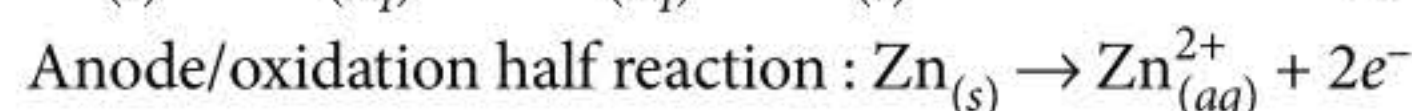
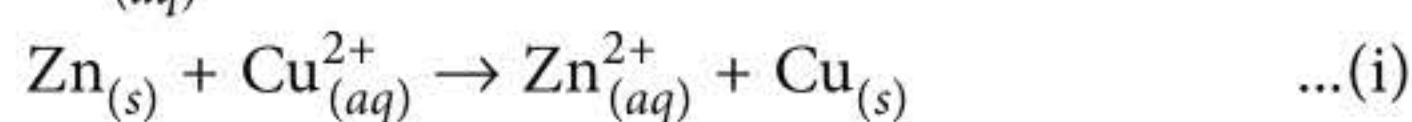


This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

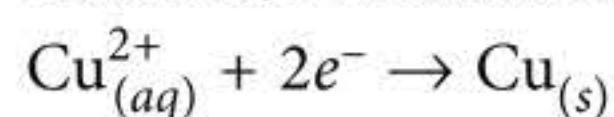
ELECTROCHEMISTRY

- Electrochemistry deals with harnessing electric energy from Gibbs energy of indirect spontaneous chemical reactions using electrochemical cells and using electric energy to bring out non-spontaneous chemical reactions using electrolytic cells.

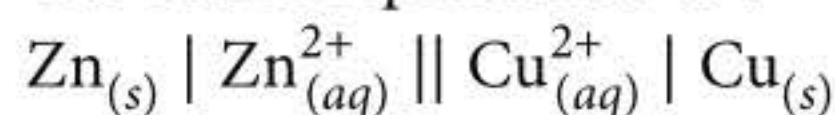
- A Daniell cell uses the reaction of $Zn_{(s)}$ with $Cu^{2+}_{(aq)}$ as :



Cathode/reduction half reaction :



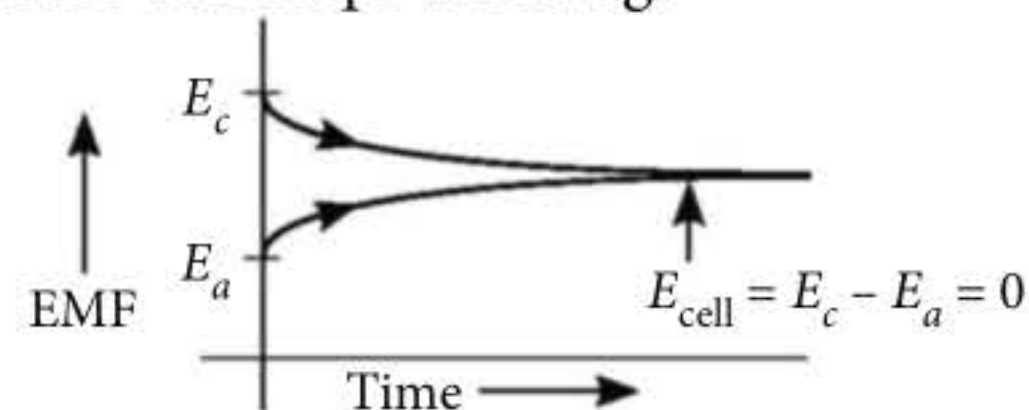
The cell is represented as :



Anode or Cathode or

Left half cell Right half cell [|| Shows salt bridge]

- $E_{cell} = E_c - E_a$
A cell works when $E_c > E_a$. EMF of half cell is directly proportional to concentration of metal ion. At cathode the concentration of metal ion decreases which decreases its emf. At anode the concentration of metal ion increases which increases its emf. The difference ' $E_c - E_a$ ' goes on decreasing and after some time cell stops working.



Under standard conditions, when $T = 298.15$ K, molarity of solution 1 M, $E_{cell}^{\circ} = E_c^{\circ} - E_a^{\circ}$

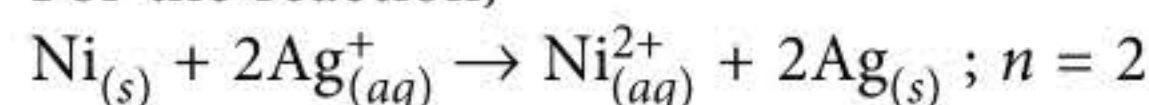
For any other concentration, according to Nernst, the emf is :

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log Q$$

[n = electrons transferred]

For Daniell cell from equation (i), $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

For the reaction,



$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \log \frac{[Ni^{2+}]}{[Ag^{+}]^2}$$

The value of $\frac{2.303RT}{F}$ in standard conditions = 0.059 V.

- The standard $E_{half\ cell}^{\circ}$ values are taken in terms of reduction potentials (IUPAC conventions) using Standard/Normal Hydrogen Electrode which consists of Pt-foil coated with Pt-black dipped in $1M [H^{+}]$ concentrated acid on which pure $H_{2(g)}$ is passed at 1 atm. Its standard reduction potential is zero volt.
- Salt Bridge :** It is inverted U-tube filled with a gel of an inert electrolyte KCl , KNO_3 , NH_4NO_3 , etc. with agar-agar, having its two ends immersed in electrolytes of two half cells. It has following functions :
 - It connects two half cells internally.
 - Only ions can pass through it.
 - It transports ions only and does not allow the two solutions to mix up.
- Equilibrium Constant of Cell reaction and Work Done**

$$E_{cell} = E_{cell}^{\circ} - \frac{2.303RT}{nF} \left(\text{or } \frac{0.059}{n} \right) \log Q$$

*By R.C. Grover, having 45+ years of experience in teaching chemistry.

