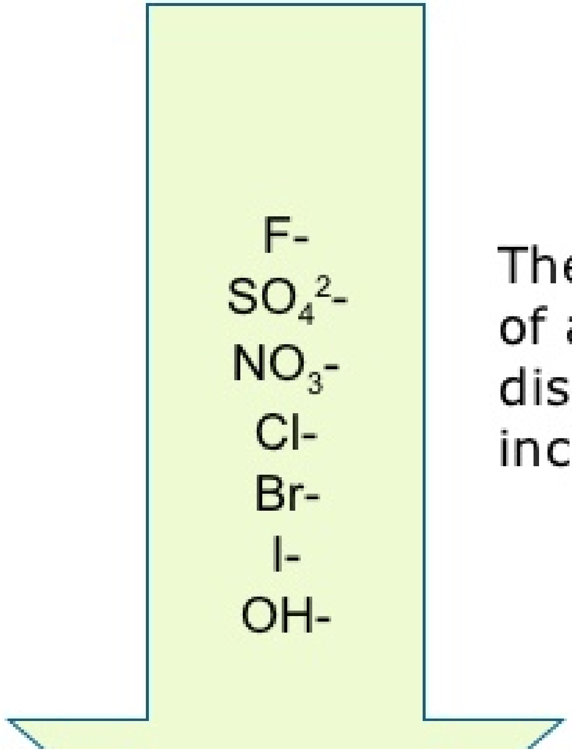
For anion $\lambda_a{}^0 = kU_a{}^0$

Note that : $\lambda^0 = k(U_c{}^0 + U_a{}^0)$ and this can be extended even if more than one cation or anion are there



Li^+
Na^+
Mg^{2+}
Al^{3+}
Zn^{2+}
Fe^{2+}
Sn^{2+}
Pb^{2+}
H^+
Cu^{2+}
Hg^+

The tendency of cation to discharge increases



F^-
SO_4^{2-}
NO_3^-
Cl^-
Br^-
I^-
OH^-

The tendency of anion to discharge increases

Solution: 1 Faraday, that is, 96500 coulombs deposits 1 gm equivalent of the substance. Now C × t amount of electricity deposits ‘m’ gm of substance

$\therefore$ 96500 C amount of electricity deposits

$$\frac{96500 \times m}{C.t} = \text{equivalent weight}$$

The answer is (c)

Example 2: One coulomb is equal to

(a) 96500 Faraday

(b) charge on 6.24×10^{18} electrons

(c) charge on 1 electron

(d) none of the above

Solution: Charge on 6.023×10^{23} electrons = 96500 C

So, 1 coulomb would be the charge on $\frac{6.023\times10^{23}}{96500} = 6.24 \times 10^{18}$ electrons.

The answer is (b)

Example 3: If three Faradays (F) of electricity is passed through the solutions of $AgNO_3$, $CuSO_4$ and $AuCl_3$, the molar ratio of the cations deposited at the cathode is

(a) 1 : 1 : 1 (b) 1 : 2 : 3

(c) 3 : 2 : 1 (d) 6 : 3 : 2

Solution: Since $Ag^+ + e^- \rightarrow Ag$, $Cu^{2+} + 2e^- \rightarrow Cu$, $Au^{3+} + 3e^- \rightarrow Au$, three Faradays of electricity will deposit 3 moles of Ag, 1.5 moles of copper, and 1 mole of gold. Therefore, the molar ratio is 3 : 1.5 : 1 or 6 : 3 : 2.

The answer is (d)

Example 4: During electrolysis of a concentrated aqueous solution of NaCl,the product at the cathode is

(a) Na (b) Cl_2

(c) O_2 (d) H_2

Solution: Chlorine gas is produced as chloride ions need a less voltage for oxidation to chlorine than needed by H_2O for oxidation to O_2 (This extra voltage needed by water is called over voltage).

