ELECTROCHEMISTRY

Module – 13.2: Faraday's law of electrolysis and applications

Faraday's laws of electrolysis:

Michael Faraday, an English scientist, studied the quantitative relationships between electricity and the amount of substance deposited on the electrode. He summarized his result of the decomposition of electrolytes by electricity in the form of two laws, commonly known as Faraday's laws of electrolysis

1. **Faraday's first law of electrolysis:**

   It states that "***the weight of a chemical substance deposited at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.***"

   Let, W = Weight (in gm) of the substance deposited

   Q = Quantity of electricity (in columns) passed, then mathematically,

   $$W \alpha Q$$

   But we know that

   Q = current (c) in amperes × time (t) in seconds

   $$i.e.,\ Q = c \times t$$

   $$W \alpha c \times t$$

   $$W = z \times c \times t$$

   Where **z** is proportionality constant and known as electrochemical equivalent (e.c.e) of the substance. Its value depends upon the nature of the ion liberated. Now when C = 1 ampere and T = 1 second, *i.e.,* when a current of 1 ampere is passed through an electrolyte for one second, then

   $$W = z \times 1 \times 1$$

   $$W = z$$

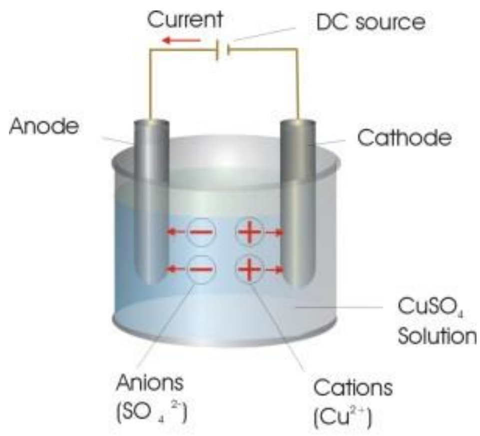
   Hence electrochemical equivalent of a substance may be defined **as the amount of the substance deposited by passing a current of one ampere for one second (*i.e.,* by passing one coulomb of electricity).** It is found that 1 gm equivalent of an ion is liberated by 96,500 coulombs nearly of electricity.

   Hence e.c.e (z) = Eq. Wt. /96,500

Let us take an example of electrolysis of aqueous copper sulphate solution using inert electrodes such as platinum electrodes.

In the aqueous solution copper sulphate dissociates into its respective ions, as shown below.

$$CuSO_4 \Rightarrow Cu^{2+} + SO_4^{\,2-}$$



An Electrolytic Cell

On passing electric current the copper ions (cations) move towards the cathode and get discharged. They are deposited as copper. Simultaneously the sulphate ions (anions) move towards the anode.

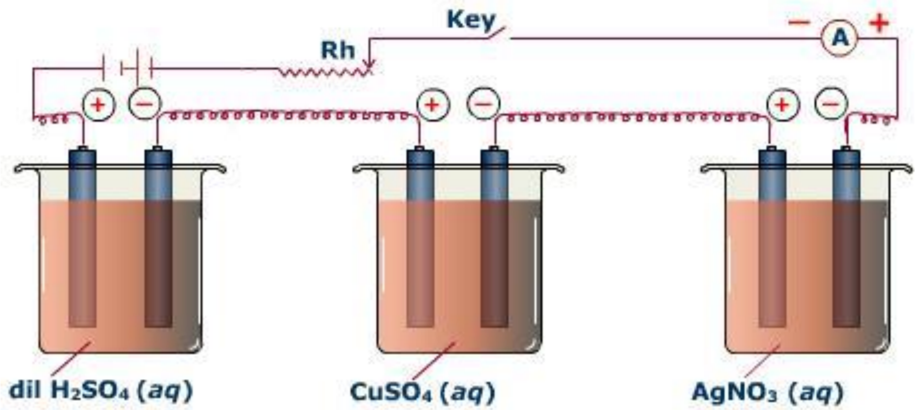
2. Faraday's second law of electrolysis:

