ELECTRO-CHEMISTRY

1. Equivalent conductance, $\Lambda = \dfrac{\sigma \times 1000}{C}$
2. Molar conductance, $\Lambda_m = \dfrac{\sigma \times 1000}{M}$
3. According to Kohlrausch's law,

   $$\Lambda_m^\infty = n_+\Lambda_{m+}^\infty + n_-\Lambda_{m-}^\infty$$

4. $$\mathrm{E}\left(\mathrm{M}^{+n}/\mathrm{M}\right) = \mathrm{E}^\circ\left(\mathrm{M}^{n+}/\mathrm{M}\right) - \frac{2.303\,RT}{nF}$$

   $$\log \frac{\left[M(s)\right]}{\left[M^{n+}(aq)\right]} \text{ (Nerns't equation)}$$

5. $\mathrm{E}^\circ{}_{\mathrm{cell}} = 2.303\,\dfrac{RT}{nF}\log \mathrm{K}_c$
6. $\Delta\,\mathrm{G}^\circ = -n\mathrm{F}\,\mathrm{E}^\circ{}_{\mathrm{cell}} = -2.303\ \mathrm{RT}\ \log\ \mathrm{K}_c$
7. $m = \mathrm{WIt}$ (Faraday's law of electrolysis)

Conductors and insulators

The substances which permit the passage of electric current through them, are called as conductors. But the substances which do not permit the passage of electric current through them, are called as non-conductors or insulators. Metals are good conductors of electricity.

Electrolytes and non-electrolytes

The substances which permit the passage of electric current through their molten state or in solution and are decomposed by it, are known as **electrolytes**. This phenomenon of passage of electric current through an electrolytic solution is known as **electrolytic conduction**. While, the substances which do not permit the passage of electric current through their molten state or in solution and are not decomposed by it, are known as **non-electrolytes**.

I. **Specific resistance or resistivity:** Specific resistance or resistivity of the material of a conductor is defined as the resistance of unit length and unit area of cross-section of that conductor.

Now specific resistance or resistivity is given as,

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

Whare R = Resistance of the conductor
A = Area of cross-section of the conductor
l = Length of the conductor.

Its SI unit is ohm metre (Ωm).

II. Conductance: The reciprocal of the resistance of a conductor is called its conductance. It is denoted by G.

So,

$$G = \frac{1}{R}$$

Its SI unit is mho or ohm^{-1} (Ω^{-1}).

III. Specific conductance or conductivity: The reciprocal of the resistivity of the material of a conductor is called its conductivity. It is denoted by σ. Hence,

$$\sigma = \frac{1}{\rho}$$

Its SI unit is ohm^{-1} metre^{-1} ($\Omega^{-1}\, m^{-1}$).

IV. **Equivalent conductance:** Equivalent conductance is defined as the conductance of a volume of solution containing one gram equivalent of an electrolyte in solution. It is denoted by symbol Λ. Its unit is ohm^{-1} cm^2 $(\text{g-equiv})^{-1}$.

Now, $$\Lambda = \frac{\sigma \times 1000}{C}$$

Where σ = specific conductance.
C = equivalents of solute per litre of solution.

V. **Molar conductance** is defined as the conductance of a volume of solution containing one gram mole of an electrolyte in solution. It is denoted by Λ_m. Its unit is $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$.

Now, $$\Lambda_m = \frac{\sigma \times 1000}{M}$$

Where σ = specific conductance.
M = concentration of the solution in moles per litre.