The answer is (b)

Example 5: Two Pt electrodes fitted in a conductance cell are 1.5 cm apart and the cross-sectional area of each electrode is 0.75 cm^2. The cell constant is

(a) 1.25 (b) 0.5 cm

(c) 2.0 cm^{-1} (d) 0.2 cm^{-1}

Solution: Cell constant = $\frac{\ell}{a} = \frac{1.5}{0.75} = 2.0$ cm^{-1}

The answer is (c)

Example 6: The ionisation constant of a weak electrolyte is 25×10^{-6} and the equivalent conductance of its 0.01 M solution is 19.6 s cm^2 eq^{-1}. The equivalent conductance at infinite dilution of the electrolyte in s cm^2 eq^{-1} is

(a) 250 (b) 196

(c) 392 (d) 384

Solution: $HA \rightleftharpoons H^+ + A^-$

$C \quad O \quad O$

$C - C\alpha \quad C\alpha \quad C\alpha$

Or $K = C\alpha^2$

Or $25 \times 10^{-6} = 10^{-2}, \alpha^2$

Or $\alpha = 5 \times 10^{-2}$ Also $\alpha = \frac{\lambda_v}{\lambda_\infty} = \frac{19.6}{\lambda_\infty}$ or $\lambda_\infty = \frac{19.6}{5\times10^{-2}} = 392$

The answer is (c)

Example 7: How many c.c. of oxygen is released by a current of 2 A flowing for 3 minutes and 13 seconds in acidulated water?

(a) 11.2 c.c. (b) 33.6 c.c.

(c) 44.8 c.c. (d) 22.4 c.c.

Solution: $Q = 2 \times 193 = 386$ C

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

And, $O_2^- \rightarrow \frac{1}{2}O_2 + 2e^-$

2 mole of electrons = 2 × 96500 C give 1/2 mole of oxygen i.e., 11,200 cm^3.

So, 386 C will give $\frac{386 \times 11,200}{2 \times 96,500} = 22.4$ c.c. of oxygen.

The answer is (d)

Example 8: The cost of electricity required to deposit 1 g of Mg is Rs. 5.00. How much would it cost to deposit 10.0 g of Al? (Al = 27, Mg = 24)

(a) Rs.10.0 (b) Rs. 27.0

(c) Rs. 44.44 (d) Rs. 66.67

Solution: $Mg^{2+} + 2e^- \rightarrow Mg$

Quantity of electricity required to deposit 1.0 g of Mg

$$= \frac{2 \times 96500}{24}$$

$Al^{3+} + 3e^- \rightarrow Al.$

Quantity of electricity required to deposit 10.0 g of Al

$$= \frac{3 \times 96500}{27} \times 10$$

Cost = $\frac{3 \times 96500}{27} \times \frac{10 \times 5 \times 24}{2 \times 96500} =$ Rs. 44.44.

The answer is (c)

1. The equilibrium constant for a reaction is 1×10^{20} at 300 K. The standard free energy change for this reaction is :
(A) –115 kJ (B) +115 kJ (C) +166 kJ (D) –166 kJ

2. Standard electrode potentials of $Fe^{2+} + 2e \longrightarrow Fe$ and $Fe^{3+} + 3e \longrightarrow Fe$ are –0.440 V and –0.036 V respectively. The standard electrode potential (E°) for $Fe^{3+} + e \longrightarrow Fe^{2+}$ is :
(A) –0.476 V (B) –0.404 V (C) +0.404 V (D) +0.772 V

3. Consider the cell , $Mg(s) \mid \underset{(0.2M)}{Mg^{2+}} \parallel \underset{(10^{-3}\,M)}{Ag^{+}} \mid Ag$

Given $E^{o}_{Ag+|Ag} = 0.8$ volt ; $E^{o}_{Mg+2|Mg} = -2.37$ volt

(i) What will the effect on emf if concentration of Mg^{2+} ion is decreased to 0.1 M
(A) decreased to 3.022 V (B) increased by 3.022 V
(C) remains same (D) none