It states that **"the weight of different substances produced, by the same quantity of electricity, is proportional to the equivalent of the substances."** If W_1 and W_2 are the weights of two elements deposited by passing a certain quantity of electricity through their salt solutions. E_1 and E_2 are their respective equivalent weights, then

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

For example, when the same current is passed through the solutions of sulphuric acid (H_2SO_4), copper sulphate ($CuSO_4$) and silver nitrate ($AgNO_3$) for the same period of time, then according to the second law of Faraday's.

$$\frac{\text{Mass of copper deposited}}{\text{Mass of hydrogen gas liberated}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of hydrogen}}$$



Experimental set up for the verification of the Second Law of Electrolysis

Metal deposited α Eq. Wt. of the metal

In other words

$$\frac{Wt.of\ metal\ M_1 deposited}{Wt.of\ metal\ M_2 deposited} = \frac{Eq.Wt\ of\ metal\ M_1}{Eq.Wt\ of\ metal\ M_2}$$

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

Where W_1 and W_2 are the weights of metal deposited at the respective electrodes and E_1 and E_2 are their respective equivalent weights.
Now according to first law

W = z × c × t

Putting the values of W in (ii), we get

$$\frac{z_1\ \times\ c\ \times\ t}{z_2\ \times\ c\ \times\ t} = \frac{E_1}{E_2}$$

$$\frac{z_1}{z_2} = \frac{E_1}{E_2}$$

In other words, the electrochemical equivalent of an element is directly proportional to its equivalent weight, *i.e.,*

E α z

E = F × z

Where F is proportionally constant and called as Faraday. The value of one Faraday is 96540 coulombs. Thus with the help of the above equation, we can determine the electrochemical equivalent of the metal as below.

$$z = \frac{E}{F}$$

Electrochemical equivalent of the metal (z)

$$= \frac{Equivalent\ wt. of\ the\ metal}{96500}$$

Definition of Faraday:

One Faraday may be defined as the quantity of electricity which can deposit one gram equivalent of the element(s) present in that electrolyte.

Applications of electrolysis:

The phenomenon of electrolysis has wide applications. The important ones are:

1. **Determination of equivalent masses of elements:**
   According to second law of electrolysis when the same quantity of electric current is passed through solutions of salts of two different metals taken in two different cells, the amounts of the metals deposited on the cathodes of the two cells are proportional to their equivalent masses of the respective metals. If the amounts of the metals deposited on the cathodes be W_A and W_B respectively, then

$$\frac{W_A}{W_B} = \frac{Equivalent\ mass\ of\ A}{Equivalent\ mass\ of\ B}$$

Knowing the equivalent mass of one metal, the equivalent mass of the other metal can be calculated. The equivalent masses of those non – metals which are evolved at anodes can also be determined by this method.

2. **Electrometallurgy:**

   The metals like sodium, potassium, magnesium, calcium, aluminum etc. are obtained by electrolysis of fused electrolytes.

Fused electrolyte	Metal isolated
$NaCl + CaCl_2 + KF$	Na
CaCl2 + CaF_2	Ca
Al_2O_3 + cryolite	Al
$MgCl_2$ (35%) + NaCl (50%) + $CaCl_2$ (15%)	Mg
NaOH	Na
$KCl + CaCl_2$	K

3. **Manufacture of non – metals:**

   Non – metals like hydrogen, fluorine, chlorine are obtained by electrolysis

4. **Electro – refining of metals:**

   The metals like copper, silver, gold, aluminum, tin etc., are refined by electrolysis

5. **Manufacture of compounds:**

   Compounds like NaOH, KOH, Na_2CO_3, $KClO_3$, $KMnO_4$ etc., are manufactured by electrolysis

