

Electrochemistry Part-II

Faraday Laws, Electrochemical cells, Electrode potentials, EMF of cell, Electro chemical series

I. Faraday's laws of electrolysis

Faraday's laws relate the quantity of electricity and the amount of the substance discharged at the electrodes.

a) First Law: The amount of the substance deposited or electrolysed is directly proportional to the quantity of electricity passed through the electrolyte

$$W \propto Q$$

w = wt. in grams

Q = quantity of electricity in coulombs

But $Q = c \times t$ where C = current in amperes, t = time in seconds

$\therefore w \propto ct$ Or $W = ect$ (Or) $W = eQ$, where 'e' is electro chemical equivalent.

The weight of the substance deposited on the electrode for 1 coulomb of electricity is called electrochemical equivalent (e). Its unit is gram/coulomb

Electrochemical equivalent depends only on the **nature of the electrolyte**.

Electrochemical equivalents are in the ratio of their equivalent weights. $e_1 / e_2 = E_1 / E_2$

It is related to GEW as: $e = \text{GEW} / 96500 \text{ g/C}$ or E/F

$$\therefore W = Ect/F \text{ or } W = Mct/ZF$$

W = wt of the substance deposited

M = atomic weight of the element

Z = valency of the element

F = 1 Faraday = 96,500C

b) **Second Law:** When the same quantity of electricity is passed through different electrolytes, the weights of the substances deposited will be in the ratio of their equivalent weights.

It is mathematically expressed as $\frac{W_1}{W_2} = \frac{E_1}{E_2}$ where W_1, W_2 are weights and E_1, E_2 are equivalent weights.

Note: when same quantity of electricity is passed through different electrolyte solutions then

- i) No. of equivalents of elements deposited are in the ratio 1:1:1...
- ii) No. of moles of elements deposited are in the ratio $1/Z_1:1/Z_2:1/Z_3...$ where $Z_1, Z_2, Z_3...$ are valency of elements.

#1 Faraday of electric current i.e. 96,500 coulombs of electricity [charge on one mole of electrons] is passed through an electrolyte 1 G.E.W of a substance will be deposited.

1 Faraday = 1 gram. eq. wt = charge on 1 mole of electrons = 96500 coulombs

1 Faraday will deposit / Liberate (at STP)

- a) 1.008 g / 11.2 Lt of Hydrogen,
- b) 35.5 g / 11.2 Lt of Chlorine gas
- c) 8 g / 5.6 Lt of Oxygen gas

II. Gram Equivalent weight [GEW] of an element = gram atomic weight / valency

Element	GEW
Hydrogen	1.008 or 1g
Oxygen	8g
Fluorine	19
Chlorine	35.5
Bromine	80
Iodine	127
Sodium	23
Magnesium	12

Aluminium	9
Zinc	32.7
Silver	108
Cu^{+2}	31.75

The number of Faradays required to deposit one mole of a metal ions = magnitude of charge on the ions.

Eg. a) 1 mole of univalent $[\text{M}^+]$ ions will be deposited by passing **one Faraday**.

Eg. $\text{Na}^+, \text{Ag}^+, \text{Cu}^+$ etc.

b) 1 mole of bivalent $[\text{M}^{+2}]$ ions will be deposited by passing **Two Faradays**

Eg. $\text{Mg}^{+2}, \text{Ca}^{+2}, \text{Cu}^{+2}, \text{Zn}^{+2}$

c) 1 mole of trivalent $[\text{M}^{+3}]$ ions will be deposited by passing **Three Faradays**

Eg. $\text{Al}^{+3}, \text{Cr}^{+3}, \text{Fe}^{+3}$

III. Electrochemical Cells (OR) Voltaic (OR) Galvanic Cells

The cell in which **chemical energy** is converted into **electric energy** is called **electrochemical cell**.

