

Electrochemical Series or EMF Series

The increasing values of standard reduction potential is as electrochemical series.

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

Electrode	Electrode reaction	E° volts	Nature
Li^+/Li	$Li^+ + e \rightleftharpoons Li$	-3.01	Anodic
Mg^{2+}/Mg	$Mg^{2+} + 2e \rightleftharpoons Mg$	-2.37	
Pb^{2+}/Pb	$Pb^{2+} + 2e \rightleftharpoons Pb$	-1.12	
Zn^{2+}/Zn	$Zn^{2+} + 2e \rightleftharpoons Zn$	-0.76	
Fe^{2+}/Fe	$Fe^{2+} + 2e \rightleftharpoons Fe$	-0.44	
Sn^{2+}/Sn	$Sn^{2+} + 2e \rightleftharpoons Sn$	-0.136	
H^+/H_2	$2H^+ + 2e \rightleftharpoons H_2$	0.00	pt. reference
Cu^{2+}/Cu	$Cu^{2+} + 2e \rightleftharpoons Cu$	+0.34	Cathodic
Ag^+/Ag	$Ag^+ + e \rightleftharpoons Ag$	+0.80	
Au^+/Au	$Au^+ + e \rightleftharpoons Au$	+1.50	
$1/2 F_2/F^-$	$1/2 F_2 + e \rightleftharpoons F^-$	+2.87	

Significance of emf series (or) Application of electrochemical series
Importance of electrode potential.

1) Calculation of Standard emf of the cell:

The standard emf of a cell (E°) can be calculated if the standard electrode potential values are known using the following reaction.

$$E^\circ_{cell} = E^\circ_{R.H.E} - E^\circ_{L.H.E}$$

2) Relative ease of oxidation (or) reduction:

Higher the value of standard reduction potential (+ve value), greater is the tendency to get reduced. (i.e. metals on the top (-ve value) are more easily ionised).

a) The fluorine has higher positive value of standard reduction potential (+2.87 V) and shows higher tendency to get reduced.

b) The lithium has highest negative value (-3.01V) and shows higher tendency towards oxidation.

3) Displacement of one element by the other. Metals which lie higher in the emf series can displace those elements which lie below them in the series.

For example, we may know whether Cu will displace Zn from the solution or vice-versa. We know that standard reduction potential of Cu & Zn.

$$E^{\circ} \text{Cu}^{2+} / \text{Cu} = +0.34\text{V} \quad \text{and} \quad E^{\circ} \text{Zn}^{2+} / \text{Zn} = -0.76\text{V}$$

So, Cu^{2+} has a great tendency to acquire Cu form, than Zn^{2+} has for acquiring Zn form.

4) Determination of equilibrium constant for the reaction:

Standard electrode potential can also be used to determine the standard free energy change (ΔG_1°) and equilibrium constant (K) for the reaction. We know that

$$-\Delta G_1^{\circ} = RT \ln K = 2.303 RT \log K$$

$$\log K = \frac{-\Delta G_1^{\circ}}{2.303 RT}$$

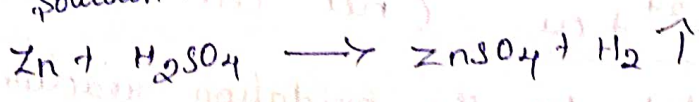
$$\therefore -\Delta G_1^{\circ} = nFE$$

$$\log K = \frac{nFE^{\circ}}{2.303 RT}$$

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

5) Displacement behaviour of hydrogen:

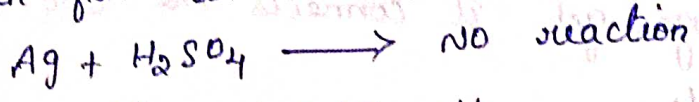
Metals with negative reduction potential will displace the hydrogen from an acid solution.



$$E^{\circ} \text{Zn} = -0.76 \text{ volt.}$$

From the values of E° , the equilibrium constant for the cell reaction can be calculated.

The metal with positive reduction potential will not displace the hydrogen from an acid solution.



$$E^{\circ} \text{Ag} = +0.80 \text{ volt.}$$