(ii) In the above question maximum work that can be obtained by operating the cell is :
(A) 611.8 kJ (B) 61.18 kJ (C) 107.2 kJ (D) 1072.5 kJ

Q.4 Consider the following cell reaction :

$Tl^{+3} + 2e^- \longrightarrow Tl^+$; $E^o = 1.26$ V

$Tl^+ + e^- \longrightarrow Tl$; $E^o = -0.336$ V

The standard potential of the $Tl^{+3}|Tl$ electrode is :

(A) 0.728 V (B) 0.824 V (C) 1.596 V (D) 2.52 V

Q.5 Two electro chemical cells are assembled in which the following reactions occur,

$V^{2+} + VO^{2+} + 2H^+ \longrightarrow 2V^{3+} + H_2O$; $E^o_{cell} = 0.616$ V

$V^{3+} + Ag^+ + H_2O \longrightarrow VO^{2+} + 2H^+ + Ag(s)$; $E^o_{cell} = 0.439$ V

then E^o for the half reaction , $V^{3+} + e^- \longrightarrow V^{2+}$, is : [Given : $E^o_{Ag^+|Ag} = 0.799$ V]

(A) –0.256 V (B) +0.256 V (C) –1.05 V (D) +1.05 V

Q.6 For the reaction , $H_2(g) + 2AgCl(s) + 2H_2O(l) \longrightarrow 2Ag(s) + 2H_3O^+(aq) + 2Cl^-(aq)$ at 25 ºC, the standard free energy of formation of AgCl(s), $H_2O(l)$ and ($H_3O^+ + Cl^-$) are : 109.7, – 237.2 and – 368.4 kJ mol^{-1} respectively . Then ΔG^o and E^o for the reaction is :

(A) – 43 kJ, 0.22 V (B) + 43 kJ, 0.22 V

(C) – 21.5 kJ, 0.11 V (D) + 21.5 kJ, 0.22 V

Q.7 Given : $Cu^{2+} + e^{-} \longrightarrow Cu^{+}$; $E^{o} = 0.15$ V

$Cu^{+} + e^{-} \longrightarrow Cu$; $E^{o} = 0.5$ V

Potential for $Cu^{2+} + 2e^{-} \longrightarrow Cu$; is :

(A) 0.325 V (B) 0.650 V (C) 0.050 V (D) 1.30 V

Q.8 Which of the following is always true regarding the spontaneity of reaction occurring in a galvanic cell ?

(A) $E^{o}_{cell} > 0, \Delta G^{o} < 0$ and $Q > K_c$ (B) $E^{o}_{cell} < 0, \Delta G^{o} < 0$ and $Q < K_c$

(C) $E^{o}_{cell} > 0, \Delta G^{o} > 0$ and $Q > K_c$ (D) $E^{o}_{cell} > 0, \Delta G^{o} < 0$ and $Q < K_c$

Q.9 If $E^{o}_{Fe2+|Fe} = x_1$ volt and $E^{o}_{Fe3+|Fe2+} = x_2$ volt, then $E^{o}_{Fe3+|Fe}$ will be :

(A) $(2x_1 + x_2)$V (B) $(3x_2 - x_1)$V (C) $\frac{(2x_1 + x_2)}{3}$V (D) $\frac{(x_1 + 2x_2)}{3}$V

Q.10 Given that $E^{o}_{Cu2+/Cu} = 0.34$ V ; $E^{o}_{Ag+|Ag} = 0.80$ V ; $E^{o}_{Mg2+|Mg} = -2.37$ and $E^{o}_{Al3+|Al} = -1.66$ V in which of the following cells the standard free energy decrease is maximum :

(A) $Mg \mid Mg^{2+} (1M) \parallel Cu^{2+} (1M) \mid Cu$ (B) $Mg \mid Mg^{2+} (1M) \parallel Ag^{+} (1M) \mid Cu$

(C) $Ag \mid Ag^{+} (1M) \parallel Al^{3+} (1M) \mid Al$ (D) $Cu \mid Cu^{2+} (1M) \parallel Ag^{+} (1M) \mid Ag$

