Electrochemical series (emf series)

A series in which elements are arranged in the ascending (increasing) order of their standard reduction potential with respect to hydrogen scale is called emf series.

Half reaction	E^{θ}/V
$Li^{+}(aq) + e^{-} \longrightarrow Li(s)$	-3,03
$Ca^{2+}(aq) + 2e^{-} \longrightarrow Ca(s)$	-2,87
$Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s)$	-1,66
$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$	-0,76
$Pb^{2+}(aq) + 2e^{-} \longrightarrow Pb(s)$	-0,13
$2H^{+}(aq) + 2e^{-} \longrightarrow H_2(g)$	0,00
$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$	+0,34
$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$	+0,80

Application / Significance of electrochemical series

(i) Relative ease of oxidation or reduction

- The metals which lie above hydrogen in the series undergo spontaneous oxidation and the metals which lie below SHE undergo reduction spontaneously (ie. Acts as Anodes and Cathodes respectively)
- The metals which lie above hydrogen are good reducing agents and which lies below hydrogen will act as good oxidizing agents

(ii) Replacement tendency

- The metal lying above in emf series displaces the metal lying below it from an electrolyte of the later.

Example 1: Ni spatula cannot be used to stir copper sulphate solution due to the following reaction

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

Example 2: when zinc is dipped in copper sulphate solution copper gets deposited (displaced)

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

(iii) Liberation of Hydrogen

- The metal with negative reduction potential will displace H_2 from an acid solution

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2\uparrow$$

Hence acids cannot be stored in galvanized steel containers.

For the same reason galvanized steels are not used to store food stuffs containing vinegar. (Vinegar is used as food preservative-vinegar is acetic acid)

(iv) Calculation of equilibrium constant (Keq)

$-\Delta G^{O} = n F E^{o}$

$-\Delta G^{O} = 2.303 RT \log K(eq)$

Therefore, $\log K = \frac{nFE'}{2.303RT}$

$$\log K = E^{\circ}/0.0591$$

(v)Calculation of Standard emf of the cell

$$E_{Cell} = E_{Cathode} - E_{anode}$$

(if both reduction potentials are considered)

(vi)Predicting the spontaneity of cell reaction

- Spontaneity of the redox reaction can be predicted from the emf value of complete cell reaction.

If the value of $\mathbf{E_{cell}}$ is **positive**, the reaction is f**easible**. G will be negative (i.e. it is an electrochemical cell)

If the value of $\mathbf{E_{cell}}$ is **negative**, the reaction is **not feasible**. G will be positive (i.e. it is an electrolytic cell).