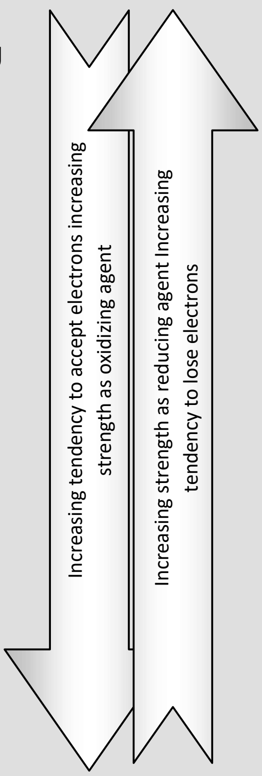
Electrochemical series.

(1) The standard reduction potentials of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. These various electrodes can be arranged in increasing or decreasing order of their reduction potentials. The arrangement of elements in order of increasing reduction potential values is called **electrochemical series**.

The electrochemical series, also called **activity series**, of some typical electrodes is being given in Table.

Standard reduction electrode potentials at 298K

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E^0, volt
Li	$Li^+ + e^- = Li$	–3.05
K	$K^+ + e^- = K$	–2.925
Ca	$Ca^{2+} + 2e^- = Ca$	–2.87
Na	$Na^+ + e^- = Na$	–2.714
Mg	$Mg^{2+} + 2e^- = Mg$	–2.37
Al	$Al^{3+} + 3e^- = Al$	–1.66
Zn	$Zn^{2+} + 2e^- = Zn$	–0.7628
Cr	$Cr^{3+} + 3e^- = Cr$	–0.74
Fe	$Fe^{2+} + 2e^- = Fe$	–0.44
Cd	$Cd^{2+} + 2e^- = Cd$	–0.403
Ni	$Ni^{2+} + 2e^- = Ni$	–0.25
Sn	$Sn^{2+} + 2e^- = Sn$	–0.14
H_2	**$2H^+ + 2e^- = H_2$**	**0.00**
Cu	$Cu^{2+} + 2e^- = Cu$	+0.337
I_2	$I_2 + 2e^- = 2I^-$	+0.535
Ag	$Ag^+ + e^- = Ag$	+0.799
Hg	$Hg^{2+} + 2e^- = Hg$	+0.885
Br_2	$Br_2 + 2e^- = 2Br^-$	+1.08
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- = Au$	+1.50
F_2	$F_2 + 2e^- = 2F^-$	+2.87



(2) **Characteristics of Electrochemical series**

(i) The negative sign of standard reduction potential indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is –0.76 volt, When zinc electrode is joined with SHE, it acts as anode (–ve electrode) i.e., oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

(ii) The substances, which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances, which are strooxidizingising agents than H^+ ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative value of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

(3) **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 electron or 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 substances 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 potentials between 0.0 and about – 2.0 volt are moderately electropositive Al, Zn, Fe, Ni, Co, etc., belong to this group.

(c) Weakly electropositive**:** 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 nonmetal from its salt solution by another nonmetal: A non-metal 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 non-metal'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.

$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$

$2I^- \rightarrow I_2 + 2e^-$ .....(Oxidation)

$Cl_2 + 2e^- \rightarrow 2Cl^-$ .....(Reduction)

[The activity or electronegative character or oxidizing 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.

$$Mn \rightarrow Mn^{n+} + ne^- \quad \text{..... (Oxidation)}$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{..... (Reduction)}$$

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. (Decreasing order of reducing netur)

Element :	Na >	Zn >	Fe
Reduction potential :	-2.71	-0.76	-0.44

Alkali and alkaline earth metals are strong reducing agents.

(v) **Oxidizing nature of non-metals**:Oxidizing 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, oxidizing nature increases from top to bottom in the electrochemical series. The strength of an oxidizing agent increases as the value of reduction potential becomes more and more positive.

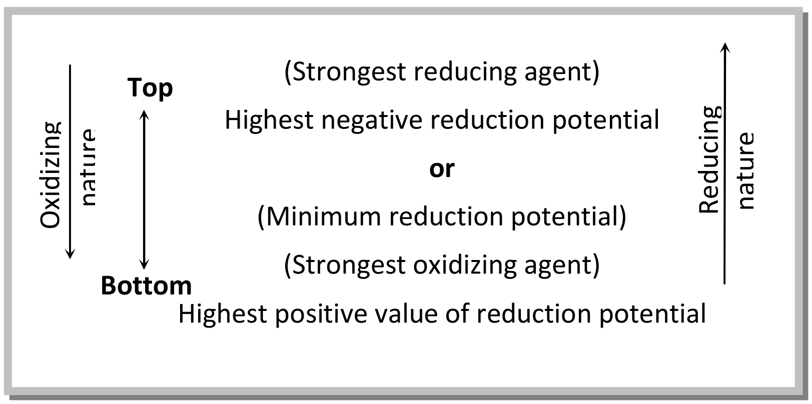
F_2 (Fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2. Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2.

Element:

Reduction potential:

$$\underset{\text{Oxidising nature increases}}{\xrightarrow[]{\begin{array}{cccc} I_2 & Br_2 & Cl_2 & F_2 \\ +0.53 & +1.06 & +1.36 & +2.85 \end{array}}}$$

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 potentials are not stable towards heat. The metals which come below copper form unstable oxides, i.e., these are decomposed on heating.

$$Ag_2O \xrightarrow{\Delta} 2Ag + \frac{1}{2}O_2 \; ; \; 2HgO \xrightarrow{\Delta} 2Hg + O_2 \; ; \; \left.\begin{array}{r} BaO \\ Na_2O \\ Al_2O_3 \end{array}\right] \xrightarrow{\Delta} \text{No decomposit ion}$$

(vii) **Extraction of metals**: A more electropositive metal can displace a less electropositive metal from its salt's solution. This principle is applied for the extraction of Ag and Au by cyanide process. Silver from the solution containing sodium argento cyanide, $NaAg(CN)_2$, can be obtained by the addition of zinc as it is more electro-positive than Ag.

$$2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$$