Q.11 The electrical work done during the reaction at 298 K : $2Hg(l) + Cl_2(g) \longrightarrow Hg_2Cl_2(s)$ is :

given that : $E^o_{Cl2|Cl^-} = 1.36$ V ; $E^o_{Hg2Cl2|Hg,\ Cl^-} = 0.27$ V : $p_{Cl2} = 1$ atm,

(A) 210.37 kJ mol^{-1} (B) 105.185 kJ mol^{-1}

(C) 420.74 kJ mol^{-1} (D) 110.37 kJ mol^{-1}

Q.12 Which of the following changes will cause the free energy of the cell reaction to decrease :

$Zn \mid ZnSO_4(aq)\ (x_1M) \parallel HCl(aq)\ (x_2M) \mid H_2(g)$, Pt

(A) increase in the volume of HCl solution from 100 ml to 200 ml
(B) increase in pressure of hydrogen from 1 atm to 2 atm
(C) increase in molarity x_2 from 0.1 to 1 M
(D) decrease in molarity x_1 from 1M to 0.1 M

Q.13 If $Sn^{2+} + 2e^- \longrightarrow Sn$ $E^o = -0.14$ V

$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$ $E^o = 0.13$ V then :

(A) Sn^{2+} is unstable and disproportionates to Sn^{4+} and Sn
(B) Sn^{2+} is stable and disproportionation reaction is not spontaneous
(C) Sn^{4+} is easily reduced to Sn
(D) none of these

Q.14 For the reactions , $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$, $E^o = 1.51$ V

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$, $E^o = 1.23$ V

then for the reaction , $MnO_4^- + 4H+ + 3e^- \longrightarrow MnO_2 + 2H_2O$, E^o is :

(A) 1.70 V (B) 5.09 V (C) 0.28 V (D) 0.84 V

Q.15 For the fuel–cell reaction : $2H_2 + O_2 \longrightarrow 2H_2O$, $\Delta G = -475$ kJ. Hence E_{cell} is :

(A) 1.23 V (B) 2.46 V (C) 0.615 V (D) 0.31 V

1. A

2. D

3. (i)A, (ii)-A

4. A

5. A

6. A

7. A

8. D

9. C

10. B

11. A

12. C,D

13. B

14. A

15. A

CONDUCTION

Specific Conductance

The resistance (R) of a metallic conductor is directly proportional to its length (ℓ) and inversely proportional to its cross-sectional area (a), i.e.,

$$R \propto \frac{\ell}{a} \quad \Rightarrow \quad R = \rho \cdot \frac{\ell}{a}$$

$$\Rightarrow \quad \frac{1}{\rho} = \frac{1}{R} \cdot \frac{\ell}{a} \qquad \ldots\ldots(1)$$

Where ρ is a constant depending upon the nature of the material and is called specific resistance of the material.

The reciprocal of the resistance is called conductance and similarly, the reciprocal of specific resistance is called specific conductance,

Thus , from equation (1)

$$\text{Specific conductance} = \text{observed conductance} \times \frac{\ell}{a} \qquad \ldots\ldots(2)$$

When $l = 1$ cm and a = 1 cm^2

Specific conductance = observed conductance

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 conductor.

The unit of resistance is ohm (Ω) so unit of conductance will be ohm^{-1}, mho or Ω^{-1} and expressing ℓ in cm and a in cm^2, the unit of specific conductance will be $ohm^{-1}cm^{-1}$, $\Omega^{-1} cm^{-1}$ or mho cm^{-1}. In SI system, the units of specific conductance are Sm^{-1} where S stands for Siemen.

The equation (2) mentioned above is also applicable for solution of an electrolyte i.e. electrolytic conductor. The specific conductance of an electrolytic solution is defined as the conductance that is observed when two electrodes each of 1 sq. cm in cross-sectional are dipped into solution at a distance of 1 cm apart. In other words, specific conductance is the conductance per c.c. solution of the electrolyte. It is denoted by the symbol κ (kappa). Sometimes κ_v or κ_c is also used, the subscript v or c standing for dilution or concentration, respectively, signifying that κ is dilution or concentration dependent.

