



19CH201 - ENGINEERING CHEMISTRY

UNIT-1 - ELECTROCHEMISTRY

1.6 Electrochemical series

ELECTROCHEMICAL SERIES (or) EMF SERIES

Definition

When the various electrodes (metals) are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called electrochemical series.

Electrode	Electrode reaction	E° , volts	Nature
Li^+/Li	$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	- 3.01	Anodic ↑ Pt-reference ↓ Cathodic
Mg^{2+}/Mg	$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	- 2.37	
Zn^{2+}/Zn	$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	- 0.76	
Fe^{2+}/Fe	$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	- 0.44	
Sn^{2+}/Sn	$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	- 0.136	
Pb^{2+}/Pb	$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	- 0.13	
H^+/H_2	$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	0.00	
Cu^{2+}/Cu	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+ 0.34	
Ag^+/Ag	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+ 0.80	
Au^+/Au	$\text{Au}^+ + e^- \rightleftharpoons \text{Au}$	+ 1.50	
$1/2\text{F}_2/\text{F}^-$	$1/2 \text{F}_2 + e^- \rightleftharpoons \text{F}^-$	+ 2.87	

Significance of emf series (or) Applications of electrochemical series (or)

Applications of Nernst equation

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 relation.

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

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) (oxidised).

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

(b) The lithium has highest negative value (- 3.01 V) 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.

i.e., $E^\circ \text{Cu}^{2+}/\text{Cu} = + 0.34 \text{ V}$ and $E^\circ \text{Zn}^{2+}/\text{Zn} = - 0.76 \text{ V}$.

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

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4. 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

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

$$\log K = \frac{-\Delta G^\circ}{2.303 RT}$$
$$= \frac{nFE^\circ}{2.303 RT}$$
$$\left[\because -\Delta G^\circ = nFE^\circ \right]$$

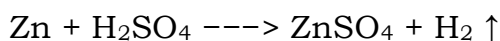


From the value of E° , the equilibrium constant for the cell reaction can be calculated.

5. Hydrogen Displacement Behaviour

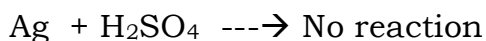
Metals with negative reduction potential (i.e., the metals placed above H_2 in the emf series) will displace the hydrogen from an acid solution.

Zinc reacts with dil H_2SO_4 to give H_2 but Ag does not, why?



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

The metal with positive reduction potential (ie., the metals placed below H_2 in the emf series) will not displace the hydrogen from an acid solution.



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

6. Predicting Spontaneity of Redox Reactions

Spontaneity of redox reaction can be predicted from the emf (E°) value of the complete cell reaction.

(i) If the E° of the cell is positive, the reaction is spontaneous.

(ii) If the E° of the cell is negative, the reaction is not feasible.

In general, an element having lower reduction potential can displace another metal having higher reduction potential from its salt solution spontaneously.