6. **Electroplating:**

   The process of coating an inferior metal with a superior metal, by electrolysis is known as electroplating. The aims of electroplating are:

   a. To prevent the inferior metal from corrosion
   b. To make it more attractive in appearance

   The object to be electroplated is made the cathode and block of the metal to be deposited is made the anode in an electrolytic bath containing a solution of a salt of the anodic metal. On passing electric current in the cell, the metal of the anode dissolves out and is deposited on the cathode – article in the form of a thin film.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$CuSO_4$ + dilute H_2SO_4

With silver	Ag	Object	$K[Ag(CN)_2]$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$K[Au(CN)_2]$
With zinc	Zn	Iron objects	$ZnSO_4$
With tin	Sn	Iron objects	$SnSO_4$

Assignment Questions:

1. State and explain Faraday's second law of electrolysis
2. How much copper will be deposited by a current of 2.4 amperes passing through a solution of copper sulphate for one hour and thirty eight minutes? (atomic weight of copper = 63) [**Ans:** 4.65 gm]
3. An electric current was passed through two voltmeter cells one containing copper sulphate (using copper electrodes) and the other containing silver nitrate solution (using silver electrodes). The increase in weight of cathodes in two cells was respectively 0.189 g and 0.648 g. Calculate the chemical equivalent of copper, taking that of silver as 108. [**Ans:** 31.5]

Example Set:

1. One Faraday is equal to ____ coulombs
   a. 9650
   b. 10,000
   c. 19640
   d. 96540

Solution: d)

2. The amount of electricity required to produce one mole of copper from copper sulphate solution will be ___ Faraday
   a. 1
   b. 1.33
   c. 2
   d. 2.33

Solution: c)

3. State Faraday's law of electrolysis

Solution:

Faraday's first law of electrolysis:

It states that **the weight of a chemical substance deposited at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.**

Faraday's second law of electrolysis:

It states that **the weight of different substances produced, by the same quantity of electricity, is proportional to the equivalent of the substances.**

4. Give any four applications of Faraday's law of electrolysis

Solution:

a. **Manufacture of non – metals:**
Non – metals like hydrogen, fluorine, chlorine are obtained by electrolysis

b. **Electro – refining of metals:**
The metals like copper, silver, gold, aluminum, tin etc., are refined by electrolysis

c. **Manufacture of compounds:**
Compounds like NaOH, KOH, Na_2CO_3, $KClO_3$, $KMnO_4$ etc., are manufactured by electrolysis

d. **Electroplating:**
The process of coating an inferior metal with a superior metal, by electrolysis is known as electroplating. The aims of electroplating are:

i. To prevent the inferior metal from corrosion

ii. To make it more attractive in appearance

Problem Set:

1. Which equation represents the first law of electrolysis correctly?

a. wz = ct

b. w = czt

c. wc = zt

d. c = wzt

Solution: b)

2. when the same electricity is passed through the solution of different electrolytes in the series, the amount of elements deposited on the electrodes are in the ratio of their

a. atomic numbers
b. atomic masses
c. molecular masses of the electrolyte
d. equivalent masses

Solution: d)

3. Calculate the time in seconds in which half gram of copper is liberated from copper sulphate solution, when a current of 0.50 ampere is passed (At. Wt. of copper = 63)

Solution:

W = o.5 gm At. Wt. of copper = 63

c = 0.50 ampere z of copper = $\frac{Eq.wt.\ of\ copper}{96,500}$

t =? $= \frac{31.5}{96,500}$

Now, applying the formula

$$W = z \times c \times t$$

$$t = \frac{W}{z \times c}$$

$$= \frac{0.5 \times 96500}{31.5 \times 0.50}$$

= 3063.5 seconds

4. An electric current of 0.5 ampere was passed through acidulated water for 30 minutes. Calculate the volume of hydrogen produced at NTP. (z for hydrogen = 0.00001)

Solution:

Given,

c = 0.5 ampere t = 30 × 60 = 1800 seconds

z = 0.00001 W =?