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 such a distance so as to enclose in between them the entire volume of solution containing one equivalent of the electrolyte. It is denoted by the symbol $\wedge$.

Let one equivalent of an electrolyte is dissolved in V mL solution. Then all the ions produced by 1 equivalent of the electrolyte will be present in this V mL solution. So, the conductance of this V c.c. solution will be the equivalent conductance of the electrolyte i.e.

$\wedge_{eq}$ = Conductance of V c.c. solution containing one equivalent of the dissolved electrolyte.

= Conductance of 1 c.c solution × V

$$= \kappa \times V \qquad \text{.......(3a)}$$

Where v = volume of solution in c.c containing 1 equivalent of the electrolyte
If C be the normality of solution i.e. concentration of electrolytic solution in equivalent/L, then

$$V = \frac{1000}{C}$$

$$\therefore \quad \wedge = \frac{1000\,\kappa}{C} \qquad \text{.......(3b)}$$

Unit of $\wedge$: $\text{Ohm}^{-1}\,\text{cm}^{-1} \times \text{cm}^{3}$ i.e. $\text{Ohm}^{-1}\,\text{cm}^{2}$ or $\Omega^{-1}\text{cm}^{2}$

Molar Conductance

The recent trend is to describe electrolytic conductance in terms of molar conductance which is defined as the conductance of solution due to all the ions produced by one mole of the dissolved electrolyte in a given solution.

It is denoted by the symbol $\wedge_m$

$\wedge_m$ and κ are inter-related as

$\wedge_m = \kappa \times v$

$$\Rightarrow \quad \wedge_m = \frac{1000\,\kappa}{C} \qquad \text{.......(4)}$$

Where v = Volume of solution in c.c. containing one mole of the electrolyte and

C = Concentration of solution in mole L^{-1} i.e. molarity

The above inter-relationship may also be expressed as

Unit of $\wedge_m$: $\Omega^{-1}cm^{2}mol^{-1}$

In SI system it is $S\ m^{2}\ mol^{-1}$

Relation between $\wedge$ and $\wedge$m;

$$\wedge_m = n\ \text{factor} \times \wedge_{eq}$$

Where n = n-factor of the electrolyte = total charge carried by either ion = $\frac{M}{E}$

11. Variation of Conductance with Dilution :

Upon dilution i.e. lowering concentration, specific conductance decreases 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 ($\wedge^{\infty}$) or zero concentration ($\wedge^{0}$) and molar conductance at infinite dilution ($\wedge_m^{\infty}$) or zero concentration ($\wedge_m^{0}$), respectively.

The increase of $\wedge_{eq}$ or $\wedge_m$ with dilution of a weak electrolyte is attributable to increase of degree of dissociation with dilution resulting into more number of ions in solution.

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

$$\wedge_m = \wedge_m^0 - \left(A + B\wedge_m^0\right)\sqrt{C}$$

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.

For aqueous medium at 25°C:

$$\wedge_m = \wedge_m^0 - \left(60.2 + 0.229\wedge_m^0\right)\sqrt{C}$$

According to this equation a plot of $\wedge_m$ vs $\sqrt{C}$ should be a straight line having the slope equal to 60.2 + 0.229 $\wedge_m^0$ and intercept equal to $\wedge_m^0$. This has been checked in the case of a number of uni-univalent electrolytes and found to be positive for $C \leq 0.02$ M. At higher concentration, the observed deviation from linearity is attributable to large inter-ionic attraction.

Determination of Conductance (κ, $\wedge_{eq}$ and $\wedge_m$)

As already mentioned above

$$\kappa = \text{Observed conductivity} \times \frac{\ell}{a}$$

For a given conductivity cell in a given experiment, $\frac{\ell}{a}$ = constant called cell constant (x).