Eg: Voltaic (or) galvanic cell

Galvanic Cell

I. A metal dipped in its ionic solution works as an **electrode**.

II. Zinc rod is dipped in zinc sulphate solution works as anode. Zinc undergoes oxidation, gives electrons; it is electron rich, so represented by negative sign. $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$

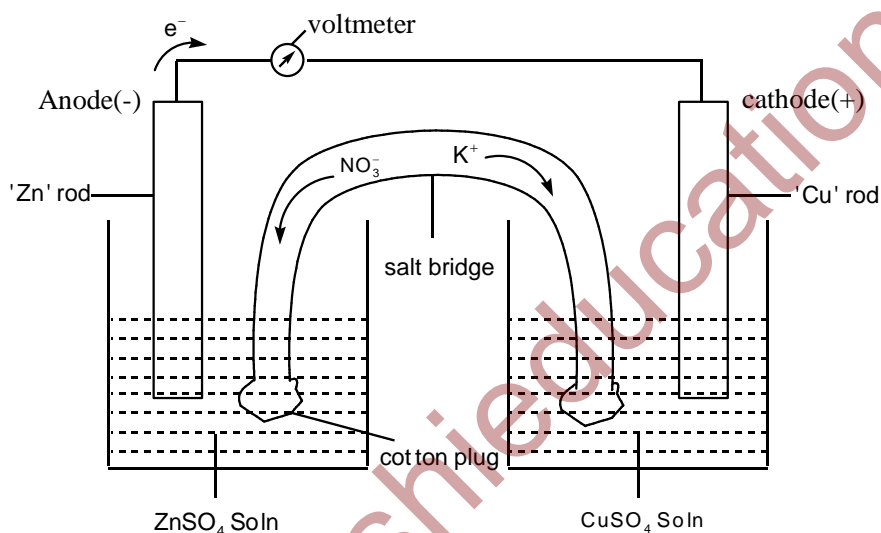
III. Cu rod dipped in CuSO_4 solution acts as cathode. Cu^{+2} present in the solution undergo reduction on Cu rod surface. Cu rod is electron poor, so it is represented by positive sign. $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

IV. Electrons flow in the external circuit from Zn to Cu

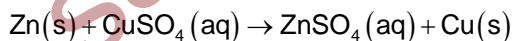
V. Two portions of the cell are also called half-cells and both are connected through a salt bridge.

VI. Salt bridge is an inverted u shaped tube, filled with Agar–Agar gel which is saturated with an electrolyte KCl (or) KNO_3 ; (or) $\text{NH}_4 \text{NO}_3$ [In these salts both the ions have equal transport number]

Salt bridge is used to prevent the accumulation of charges at the electrodes and to maintain electrical neutrality in both the half cells. If salt bridge is removed the cell reaction stops.



The reaction taking place in the electrochemical cell is a redox reaction.



Emf of Galvanic cell i.e. $E_{cell} = 1.1$ volts.

#In Daniel cell instead of salt bridge, porous pot (or) porous diaphragm is used.

#. Daniel cell or Galvanic cell is a reversible cell.

During the working of galvanic cell and with the passage of time the following changes takes place

- i) Spontaneity of the cell reaction decreases
- ii) E_{cell} Decreases
- iii) Reaction quotient Q increases.

IV. Reversible Cell

A voltaic cell may be reversible or irreversible.

The anodic and the cathodic reactions in a reversible Galvanic cell are always in a state of equilibrium.

A reversible cell shall satisfy the following conditions.

- i) When the cell is connected to an external source (a battery), whose emf is exactly equal to that of voltaic cell, no current flow into or out of the voltaic cell.
- ii) If the emf of the external battery is more than the emf of the voltaic cell, current flows from the battery into the voltaic cell.
- iii) If the emf of the external battery is less than the emf of the voltaic cell the current flows from the cell to the battery.

