ELECTROCHEMICAL SERIES OR EMF SERIES

The standard reduction potential of a number of electrodes is given in the table. These values are determined potentiometrically by combining the electrode with another standard electrode, whose electrode potential is zero.

Electrode	Electrode reaction	Potential E_0 (V)	Nature
Li^+ / Li	$Li^+ + e^- \rightleftharpoons Li$	– 3.01	Anodic ↑
Ca^{2+} / Ca	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	– 2.93	
Na^+ / Na	$Na^+ + e^- \rightleftharpoons Na$	– 2.90	
Mg^{2+} / Mg	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	– 2.71	
Al^{3+} / Al	$Al^{3+} + 3e^- \rightleftharpoons Al$	– 2.37	
Pb^{2+} / Pb	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	– 1.66	
Zn^{2+} / Zn	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76	
Cr^{3+} / Cr	$Cr^{3+} + 3e^- \rightleftharpoons Cr$	-0.74	
Fe^{2+} / Fe	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44	
Co^{2+} / Co	$Co^{2+} + 2e^- \rightleftharpoons Co$	-0.28	
Ni^{2+} / Ni	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	-0.23	
Sn^{2+} / Sn	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	-0.14	
Fe^{3+} / Fe	$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04	
H^+ / H_2	$2H^+ + 2e^- \rightleftharpoons H_2$	+0.00	Reference Electrode
Cu^{2+} / Cu	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34	
Ag^+ / Ag	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80	
Pt^{2+} / Pt	$Pt^{2+} + 2e^- \rightleftharpoons Pt$	+0.86	
Au^+ / Au	$Au^+ + e^- \rightleftharpoons Au$	+1.69	
$1/2\ F_2 / F^-$	$1/2F_2 + e^- \rightleftharpoons F^-$	+2.87	↓ Cathodic

Definition :

"An increasing order of the standard reduction potentials is called electrochemical series".

Significance of EMF series or
Application of Electrochemical series or
Importance of Electrode Potential

1) Ca***lculation of standard emf of the cell***

The standard emf of a cell (E_o) can be calculated if the standard electrode potential values are known by using the following formula :

$$E^0cell = E^0R.H.E. - E^0L.H.E.$$

$$= E^0R - E^0L$$

The standard free energy change of a cell reaction can be calculated.
Where, n = number of electrons involved in cell reaction.
F = 96500 coulombs
E_o = Standard emf of the cell.

2) ***The relative case of oxidation or reduction***

By using the given formula :

$$\Delta G^o = nFE^o$$

A metal ion with higher reduction potential has a greater tendency to undergo reduction. A metal ion with lower reduction potential has a greater tendency to undergo oxidation.
The elements present above the hydrogen in the series undergo oxidation whereas the elements present below hydrogen in the series undergo reduction.

From the series, the fluorine has higher positive value of standard reduction potential (+2.87 V) and shows higher tendency towards reduction.
Similarly, lithium has the highest negative value (–3.01 V) and shows higher tendency towards oxidation.

The reduction potential of Cu is 0.34 V while Zn is – 0.76 V.Even though both of them are ready to undergo reduction reactions, Cu undergoes reduction reaction more readily than Zn because Cuhas higher value of reduction potential than Zn.

3) T***he replacement or displacement tendency of one element by the other***

Metals with a lower reduction potential have a greater tendency to replace another metal which has higher reduction potential.

In otherwords, the more electropositive metal is reduced and less electropositive metal is oxidised. The driving force for the displacement increases with increased separation of metals in the emf series.

Example: The reduction potential of zinc (–0.76 V) is lower than copper (0.34 V). Hence, zinc displaces copper from its salt solution.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu.$$

4) ***Displacement behavior of hydrogen***

Metals with negative reduction potential displaces the hydrogen from acid solution.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

$$E^0_{Zn2+/Zn} \longrightarrow -0.76\ V$$

5)*Determination of equilibrium constant for the reaction*

Standard electrode potential can also be used to determine the equilibrium constant (K) for the reaction we know that

$$-\Delta G^0 = RT\ln K = 2.303\ RT \log K$$

$$\log K = --\Delta G^0 / 2.303RT$$

$$= nFE^o / 2.303RT$$

From the value of E0, the equilibrium constant for the cell reaction can be calculated.