VI. **Electrolytic cell:** It is a device used to convert electrical energy into chemical energy. Reduction takes place at cathode and oxidation takes placed at anode. When electricity is passed through electrolyte, it dissociates into its ions, cations move towards the cathode and anions move towards the anode. When electricity is passed through molten sodium chloride, then,

Electrochemical reaction, NaCl $\rightleftharpoons Na^+ + Cl^-$

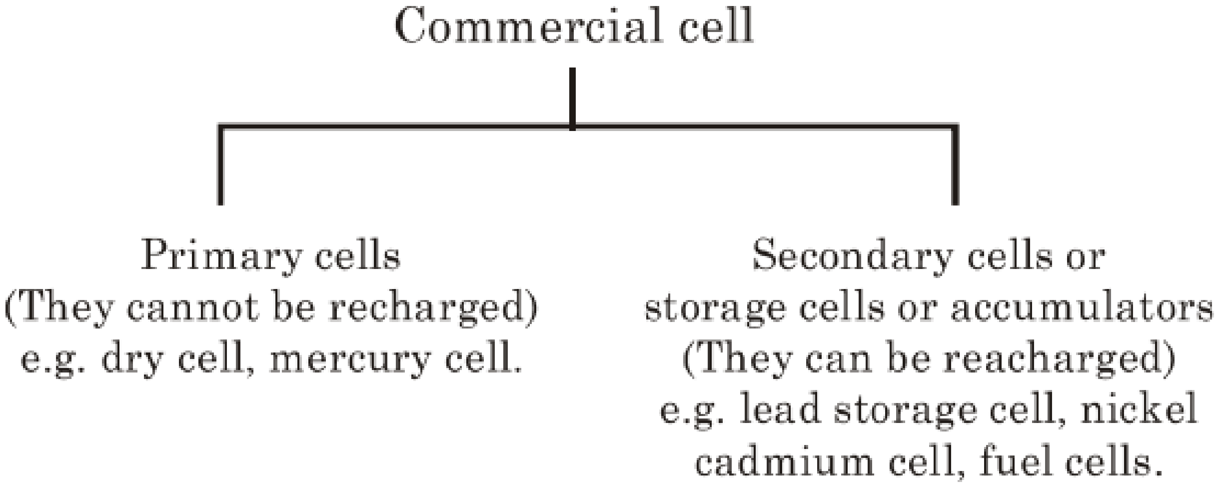
At cathode : $Na^+ + e^- \rightarrow Na$ (reduction)
At anode : $Cl^- - e^- \rightarrow Cl$ (oxidation)
$Cl + Cl \rightarrow Cl_2$

VII. Faraday's laws of electrolysis:

First law of electrolysis: During electrolysis, the mass of the substance produced or consumed at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.
Hence, $m = WIt$

Second law of electrolysis: When the same quantity of electricity is passed through different electrolytes connected in series, the weight of different substances produced at the electrodes are proportional to their equivalent weight.

VIII. Commercial cell or batteries: A battery is a series combination of two or more electrochemical cells used as a source of electrical energy. Following are the types of commercial cells.


Commercial cell

Primary cells
(They cannot be recharged)
e.g. dry cell, mercury cell.

Secondary cells or
storage cells or accumulators
(They can be reacharged)
e.g. lead storage cell, nickel
cadmium cell, fuel cells.

IX. **Electrolytic corrosion:** Corrosion is the gradual deterioration of metal by atmospheric attack. It is an electrochemical reaction. Corrosion of iron is called as rusting. Rust is mainly a mixture of ferric hydroxide [$Fe(OH)_3$] and ferric oxide [Fe_2O_3.].

Factors Affecting Molar Conductance

(a) **Nature of electrolytes:** If greater the number of ions in the solution, then greater is the conductance. Strong electrolytes dissociate completely into its ions and give large number of ions, therefore have high conductance. Weak electrolytes ionize to small extent and give lesser number of ions, so have low conductance.

(b) Concentration of the solution: Molar conductance of an elctrolyte increases with decrease in concentration.

For strong electrolytes, variation of molar conductance with concentration is given as,

$$\Lambda_m = \Lambda_m^{\infty} - b\sqrt{C}$$

Where Λ_m^{∞} = molar conductance at infinite dilution

C = concentration

b = a constant

(c) Temperature: The conductance of electrolytes increases with increase in temperature.