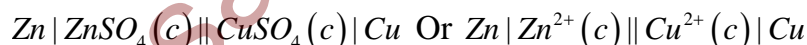
V. Representation of galvanic cells (iupac convention) (or) sign convention of the electrochemical cell:

In writing the electrochemical cell, keep anode (or) oxidation electrode in the left hand side and reduction electrode or cathode in the right hand side.

Electrode can be represented by semicolon (or) single vertical line.

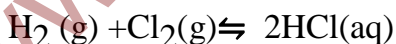
Double vertical line represents salt bridge.

Eg: Galvanic cell, $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$ is represented as



Daniel cell is represented as $Zn; Zn^{2+}(c) | Cu^{2+}(c); Cu$

#if the same electrolyte is present at both electrodes



The cell representation is $Pt, H_{2(g)}(1 atm.) | HCl(1.0M) | Cl_{2(g)}(1 atm.), Pt$

An inert metal rod such as platinum is needed to be placed in the solution, if non-metal is present in the reaction.

VI. Emf of the cell

The difference between two electrodes potentials present in the electrochemical cell is called electromotive force of the cell.

$$\begin{aligned}\text{EMF of the cell} &= \text{LHE oxidation potential} + \text{RHE reduction potential} \\ &= \text{LHE oxidation potential} - \text{RHE oxidation potential} \\ &= \text{RHE reduction potential} - \text{LHE reduction potential} \\ &= E_{\text{right}} - E_{\text{left}} \\ &= E_{\text{cathode}} - E_{\text{anode}}\end{aligned}$$

*High reduction potential **metal electrode works as right hand electrode (or) cathode in the electrochemical cell.**

- I. If EMF of the cell is +ve, cell reaction is spontaneous or irreversible.
- II. If EMF of the cell is negative (-ve), cell reaction is non-spontaneous or reversible.
- III. If EMF of the cell is zero, cell reaction is at equilibrium.

VII. Single Electrodes

A metal rod immersed in the aqueous solution of its salt or a gaseous non-metal in contact with the aqueous solution of its anion in the form of salt (or acid or alkali) functions as single electrodes.

Metal Electrodes

1. Zinc electrode: Zn aqueous solution
2. Copper electrode: aqueous solution
3. Magnesium electrode: aqueous solution
4. Silver electrode: aqueous solution
5. Iron electrode: aqueous solution; etc.

Non metal electrodes

1. Hydrogen electrode : $\text{H}^+(\text{aq}) / \text{H}_2(\text{g}), \text{Pt}$
2. Chlorine electrode : $\text{Pt}; \text{Cl}_2(\text{g}) / \text{Cl}^-(\text{aq})$

3. Oxygen electrode : Pt;O₂(g) / OH⁻(aq)

4. Bromine electrode: Pt;Br₂(g) / Br⁻(aq)

#Hydrogen electrode is a non-metal electrode but behaves like a metal electrode.

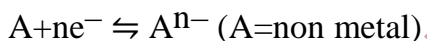
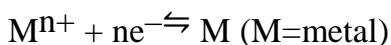
VIII. Single Electrode Potentials

I. A metal (or) non-metal in contact with the solution of its ions tends to develop electric potential at the metal/ metal ion (or) non-metal/ non-metal ion interface. It is called single electrode potential.

or The potential difference developed between the electrode and the electrolyte is called electrode potential.

The magnitude of the potential (E) depends on

- Chemical nature of the metal or the non-metal
- The number of electrons transferred (n) in the half cell reaction namely



- The concentration of the ions(c) (Mⁿ⁺ or Aⁿ⁻) in the solution.
- The temperature of the system (T)

25⁰c (or) 298K, 1 atmosphere pressure are called standard conditions.

II. Standard Electrode potential (E⁰): Standard electrode potential (E⁰) is the potential developed by single electrode if concentration of ions is 1 M (unit conc.) at 298 K and 1 atmosphere pressure.

The potentials are standard reduction potentials only (SRP).