Now W = z × c × t

= 0.00001 × 0.5 × 1800

= 0.009 gm

Now we know that 2 gm of hydrogen at NTP = 2.24 litres

0.009 gm of hydrogen at NTP $= \frac{22.4}{2} \times 0.009$ L

= 0.1008 litre

5. Calculate the time required for a current of 0.10 amperes to deposit 160 mg. of copper from a solution of copper sulphate. [chemical equivalent of Cu = 32]

Solution:

Chemical equivalent (equivalent wt.) of Cu = 32

Thus 32 gm of Cu is deposited by = 96500 coulombs

160 mg. or 0.16 gm of Cu will be deposited by $= \frac{96500}{32} \times 0.16 = 482.5\ coulombs$

In other words, quantity of electricity (Q) = 482.5 coulombs

c = 0.10 amperes t =?

Now since Q = c × t

482.5 = 0.10 × t

$= \frac{482.5}{0.10}$

= 4825 seconds

6. 0.600 g of a metal was deposited during the electrolysis of its salt solution with a current of 0.10 amperes for $2\frac{1}{2}$ hours. Determine the equivalent weight and valency of the metal in the salt (Atomic weight of the metal is 64)

Solution:

Given c = 0.10 amperes

t = 150 × 60 = 9000 seconds

Q = c × t

= 0.10 × 9000 = 900 coulombs

Now 900 coulombs of electricity deposits 0.600 gm of metal

96500 coulombs of electricity will deposit = $\frac{0.600}{900} \times 96500$

$= 64.33$

Hence the eq. wt. of the metal = 64.33

Therefore valency of the metal = $\frac{At.Wt.}{Eq.wt.} = \frac{64}{64.33} = 1$

Exercise questions:

1. In electrolysis experiment current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold chloride and the second contains copper sulphate solution on passing current 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode of the second cell. Also calculate the magnitude of the current in amperes.
(At. Wt. of Au = 197 and At. Wt of Cu = 63.5)
2. How long a current of 3 amperes has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer?
(Density of silver is 10.5 g / cm^3.)
3. A 100 watt, 110 volt incandescent lamp is connected in series with an electrolyte cell containing cadmium sulphate solution. What weight of cadmium will be deposited if the current flows for 10 hours
4. Calculate the quantity of electricity that will be required to liberate 710 g of Cl_2 gas by electrolyzing a conc. Solution of NaCl. What weight of NaOH and what volume of H_2 at 27^0 C and 1 atm. pressure is obtained during this process?
5. How long would it take to deposit 100 g of Al from an electrolytic cell containing Al_2O_3 using a current of 125 ampere
6. An ammeter and copper voltmeter are connected in series in an electric circuit through which a constant direct current flows. The ammeter shows 0.525 ampere. If 0.6354 g of Cu is deposited in one hour, what is percentage error of ammeter? (At. Wt. of Cu = 63.54)
7. Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation. (At .Wt of Cr = 52)
$CrO_{3\,(aq.)} + 6H^+ + 6e \rightarrow Cr_{(s)} + 3H_2O$
Calculate:
   a. How many grams of chromium will be plated out by 24000 coulombs?
   b. How long will it take to plate out 1.5 g of Cr by using 12.5 amperes current?

8. An aqueous solution of NaCl on electrolysis give $H_{2_{(g)}}$, $Cl_{2_{(g)}}$ and NaOH according to the reaction $2Cl^-_{(aq)} + 2H_2O \rightarrow 2OH^-_{(aq)} + H_{2_{(g)}} + Cl_{2_{(g)}}$. A direct current of 25 amperes with a current efficiently of 62% is passed through 20 litres of NaCl solution (20% by weight). Write down the reactions taking place at the anode and the cathode. How long will it take to produce 1 kg of Cl_2, What will be the molarity of the solution with respect to hydroxide ion? (Assume no loss due to evaporation).
9. In a fuel hydrogen and oxygen react to produce electricity. In the process hydrogen gas is oxidized at the anode and oxygen at the cathode. If 6.72 litre of H_2 at STP react in 15 minutes, what is the average current produced? If the entire current is used for electro deposition of copper from coperr (II) solution, how many grams of copper will be deposited?