Thus,

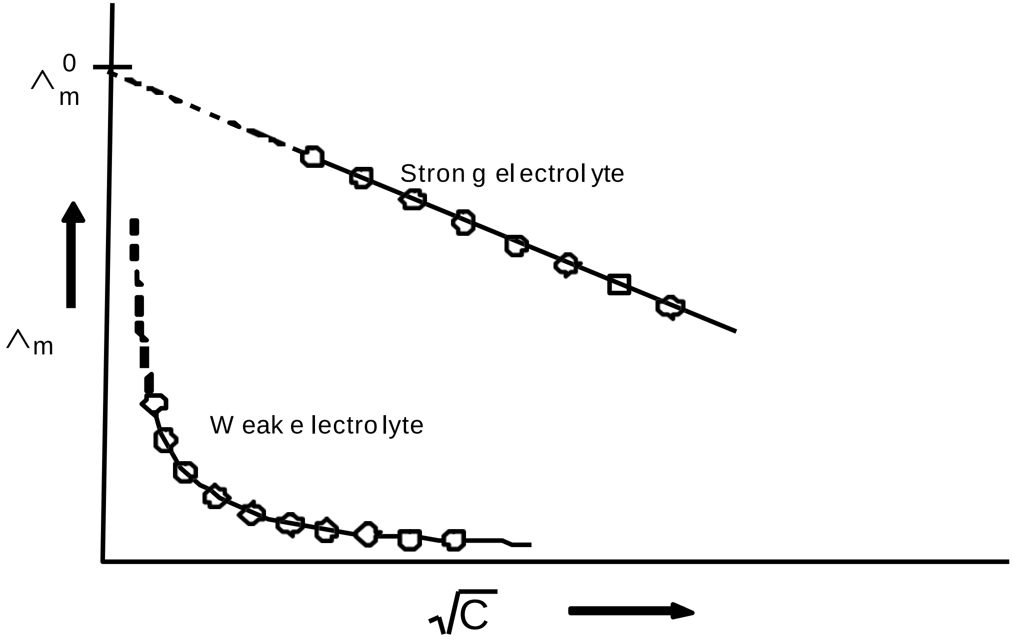
$$\kappa = \text{Observed conductance} \times x = \frac{1}{\text{Observed resistance}} \times x$$

The resistance of a solution is determined by Wheatstone bridge method using a meter bridge the conductivity cell remains dipped in the test solution. The current used is AC. removed from the cell, it is washed with conductivity water and then filled with test solution. The resistance of the test solution is measured and since cell constant is already known so specific

From specific conductance, we determine $\wedge_{eq}$ and $\wedge_m$ using the equation (3) and equation (4) respectively.

Determination of $\wedge_m^0$ or $\wedge^0$

A plot of $\wedge_m$ vs $\sqrt{C}$ as found experimentally is as shown below graphically .



The $\wedge_m$ vs $\sqrt{C}$ plot of strong electrolyte being linear it can be extrapolated to zero concentration. Thus, $\wedge_m$ values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

$\wedge_m$ values are then plotted against $\sqrt{C}$ when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects $\wedge_m$ axis is $\wedge^0_m$ of the strong electrolyte.

However, the plot in the case of weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to $\wedge_m$ axis. Hence extrapolation in this case is not possible. Thus , $\wedge_0$ of a weak electrolyte cannot be determined experimentally. It can , however , be done with the help of Kohlrausch’s law to be discussed later.

Q.

1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.

Solution :

Given l = 2.1 cm , a = 4.2 sq. cm , R = 50 ohm

Specific conductance, $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

or $\kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$

Equivalent conductivity = $\kappa \times V$

V = the volume containing 1 g equivalent = 1000 ml

So Equivalent conductivity = 0.01 × 1000

= 10 $\text{ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$

Q.

Specific conductance of a decinormal solution of KCl is 0.0112 ohm^{-1} cm^{-1}. The resistance of a cell containing the solution was found to be 56. What is the cell constant?