Standard oxidation potential (SOP) is equal to SRP in magnitude with opposite sign.

E.g.: SRP of Zn²⁺/Zn electrode is -0.76v and its SOP is +0.76V.

III. Single electrode potential is obtained by using a reference electrode N.H.E. or S.H.E. It is represented as $\text{Pt, H}_2 (\text{g}) (1\text{atm}) / \text{H}^+ (1\text{M})$. This electrode acts as “reversible electrode”.

The potential of SHE is assumed to be “zero” volts.

a) R.P of Hydrogen electrode = $-0.059 \times \text{pH}$

b) O.P of Hydrogen electrode = $+0.059 \times \text{pH}$

*A saturated calomel electrode is now used as secondary reference electrode. It is represented as $\text{Hg/ Hg}_2\text{Cl}_2 (\text{s}), \text{KCl} (\text{saturated})$ and potential of saturated calomel electrode is -0.2422 volts.

IX. ELECTROCHEMICAL SERIES AND THE STANDARD REDUCTION POTENTIALS.

In the IUPAC system of referring the electrode potentials, standard reduction potentials are simply called a standard potential.

Electrochemical Series is the arrangement of various electrode systems in the ascending order of their SRP values. It is also called as “activity series”.

i. All the metals which are present above the hydrogen in the electrochemical series are called active metals. They have $-ve$ SRP values. They liberate hydrogen from dilute mineral acids.

ii. All the elements which are present below the hydrogen in the activity series have $+ve$ SRP values.

iii. Metal with less SRP

a) Has high tendency to lose electrons.

b) Undergoes oxidation and acts as reducing agent.

c) Is represented on LHS in galvanic cell.

d) Displaces other metal ions which have more SRP from their salt solution.

iv. Metal with more SRP

- a) Has high tendency to gain electrons.
 - b) Undergoes reduction and acts as oxidant.
 - c) Is represented on RHS in galvanic cell.
 - d) Is replaced by other metals which have less SRP from its salt solution.
- v. An element with a lower reduction potential (higher negative potential) is a more powerful reducing agent. $\text{Li} > \text{K} > \text{Ca} > \text{Zn} > \text{Cu}$
- vi. An element with a higher reduction potential (higher positive potential) is a more powerful oxidising agent.
- i) $\text{Ag}^+ > \text{Cu}^{2+} > \text{Sn}^{2+} > \text{Ni}^{2+} > \text{Fe}^{2+} > \text{Zn}^{2+}$
 - ii) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- vii. A salt solution can't be stored in a container made up of Lower SRP metal. Metals with $-ve$ SRP only displaces hydrogen from dilute acids.
- viii. In a galvanic cell lower SRP electrode acts as 'anode' and higher SRP electrode acts as 'cathode'.

Electro chemical or Activity series

Electrode	potential in volts
Li^+ / Li	-3.045
Cs^+ / Cs	-2.95
K^+ / K	-2.925
$\text{Ba}^{+2} / \text{Ba}$	-2.90
$\text{Ca}^{+2} / \text{Ca}$	-2.870
Na^+ / Na	-2.714
$\text{Mg}^{+2} / \text{Mg}$	-2.375
$\text{Al}^{+3} / \text{Al}$	-1.66
$\text{Zn}^{+2} / \text{Zn}$	-0.762
$\text{Fe}^{+2} / \text{Fe}$	-0.441

H⁺/H₂, Pt	0.000
AgBr/Ag	+0.10
AgCl/Ag	+0.22
Cu ²⁺ /Cu	+0.337
Cu ⁺ /Cu	+0.52
Pt, I ₂ / 2I ⁻	+0.536
Ag ⁺ / Ag	+0.800
Pt, Br ₂ /2Br ⁻	+1.065
Pt, Cl ₂ /2Cl ⁻	+1.360
Au ³⁺ / Au	+1.50
Pt, F ₂ / 2F ⁻	+2.87

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