Kohlrausch's Law of Independant Migration of Ions

According to this law *at infinite dilution, if dissociation for all electrolytes is complete and if all inter-ionic effects disappear each ion migrates independently, and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature and not at all on that of the ion with which it is* *associated. So, Λ_m of any electrolyte is the sum of the molar conductances of the ions composing it. Molar conductances of cations and anions at infinite dilution are represented as*

Λ^{∞}_{m+} and $\Lambda^{\infty}_{\mathrm{m}-}$ respectively. Now,

$$\Lambda^{\infty}_{m} = n_+ \Lambda^{\infty}_{m+} + n_- \Lambda^{\infty}_{m-}$$

where n_+ and n_- are the number of cations and anions per formula unit of electrolyte.

For NaCl, $\Lambda^{\infty}_{m}(\mathrm{NaCl}) = \Lambda^{\infty}_{m+}\left(\mathrm{Na}^{+}\right) + \Lambda^{\infty}_{m-}\left(\mathrm{Cl}^{-}\right)$.

For $\mathrm{Al_2(SO_4)_3}$, $\Lambda^{\infty}_{m}\left[\mathrm{Al_2(SO_4)_3}\right] = 2\Lambda^{\infty}_{m+}\left(\mathrm{Al}^{3+}\right) + 3\Lambda^{\infty}_{m-}\left(\mathrm{SO_4^{2-}}\right)$

Differences Between Electrochemical Cell and Electrolytic Cell

	Electrochemical Cell (or galvanic cell or valtaic cell)		**Electrolytic cell**
I.	It is a device used to convert chemical energy into electrical energy	I.	It is a device used to convert electrical energy into chemical energy.

II. Cell reaction is spontaneous.	II. Cell reaction is non-spontaneous.
III. Free energy decreases as the cell reaction proceeds.	III. Free energy increases as the cell reaction proceeds.
IV. Work is obtained from the cell.	IV. Work is done on the cell.
V. The two electrodes are placed in different containers called *half cells*, connected through *salt bridge*.	V. Both the electrodes are placed in the same container.
VI. Oxidation occurs at anode (negative terminal) and reduction occurs at cathode (positive terminal).	VI. Oxidation occurs at cathode (negative) and reduction occurs at anode (positive).

Electrochemical Cell

In electrochemical cell, electricity is produced by spontaneous chemical reaction. In redox-reaction simultaneous loss and gain of electrons takes place. The electrons lost by reducing agents are taken up by oxidising agent, which causes the transfer of electrons and produced electricity. Electrochemical cells are also called as voltaic cells or galvanic cells.

Voltaic cell consists of zinc rod dipped in 1.0M copper sulphate solution. Electrons pass from zinc atoms to copper ions in which they are in direct contact with each other.

Oxidation half reaction:

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

Reduction half reaction:

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

Overall reaction:

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

Zinc Cupric ion Zinc ion Copper

Hence, It is represented as Zn (s) | Zn^{2+} (1M) || Cu^{2+} (1M) | Cu (s).

Daniel cell: It consists of two half cells, anode half cell and cathode half cell. The anode half cell consists of zinc electrode (anode) immersed in zinc sulphate solution and cathode half cell consists of copper electrode (cathode) immersed in copper sulphate solution. These two electrodes are connected with a copper wire through ammeter. The two solutions are connected through salt bridge.

At anode:

$$Zn(s) \rightarrow Zn^{2+}\ (aq) + 2e^{-} \quad \text{(oxidation)}$$

At cathode:

$$Cu^{2+}\ (aq) + 2e^{-} \rightarrow Cu\ (s) \qquad \text{(reduction)}$$

Electrochemical reaction:

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

As the reaction starts, the mass of zinc rod decreases and that of copper rod increases.