Solution :

We know that

Sp. conductance = Cell constant × conductance

$$\text{or}\quad \text{Cell constant} = \frac{\text{Sp. conductance}}{\text{Conductance}}$$

$$= \text{Sp. conductance} \times \text{Resistance}$$

$$= 0.0112 \times 56$$

$$= 0.6272\ \text{cm}^{-1}$$

Illustration 27.

The specific conductivity of 0.02 M KCl solution at 25 ºC is 2.768 × 10^{-3} ohm^{-1} cm^{-1}. The resistance of this solution at 25 ºC when measured with a particular cell was 250.2 ohms. The resistance of 0.01 M $CuSO_4$ solution at 25 ºC measured with the same cell was 8331 ohms. Calculate the molar conductivity of the copper sulphate solution.

Solution :

$$\text{Cell constant} = \frac{\text{Sp. cond. of KCl}}{\text{Conductance of KCl}}$$

$$= \frac{2.768 \times 10^{-3}}{1/250.2}$$

$$= 2.768 \times 10^{-3} \times 250.2$$

For 0.01 M $CuSO_4$ solution

Sp. conductivity = Cell constant × conductance

$$= 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$$

Molar conductance = Sp. cond. × $\frac{1000}{C}$

$$= \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100}$$

$$= 8.312 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

Q

A 0.05 N solution of a salt occupying a volume between two platinum electrodes separated by a distance of 1.72 cm and having an area of 4.5 cm^2 has a resistance of 250 ohm. Calculate the equivalent conductance of the solution.

Solution :

Specific conductance = conductance × cell constt.

$$K = C \times \frac{l}{A} \qquad = \frac{1}{R} \times \frac{l}{A} \qquad = \frac{1}{250} \times \frac{1.72}{4.5}$$

$$= 1.5288 \times 10^{-3}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\Lambda_e = K \times \frac{1000}{N} = 1.5288 \times 10^{-3} \times \frac{1000}{0.05} = 30.56\ \text{ohm}^{-1}\ \text{cm}^{2}\ \text{eq}^{-1}$$

12. Kohlrausch's Law of Independent Migration of Ions :

Kohlrausch determined $\wedge_0$ values of pairs of some strong electrolytes containing same cation say KF and KCl , NaF and NaCl etc., and found that the difference in $\wedge_0$ values in each case remains the same .

$$\wedge^0_m(\text{KCl}) - \wedge^0_m(\text{KF}) = \wedge^0_m(\text{NaCl}) - \wedge^0_m(\text{NaF})$$

He also determined $\wedge_0$ values of pairs of strong electrolytes containing same anion say KF and NaF , KCl and NaCl etc. and found that the difference in $\wedge_0$ values in each case remains the same .

$$\wedge^0_m(\text{KF}) - \wedge^0_m(\text{NaF}) = \wedge^0_m(\text{KCl}) - \wedge^0_m(\text{NaCl})$$

This experimental data led him to formulate the following law called Kohlrausch’s law of independent migration of ions.

At infinite dilution when dissociation is complete , every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contributions of the two ions . Thus

$$\wedge_m^0 = \lambda_+^0 + \lambda_-^0 \qquad \ldots\ldots(5)$$

Where λ_+^0 is the contribution of the cation and λ_-^0 is the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductance of anion, at infinite dilution. The above equation (5) is, however, correct only for binary electrolyte like NaCl, $MgSO_4$ etc.

For an electrolyte of the type of A_xB_y, we have :

$$\wedge_m^0 = x\lambda_+^0 + y\lambda_-^0$$

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 electrolytes :

(a) A strong electrolyte containing same cation as in the test electrolyte , say HCl

(b) A strong electrolyte containing same anion as in the test electrolyte , say CH_3COONa

(c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

Λ_m^0 of CH_3COOH is then given as :

$$\Lambda_m^0(CH_3COOH) = \Lambda_m^0(HCl) + \Lambda_m^0(CH_3COONa) - \Lambda_m^0(NaCl)$$