At equilibrium $Q = K_c$ (Equilibrium constant), $E = 0$

$$\Rightarrow E_{\text{cell}}^{\circ} = \frac{2.303RT}{nF} \log K_c$$

Also $\Delta G^{\circ} = -nFE^{\circ} = -2.303 RT \log K_c = \text{Work done}$

○ Concentration Cell

When the two half cells of a cell are same, the cell will work if $[M^{x+}]_c > [M^{x+}]_a$. It is called concentration cell.

$$E_{\text{cell}} = \frac{0.059}{n} \log Q; \text{ because } E_{\text{cell}}^{\circ} = 0$$

○ EMF Series and its Applications

When elements are arranged in decreasing order of emf from top to bottom it is called electrode potential series or activity series or EMF series or electromotive series or electrochemical series. Some of the applications of this series are :

- Metal of lower emf cannot be used to make a container for salt solution of metal of higher emf.
- When two half cells are joined to make an electrochemical cell, the metal of lower emf will work as anode and other as cathode.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

- Lower the $E_{\text{metal}^{x+}/\text{metal}}^{\circ}$ better is the reducing power of the metal.
- The value of $E_{\text{Li}^+/\text{Li}}^{\circ}$ is the lowest -3.05 V, showing it to be the best reducing metal.
- The value of $E_{\text{F}_2/\text{F}^-}^{\circ}$ is the highest $+2.87$ V, showing it to be the best oxidising element.
- Metals having negative E° values can displace H_2 gas from acids.

○ Electrolysis

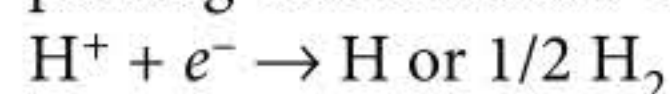
Sorting, shifting and deposition of ions on electrodes by passing electric current through electrolyte, is called electrolysis.

(a) **Faraday's 1st Law of Electrolysis** : The mass (m gram) of a substance consumed or deposited at an electrode is directly proportional to the quantity of charge (Q Coulombs) passed through the electrolyte during electrolysis.

$$\text{mass } m \propto Q \text{ (Coulombs)} \propto I \text{ (ampere)} \times t \text{ (seconds)}$$

$$m = ZIt$$

Z is proportionality constant known as electrochemical equivalent of a substance, which is the mass produced or consumed at electrode by passing one coulomb charge through electrolyte.



Practically, 0.000010364 g hydrogen is deposited by 1 C charge.

$$\Rightarrow 1 \text{ g hydrogen is deposited by } \frac{1}{0.000010364} \text{ C charge}$$

$$= 96488 \text{ C} \approx 96500 \text{ C} = 1 \text{ F (Faraday)}$$

Similarly, 1 mole of Na, Cu and Al will be collected from Na^+ , Cu^{2+} and Al^{3+} by using 1 F, 2 F and 3 F charge respectively.

(b) **Faraday's 2nd Law of Electrolysis** : When the same quantity of charge is passed through different electrolytes, the ratio of masses deposited or consumed at electrodes to their equivalent weights is constant.

(c) Products of Electrolysis of Aqueous Solutions

- Metal can be deposited at cathode only if its EMF is more than -0.83 V, otherwise H_2 is liberated.
- Non metal is deposited at anode only if its EMF is less than 1.23 V, otherwise O_2 gas will be liberated.
- Aqueous solutions of metal sulphates and metal nitrates, on electrolysis, produce O_2 gas at anode.
- When two or more reactions are possible at an electrode, the reaction with lower discharge potential is preferred *i.e.*, at anode, reaction of lower reduction potential and at cathode, reaction of higher reduction potential will occur. It is called competing electrolysis.

○ Applications of Electrolysis

- Determination of equivalent weight of elements
- Electrometallurgy
- Electrorefining of metals
- Electroplating
- Manufacture of compounds

MULTIPLE CHOICE QUESTIONS

- If $\text{Zn}_{(s)} | \text{Zn}_{(1\text{M})}^{2+} || \text{Cu}_{(1\text{M})}^{2+} | \text{Cu}$; $E_1^{\circ} = 1.1$ V and $\text{Cu}_{(s)} | \text{Cu}_{(1\text{M})}^{2+} || \text{Ag}_{(1\text{M})}^+ | \text{Ag}_{(s)}$; $E_2^{\circ} = 0.46$ V, What is the EMF of $\text{Zn}_{(s)} | \text{Zn}_{(1\text{M})}^{2+} || \text{Ag}_{(1\text{M})}^+ | \text{Ag}_{(s)}$?
 (a) 0.64 V (b) 0.08 V
 (c) 1.56 V (d) 1.74 V
- Which of the following is the correct E_{cell} of the following if E_{cell}° is 3.17 V?
 $\text{Mg}_{(s)} | \text{Mg}_{(0.2\text{M})}^{2+} || \text{Ag}_{(0.001\text{M})}^+ | \text{Ag}_{(s)}$
 (a) 3.17 V (b) 3.318 V
 (c) 3.46 V (d) 3.01 V