$$\text{Anode reaction: } H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$$

$$\text{Cathode reaction: } O_2 + 2H_2O + 2e^- \longrightarrow 4OH^-$$

10. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g/ml, Sulphuric acid of density 1.294 g/ml is 39% by weight and that of 1.139 g/ml is 20% H_2SO_4 by weight. The battery holds 3.5 litres of the acid and the volume remained practically constant during the discharge

Calculate the number of ampere – hours for which the battery must have been used. The charging and discharging reactions are:

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \text{ (charging)}$$

$$PbO_2 + 4H^+ SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \text{ (discharging)}$$

Solutions to exercise questions:

1. Equivalent of gold formed = Equivalent of Cu formed

Therefore $\frac{wt.of\ Au}{eq.wt.of\ Au} = \frac{wt.of\ Cu}{eq.wt.of\ Cu}$

Therefore $Au^{3+} + 3e^- \rightarrow Au$

and $Cu^{2+} + 2e^- \rightarrow Cu$

Therefore $\frac{9.85}{197/3} = \frac{W_{Cu}}{63.5/2}$

$$W_{Cu} = \frac{9.85 \times 3 \times 63.5}{197 \times 2} = \frac{1876.425}{394} = 4.763\ g$$

Also, $w = \frac{Eit}{96500}$

Therefore $4.763 = \frac{63.5 \times i \times 5 \times 60 \times 60}{2 \times 96500}$

Therefore $i = \frac{4.763 \times 2 \times 96500}{63.5 \times 5 \times 60 \times 60}$

$= \frac{919259}{1143000}$

= 0.804 ampere

2. Volume of the surface (V) = area × thickness

   Given,

   Area = 80 cm^2, thickness = 0.005 mm = 0.0005 cm

   Therefore V = 80 × 0.0005 = 0.04 cm^3

   Mass of Ag (w) = V × density

   = 0.04 × 10.5 = 0.42 g

   $Ag^+ + e^- \rightarrow Ag$

   Therefore $W_{Ag} = \frac{Eit}{96500}$

   $0.42 = \frac{108 \times 3 \times t}{96500}$

   Therefore $t = \frac{0.42 \times 96500}{108 \times 3} = \frac{40530}{324} = 125.09\ s$

3. Watt = Ampere × Volt

   Therefore Ampere (i) = $\frac{Watt}{Volt} = \frac{100}{110}$

   Now, $w = \frac{Eit}{96500}$

   Therefore $w_{Cd} = \frac{112.4 \times 100 \times 10 \times 60 \times 60}{2 \times 110 \times 96500}$

$= \frac{404640000}{21230000} = 19.06\ g$

4. $2Cl^- \rightarrow Cl_2 + 2e$

   $w = \frac{E.i.t}{96500} = \frac{E.Q}{96500}$

   $Q = \frac{96500w}{E} = \frac{96500 \times 710}{35.5} = 20F$

   Q = 1930000 coulomb

   Therefore 1F gives 1g eq. or 40g NaOH

   Therefore 20F gives 20g eq. or 40 × 20g NaOH = 800g NaOH

   Therefore 1F gives 1g eq. or 1g H_2

   Therefore 20F gives 20g eq. or 20g H_2

   From $PV = \frac{w}{m} RT$

   $1 \times V = \frac{20}{2} \times 0.0821 \times 300$

   $V_H = 246.3$ litre

5. $Al_2^{3+} + 6e \rightarrow 2Al$

   $E_{Al} = \frac{At.wt}{3} = \frac{27}{3} = 9$

   Now $w = \frac{E.i.t}{96500}$

   $100 = \frac{27 \times 125 \times t}{3 \times 96500}$

   t = 8577.77 second

6. Current flown = 0.525 ampere as shown by ammeter

   Actual current flown (i) = $\frac{w}{E \times t} \times 96500 = \frac{0.6354 \times 96500}{(\frac{63.54}{2}) \times 60 \times 60}$ ($\because t = 60 \times 60$ sec)