Proof :

$$\Lambda_m^0(HCl) = \lambda_H^0 + \lambda_{Cl^-} \qquad \ldots \text{ I}$$

$$\Lambda_m^0(CH_3COONa) = \lambda^0_{CH_3COO^-} + \lambda_{Na^+} \qquad \ldots \text{ II}$$

$$\Lambda_m^0(NaCl) = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \qquad \ldots \text{ III}$$

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

$$\wedge^0_{(HCl)} + \wedge^0_{(CH_3COONa)} - \wedge^0_{(NaCl)} = \lambda^0_{(H^+)} + \lambda^0_{(CH_3COO^0)} = \wedge_{0(CH_3COOH)}$$

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

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

(iii) Determination of solubility of sparingly soluble salt :

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to $\wedge^0_m$ as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\wedge^0_m = \frac{1000\kappa}{C},$$

Where C is the molarity of solution and hence the solubility.

(iv) Determination of ionic product of water :

From Kohlrausch’s law , we determine $\wedge_m^0$ of H_2O where $\wedge_m^0$ is the molar conductance of water at infinite dilution when one mole of water is completely ionised to give one mole of H^+ and one mole of OH^- ions i.e.

$$\wedge_m^0 (H_2O) = \lambda^0_{H^+} + \lambda^0_{OH^-}$$

Again using the following

$$\wedge_m = \frac{\kappa \times 1000}{C}$$, where C = molar concentration i.e. mol L^{-1} or mol dm^{-3}

$$\Rightarrow \quad \wedge_m = \frac{\kappa}{C}$$, where C = concentration in mol m^{-3}

Assuming that $\wedge_m$ differs very little from $\wedge_m^0$

$$\wedge_m^0 = \frac{\kappa}{C} \Rightarrow C = \frac{\kappa}{\wedge_m^0}$$

Specific conductance (κ) of pure water is determined experimentally. Thereafter, molar concentration of dissociated water is determined using the above equation . K_w is then calculated as : $K_w = C^2$

Q.

The equivalent conductances of sodium chloride , hydrochloric acid and sodium acetate at infinite dilution are 126.45 , 426.16 and 91.0 ohm^{-1} cm^{2} equiv^{-1}, respectively at 25 ºC. Calculate the equivalent conductance of acetic acid at infinite dilution.

Solution :

According to Kohlrausch's law,

$$\Lambda_{\infty CH_3COONa} = \lambda_{CH_3COO^-} + \lambda_{Na^+} = 91.0 \qquad ....(i)$$

$$\Lambda_{\infty HCl} = \lambda_{H^+} + \lambda_{Cl^-} = 426.16 \qquad ......(ii)$$

$$\Lambda_{\infty NaCl} = \lambda_{Na^+} + \lambda_{Cl^-} = 126.45 \qquad ....(iii)$$

Adding equations (i) and (ii) and substracting (iii),

$$\lambda_{CH_3COO^-} + \lambda_{Na^+} + \lambda_{H^+} + \lambda_{Cl^-} - \lambda_{Na^+} - \lambda_{Cl^-}$$

$$= 91.0 + 426.16 - 126.45$$

$$\lambda_{CH_3COO^-} + \lambda_{H^+} = \Lambda_{\infty CH_3COOH} = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

Q.

A decinormal solution of NaCl has specific conductivity equal to 0.0092. If ionic conductance of Na^{+} and Cl^{-} ions at the same temperature are 43.0 and 65.0 ohm^{-1} respectively, calculate the

degree of dissociation of NaCl solution.

Solution :

Equivalent conductance of N/10 NaCl solution

Λ_υ = Sp. conductivity × dilution

= 0.0092 × 10000

= 92 ohm–1

$$\Lambda_\infty = \lambda_{Na^+} + \lambda_{Cl^-}$$

$= 43.0 + 65.0 \quad = 108 \text{ ohm}^{-1}$

Degree of dissociation , $\alpha = \frac{\Lambda_\upsilon}{\Lambda_\infty} = \frac{92}{108} = 0.85$