ELECTROCHEMICAL SERIES

- **Electrochemistry:** The branch of physical chemistry that study the relationship between elctricity,as a measurable and quantitative phenomenon and indefinite chemical change with either electricity cons0idered an outcome of a particular chemical change or vice versa.
- It deals with the interaction between the electrical and chemical change.
- English chemist Jhon Daniell and physicist Michael Faraday both considered as a founder of electrochemistry today.

ELECTROCHEMICAL SERIES:

- When elements are arranged in order of their standard electrode potentials or in the decreasing order of their standard reduction potentials is called Electrochemical Series.
- They are also known as Electromotive Force or e.m.f. series.

Characteristics of Electrochemical Series:

- In this series, all reduction potentials are given on hydrogen scale whose Eo is taken as zero.
- The standard reduction potential of an element is a measure of the tendency of that element to get reduced.
- The elements which have greater reduction potential will get easily reduced. While the elements with low reduction potential will get easily oxidized.
- Elements that lose electrons more easily have lower reduction potential and those which lose electrons with greater difficulty instead of loosing electrons, they accept electrons more easily, have higher reduction potential.
- In EMF series elements having higher reduction potential is placed at the top. While those having lower reduction potential are placed at the bottom. SHE has middle position in electrochemical series.

  The substance which are stronger reducing agents than hydrogen are placed below hydrogen in the series and have negative reduction potential. The substance which are weaker reducing agents than hydrogen are placed above hydrogen and have positive standard reduction potential. Thus as we move down the groups strength of reducing agent while strength of oxidizing agent decrease.

- An important point to remember in using reduction potential values is that they relate only to standard condition i.e. 1 M solution of ions, one atmospheric pressure at room temperature.

- Change in temperature, concentration and pressure will affect the values of reduction potential.

- The electrode potential has given in reduction mode as recommended by **International Union of Pure and Applied Chemistry** (IUPAC).

Standard reduction potentials of elements at 298 K

Stronger oxidizing agent ⬆	$F_2(g) + 2e^-$	⟶ $2F^-(aq)$	2.87
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	⟶ $2H_2O(l)$	1.78
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	⟶ $Mn^{2+}(aq) + 4H_2O(l)$	1.51
	$Cl_2(g) + 2e^-$	⟶ $2Cl^-(aq)$	1.36
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	⟶ $2Cr^{3+}(aq) + 7H_2O(l)$	1.33
	$O_2(g) + 4H^+(aq) + 4e^-$	⟶ $2H_2O(l)$	1.23
	$Br_2(l) + 2e^-$	⟶ $2Br^-(aq)$	1.09
	$Ag^+(aq) + e^-$	⟶ $Ag(s)$	0.80
	$Fe^{3+}(aq) + e^-$	⟶ $Fe^{2+}(aq)$	0.77
	$O_2(g) + 2H^+(aq) + 2e^-$	⟶ $H_2O_2(aq)$	0.70
	$I_2(s) + 2e^-$	⟶ $2I^-(aq)$	0.54
	$O_2(g) + 2H_2O(l) + 4e^-$	⟶ $4OH^-(aq)$	0.40
	$Cu^{2+}(aq) + 2e^-$	⟶ $Cu(s)$	0.34
	$Sn^{4+}(aq) + 2e^-$	⟶ $Sn^{2+}(aq)$	0.15
	$2H^+(aq) + 2e^-$	⟶ $H_2(g)$	0
	$Pb^{2+}(aq) + 2e^-$	⟶ $Pb(s)$	−0.13
	$Ni^{2+}(aq) + 2e^-$	⟶ $Ni(s)$	−0.26
	$Cd^{2+}(aq) + 2e^-$	⟶ $Cd(s)$	−0.40
	$Fe^{2+}(aq) + 2e^-$	⟶ $Fe(s)$	−0.45
	$Zn^{2+}(aq) + 2e^-$	⟶ $Zn(s)$	−0.76
	$2H_2O(l) + 2e^-$	⟶ $H_2(g) + 2OH^-(aq)$	−0.83
	$Al^{3+}(aq) + 3e^-$	⟶ $Al(s)$	−1.66
	$Mg^{2+}(aq) + 2e^-$	⟶ $Mg(s)$	−2.37
Weaker oxidizing agent	$Na^+(aq) + e^-$	⟶ $Na(s)$	−2.71
	$Li^+(aq) + e^-$	⟶ $Li(s)$	−3.04

Weaker reducing agent ⬇ ... Stronger reducing agent

Down the series:

Reduction potentials decrease
Oxidation potentials increase
Non metalic properies decrease
Metalic properties increase
Strength of reducing agent increase
Strength of oxidising agent decrease
Reactivity of non metals decrease
Reactivity of metals increase
Electronegativity of non metals decrease
Electronegativity of metals decrease
Electropositivity of non metals increase
Electropositivity of metals increase
Thermal Stability of metal oxide increases

Down the Series

Application of Electrochemical Series

1. Oxidizing and Reducing Strengths

Electrochemical series helps us to identify a good oxidizing agent or reducing agent. All the substance appearing on the top of the electrochemical series are a good oxidizing agent i.e., they have positive Value of standard reduction potential whereas those appearing on the bottom of the electrochemical series are a good reducing agent i.e., they have a negative value of standard reduction potential. For Example, F2 electrode with the standard reduction potential value of +2.87 is a strong oxidizing agent and Li+ with standard reduction potential value of -3.05 volts is a strong reducing agent.

2. Calculation of Standard e.m.f. (E0) of Electrochemical Cell

The standard e.m.f of the cell is the sum of the standard reduction potential of the two half cell: reduction half cell and oxidation half cell

$$E^o_{cell} = E^o_{red} + E^o_{ox}$$

By convention, the standard oxidation potential is always expressed in terms of reduction potential.

Thus, standard oxidation potential $(E^o_{ox}) = -$ standard reduction potential E^o_{red}

Therefore,

E^o_{cell} = (standard reduction potential of reduction half cell) – (standard reduction potential of oxidation half cell)

As oxidation takes place at anode and reduction takes place at the cathode. Hence,

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

Example:

For a reaction, 2Ag+ (aq) + Cd → 2Ag + Cd+2(aq)

The standard reduction potential given are: Ag+/ Ag =0.80 volt, Cd+2/ Cd = -0.40 volt

From the reaction, we can see that Cd losses electron and Ag+ gains. Hence, oxidation half cell or anode is Cd.

Using the formula,

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$=0.80 -(-0.40)$$

$$= 1.20 \text{ volt}$$

3. Predicting the Feasibility of Redox Reaction

Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative. The free energy is related to cell e.m.f. in the following manner:

$\Delta G^o = nFE^o$

Where n is the number of electrons involved, F is the Faraday constant and E^o is the cell emf.

- ΔG^o can be negative if E^o is positive.
- When E^o is positive, the cell reaction is spontaneous and serves as a source of electrical energy.
- If it comes out to be negative then the spontaneous reaction cannot take place.
- The resultant value of E^o for redox reaction is important in predicting the stability of a metal salt solution when stored in another metal container.
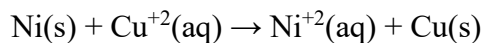
Also Read: Gibbs Free Energy

For example, let us find out whether we can store copper sulphate solution in a nickel vessel or not.

Given: Ni^{+2}/Ni = -0.25 volt, Cu^{+2}/Cu = 0.34 volt

$Ni + CuSO_4 \rightarrow NiSO_4 + Cu$
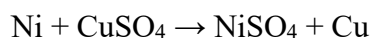
We want to see whether Ni metal will displace copper from copper sulphate solution to give NiSO4 by undergoing oxidation reaction.

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

From the above reaction, it is clear oxidation terminal will be Ni electrode.

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$= 0.34 - (-0.25)$

$= 0.59$ volt

As the e.m.f. comes out to be positive, it implies copper sulphate reacts when placed in a nickel vessel and hence cannot be stored in it.

4. Predicting the Product of Electrolysis

In case, two or more types of positive and negative ions are present in solution, during electrolysis certain metal ions are discharged or liberated at the electrodes in preference to others. In general, in such competition, the ion which is a stronger oxidizing agent(high value of standard reduction potential) is discharged first at the cathode.

Thus, when an aqueous solution of NaCl containing Na+, Cl-, H+ and OH- ions is electrolyzed, H+ ion is preferentially deposited at cathode (reduction) instead of Na+ being reduced, this is because reduction potential of hydrogen(0.00 volt) is higher than the reduction potential of sodium(-2.71 volt). At the anode where oxidation takes place, the anion that has lower reduction potential will be oxidized. Therefore, OH- with standard reduction potential 0.40 volt will be oxidized in preference to Cl- with standard reduction potential of 1.36 volt.

5. Relative chemical reactivity of Metals:

Greater the value of standard of standard reduction potential of a metal,smaller is its tendency to loose electrons to change into positive ion and hence lower will be its reactivity.

For example, metals like Li, Na,K, and Rb are highly reactive. Coinage metals,Cu, Ag, and Au are the least reactive because they have positive reduction potential.