Salt bridge: Salt bridge contains an inert paste of a strong electrolyte (Na_2SO_4 or KCl) and agar gel. Which prevents the mixing of two electrolytes and allows the migration of ions from cathode half cell to anode half cell.

Electrode Potential and E.M.F. of a Cell

Electrode potential: Electrode potenital is defined as the tendency of a metal to lose or gain electrons when placed in contact with its ions. It is of two types :

(a) **Oxidation potential:** The tendency of an electrode to lose electrons is known as its oxidation potential.

$Zn \rightleftharpoons Zn^{2+}(aq) + 2e^-$

(b) **Reduction potential:** The tendency of an electrode to gain electrons is known as its reduction potential.

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

Oxidation potential is equal and opposite of reduction potential.

The electrode potential depends upon

- (*a*) Concentration of metal ions in solution.
- (*b*) Nature of the metal and its ions.
- (*c*) Temperature.

E.M.F. or Cell Potential

The difference between the electrode potentials of the two electrodes providing an electrochemical cell is called, as electromotive force (E.M.F.) or cell potenital of a cell. Which is represented as E_{cell} and expressed in volts.

$$E_{cell} = E_{cathode} - E_{anode}$$

Distinctions Between E.M.F. and Potential Difference

	E.M.F		Potential difference
I.	It is the potential difference between the two electrodes when no current is being drawn from the cell i.e., in open circuit.	I.	It is the difference of potentials of two electrodes when current is being drawn from the cell i.e., in closed circuit.
II.	It is measured with the help of a potentiometer.	II.	It is measured with the help of a voltmeter.

III. It is the maximum voltage that can be drawn from the cell.	III. It is less than the E.M.F. of the cell.
IV. It is a measure of maximum useful work obtainable from the cell.	IV. It gives work which is less than the maximum obtainable work.

Electrode Potential, Electrolysis and E.M.F.

(*i*) $M^{n+} + ne = M$

(*ii*) $E_{OX.} + E_{Red}$ = e.m.f. (of cell) in volt

(*iii*) $\Delta G = -nEF$.

where, ΔG = Change in free energy

n = no. of electrons used in the reaction

E = e.m.f. of cell and

F = Faraday's constant = 96,500 coulombs

(*iv*) $\log K_e = \frac{nEF}{2.303RT}$, At 25°C, T = 273 + 25

= 298K and

$\frac{2.303}{F} = 0.059$ so, at 25°C, $\log K_e = \frac{nE}{0.059}$

where, K_e = equilibrium constant
E = e.m.f. of cell and
n = no. of electrons used in the reaction.

(*v*) Nernst equation : For $M_1^{n+} + M_2 \rightleftharpoons M_1 + M_2^{n+}$

$$E_{ox} = E_{ox}^0 - \frac{2.303RT}{nF} \log K_e;$$ where, E_{ox} = Oxidation potential and E_{ox}^o = standard oxidation potential

(*vi*) $W = ZQ = Z.i.t$ (Ist law of electrolysis)

(*vii*) $Z = \frac{E}{F} \therefore W = \frac{E}{F} i.t.$

(*viii*) $1F = 96{,}500$ coulomb $= N \times e = 6.023 \times 10^{23} \times 1.6 \times 10^{-19}$ coulombs

(*ix*) $\frac{W_A}{W_B} = \frac{E_A}{E_B}$ (2nd law of electrolysis)

(*x*) $\frac{Z_A}{Z_B} = \frac{E_A}{E_B}$; where, Z is called electrochemical equivalent and E is called chemical equivalent of the substance.

(*xi*) Oxidation occurs at anode.

(*xii*) Reduction occurs at cathode.

(*xiii*) 1F ≡ 1 gram equivalent of a substance
= 11,200 ml H_2 at N.T.P. = 5,600 ml O_2 at N.T.P.

(*xiv*) 1 Ampere = 1 Coulomb × 1 sec.

(*xv*) Unit of Z is the unit of mass per unit charge.