   i = 0.536 ampere

   Thus error in (i) = 0.536 – 0.525 = 0.011

   Therefore % error in ammeter = $\frac{0.11 \times 100}{0.536} = 2.05\%$

7. Eq. wt. of Cr = $\frac{At.wt.}{No.of\ electrons\ lost\ or\ gained\ by\ one\ molecule\ of\ Cr} = \frac{52}{6}$

   a. Therefore 96500 coulomb deposit = $\frac{52}{6} \times \frac{24000}{96500} g\ Cr = 2.1554\ g\ of\ Cr$

   b. Also given, $w_{Cr} = 1.5$ g, i = 12.5 ampere, t =?, $E_{Cr} = \frac{52}{6}$

$$w = \frac{E.i.t}{96500}$$

$$1.5 = \frac{52 \times 12.5 \times t}{6 \times 96500}$$

t = 1336.15 second

8. $2Cl^{-}_{(aq)} + 2H_2O \rightarrow 2OH^{-}_{(aq)} + H_{2_{(g)}} + Cl_{2_{(g)}}$

Reaction at anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Reaction at cathode : $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$$i = \frac{62}{100} \times 25 = 15.4 \text{ amperes}$$

Weight of Cl_2 deposited = 1 kg or 1000 gm

We know that $\frac{W}{E} = \frac{Q}{F} = \frac{it}{F}$

$$\frac{1000}{35.5} = \frac{15.4 \times t}{96500}$$

t = 175300 sec. (or) 48.69 hours

Number of moles of Cl_2 thus produced

$$= \frac{1000}{71} = 14.08$$

Amount of OH^- released in the electrolysis = 2 x 14.08 moles = 28.16 moles

∴ Molarity with respect of

$$OH^- = \frac{28.16 \text{ moles}}{20 l} = 1.408 \text{ M}$$

9. For the given reactions, it is obvious that 22.4 litres of H_2 gas require 2 Faraday electricity.

∴ 6.2 litres of H_2 will requires = 6 Faraday electricity

Q = C x t

6 x 96500 = C x 15 x 60

$$C = \frac{6 \times 96500}{15 \times 60} = 643.3 \text{ ampere}$$

Calculation of amount of Cu deposited by 6 F since 1 F deposits $= \frac{63.5}{2} = 31.75$ g of Cu

$6\,F$ will deposits = $31.75 \times 6\,g = 190.50$ g of Cu

10. When we add charging the discharging reaction, we get

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow PbSO_4 + 2H_2O$

$NH_2SO_4 = M_{H_2SO_4}$ ($\therefore$ $2SO_4^{2-}$ requires $2e^-$)

$\therefore$ Normality = Molarity

Molarity of H_2SO_4 before electrolysis

$$= \frac{39 \times 1.2 \times 294 \times 1000}{98 \times 100} = 5.15$$

Molarity of H_2SO_4 after electrolysis

$$= \frac{20 \times 1.39 \times 1000}{98 \times 100} = 2.325$$

Moles of H_2SO_4 before electrolysis = 5.15 x 3.5 = 18.025

Moles of H_2SO_4 after electrolysis = 2.325 x 3.5 = 8.1375

$\therefore$ Moles (or equivalent) of H_2SO_4 used = 18.025 – 8.1375 = 9.8875

$$w = \frac{Eit}{96500} \quad \text{or} \quad i \times t = \frac{w \times 96500}{E} = 9.8875 \times 96500$$

= 954143.75 ; or **265.02 Amp.hr.**