Similarly, metals like Pb, Sn, Ni, Co and Cd which are very close to SHE react very slowly with steam to liberate hydrogen gas, while the metals like Fe, Cr, Mn, Al and Mg which have more negative reduction potential react with steam to produce the metallic oxides and hydrogen gas.

6. Reaction of metals with dilute acids:

Greater the value of standard reduction potential of a metal, lesser is its tendency to loose electrons to form metal ions and so weaker is its tendency to displace hydrogen gas from acids.

For example, metals like Au, Pt, Ag, and Cu which have sufficiently high positive values of reduction potential and do not liberate hydrogen from acids. While metals like Zn, Mg and Ca which are close to the top of the series and have very low reduction potentials, liberate hydrogen gas, when they react with acids.

It involves Lowery Bronsted concept: The term Bronsted lowry base is a substance that accepts proton in the form of hydrogen atom. In contrast the lowery Bronsted acid is the substance that donates the proton. As a result, the Bronsted lowry acid base reaction produce a conjugate acid and conjugate base.

7. Displacement of one metal by another from its solution:

Metals will displace another metal from the aqueous solution of its salt if it lies above the electrochemical series.

For example, Fe can displace Cu from $CuSO_4$, Zn does not displace Mg from $MgSO_4$. displacement reactions occur when a metal from electrochemical series is mixed with the ions of a metal lower down in electrochemical series. The atoms of more reactive metal push their electrons onto ions of ions of less reactive metals.

Metals having higher oxidizing potential will replace the metal having lower oxidizing potential.

8. Comparison of relative tendency of metals and non metals to get oxidized or reduced:

The value of the reduction potential of a metal or non metals tell us tendency to loose electrons and act as reducing agents. It gives the information about the tendency of species to gain electrons and act as oxidizing agent. Greater the value of standard reduction potential of a given species, greater is its tendency to accept electrons to undergo reduction and hence act as an oxidizing agent.

For example, the non metals elements like halogens which lie below the SHE, have strong tendency to gain electrons and undergo reduction.

The series tells us that strong oxidizing agent like halogens have large positive values of standard reduction potentials, while strong reducing agent have large negative value like Li, K, Ca, Na etc. which lie above SHE.

9. For Corrosion treatment:

When two metals which are in contact with each other are exposed to atmosphere, the elements lower in series will be oxidized. i.e. it is rusted and destroyed.

If there is scratch on galvanized sheet of iron is exposed then zinc is rusted and iron is protected. This is because in e.m.f. series iron is below tin. The electrochemical corrosion process consists of two partial electrochemical reactiocs: The anodic partial reactions, and cathodic partial reactions consisting of the reduction of water,hydrogen or oxygen gas. Corrosion monitoring is a process that evaluates and monitors equipment's components,structures,process units and facilities for the signs of corrosions.Monitoring programs aims to identify certain conditions in order to extend the life and serviceability of assets while increasing safety and reducing replacement costs.

10. To find thermal stability of metallic oxides:

The thermal stability of metal oxide on its electropositive nature. As the electropositivity increase from top to bottom, the thermal stability of oxide also increase from to top to bottom.

The oxides of metals having high positive reduction potential are not stable towards heat. The metals which are above copper form unstable oxides i.e. they are decomposed on heating.it is demonstrated that the melting point and thermal stability of oxides are determined by the nature of the distribution of valent electrons from the components over localized and non-localized once and by the probability of formation of stable electronic configuration of transition metal and oxygen atoms.

11. To ascertain the electropositivity of metals:

- **Strongly electropositve metals:**

  Metals having high standard reduction potential near about -2.0 V or more negative like alkali metals or alkaline earth metals are strongly electropositve in nature.

- **Moderately electropositve metals:**
  Metals having value of standard reduction potentials between 0.0 V and about -2.0 V are moderately electropositve. Al, Zn, Fe, Ni and Co etc. belong to this group.
- **Weakly electropositve metals:**

  The metals which are above hydrogen and possess positive values of standard reduction potentials are weakly electropositve in nature.

  For example, Cu, Hg, Ag etc. belong to this group.

12. For construction of a cell:

Various cells can be constructed by combining standard electrodes given in EMF series as per requirement of e.m.f.

For example if a cell if e.m.f. 1.1V is required, then from e.m.f series we can locate zinc and copper electrodes whose combination gives required e.m.f. electrochemical cells which generate an electric current are called voltaic cells or galvanic cells and those that generates chemical reactions,via electrolysis for example,are called electrolytic cells. A common example of galvanic cell is standard 1.5 volt cell meant for consumers use.