TOPIC-4
Faraday’s laws of electrolysis and applications

VERY SHORT ANSWER QUESTIONS

1. **Explain Faraday’s First law of electrolysis?**

   **Ans:** **Faraday's First Law:** When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

   If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation:

   \[ W \propto Q \]

   A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

   \[ Q = \text{current in amperes} \times \text{time in seconds} = I \times t \]

   So \[ W \propto I \times t \]

   or \[ W = z \times I \times t \]

   where z is a constant, known as electro-chemical equivalent, and is characteristic of the substance deposited.

2. **Explain faraday’s Second law of electrolysis?**

   **Ans:** When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

   Again according to first law,

   \[ W = Z \times Q \]

   Then \[ Q = 96500 \text{ coulomb} \], W becomes gram equivalent mass (E).

   Thus, \[ E = Z \times 96500 \]
or \[ Z = \frac{E}{96500} \]

\[ \frac{z_1}{z_2} = \frac{E_1}{E_2} \]

3. **Explain how fundamental unit of charge can be found out?**

**Ans:** **Fundamental unit of charge:** As one g-equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by one g-equivalent of an ion is 96500 coulomb. If the valency of an ion is 'n', then one mole of these ions will carry a charge of \( nF \) coulomb. One g-mole of an ion contains \( 6.02 \times 10^{23} \) ions.

Then,

The charge carried by an ion = \( \frac{nF}{(6.02 \times 10^{23})} \) coulomb

For \( n = 1 \),

The fundamental unit of charge = \( \frac{F}{(6.02 \times 10^{23})} \)

i.e., \( \frac{96500}{(6.02 \times 10^{23})} = 1.6 \times 10^{-19} \) coulomb

or \( 1 \) coulomb* = \( 6.24 \times 10^{18} \) electrons

The rate of following of electric charge through a conductor is called the electric current.

4. **Find the charge in coulomb on 1 g-ion of?**

**Solution:** Charge on one ion of N\(_3^-\):

\[ = 3 \times 1.6 \times 10^{-19} \text{ coulomb} \]

Thus, charge on one g-ion of N\(_3^-\):

\[ = 3 \times 6.02 \times 10^{23} \]

\[ = 2.89 \times 10^5 \text{ coulomb} \]

5. **How much charge is required to reduce (a) 1 mole of Al\(^{3+}\) to Al and (b) 1 mole of to Mn\(^{2+}\)?**

**Solution:**

(a) The reduction reaction is

\[ \text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al} \]

1 mole 3 mole
Thus, 3 mole of electrons are needed to reduce 1 mole of $\text{Al}^{3+}$.

\[ Q = 3 \times F \]
\[ = 3 \times 96500 = 289500 \text{ coulomb} \]

(b) The reduction is

\[ \text{Mn}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \]

| 1 mole | 5 mole |

\[ Q = 5 \times F \]
\[ = 5 \times 96500 = 48500 \text{ coulomb} \]

**LONG ANSWER QUESTIONS**

1. **Explain the Faraday’s Law of Electrolysis?**

*Ans:* The relationship between the quantity of electric charge passed through an electrolyte and the amount of the substance deposited at the electrodes was presented by Faraday in 1834, in the form of laws of electrolysis.

(i) **Faraday's First Law**

When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If $W$ be the mass of the substance deposited by passing $Q$ coulomb of charge, then according to the law, we have the relation:

\[ W \propto Q \]

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

\[ Q = \text{current in amperes} \times \text{time in seconds} \]
\[ = I \times t \]

So  \[ W \propto I \times t \]

or  \[ W = z \times I \times t \]
where $z$ is a constant, known as electro-chemical equivalent, and is characteristic of the substance deposited.

When a current of one ampere is passed for one second, i.e., one coulomb ($Q = 1$), then

$$W = Z$$

Thus, electrochemical equivalent can be defined as the mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second. For example, when a charge of one coulomb is passed through silver nitrate solution, the amount of silver deposited is 0.001118 g. this is the value of electrochemical equivalent of silver.

**Faraday's Second Law**

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

![Diagram of voltametres](image)

The law can be illustrated by passing same quantity of electric current through three voltametres containing solutions of $\text{H}_2\text{SO}_4$, $\text{CuSO}_4$ and $\text{AgNO}_3$ respectively as shown in Fig.12.1. In the first voltameter, hydrogen and oxygen will be liberated; in the second, copper will be deposited and in the third, silver will be deposited.

$$(\text{Mass of hydrogen})/(\text{Mass of copper}) = (\text{Equivalent mass of hydrogen})/ (\text{Equivalent mass of copper})$$

or $$(\text{Mass of copper})/(\text{Mass of silver}) = (\text{Equivalent mass of copper})/ (\text{Equivalent mass of silver})$$

or $$(\text{Mass of silver})/(\text{Mass of hydrogen}) = (\text{Equivalent mass of silver})/ (\text{Equivalent mass of hydrogen})$$

It is observed that by passing one coulomb of electric charge.
Hydrogen evolved = 0.00001036 g.

Copper deposited = 0.0003292 g.

and Silver deposited = 0.001118 g

These masses are in the ratio of their equivalent masses. From these masses, the amount of electric charge required to deposit one equivalent of hydrogen or copper or silver can be calculated.

For hydrogen = 1/0.0001036 = 96500 coulomb

For copper = 31.78/0.0003292 = 96500 coulomb

For silver = 107.88/0.001118 = 96500 coulomb

This follows that 96500 coulomb at electric charge will deposit one g equivalent of any substance. 96500 coulomb us termed as one Faraday and is denoted by F.

Again according to first law,

\[ W = Z \times Q \]

Then \( Q = 96500 \) coulomb, \( W \) becomes gram equivalent mass (E).

Thus, \( E = Z \times 96500 \)

or \( Z = E/96500 \)

\[ z_1/z_2 = E_1/E_2 \]

2. Explain the applications of Faraday’s Laws of electrolysis?

Ans:

Applications of Electrolysis

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

1. **Determination of equivalent masses of elements:**

   According to second law of electrolysis when the same quantity of electronic current is passed through solutions of salts of 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
\[ \frac{W_A}{W_B} = \frac{\text{Equivalent mass of A}}{\text{Equivalent mass of B}} \]

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

(2) **Electron metallurgy:**

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

<table>
<thead>
<tr>
<th>Fused electrolyte</th>
<th>Metal isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl + CaCl₂ + KF</td>
<td>Na</td>
</tr>
<tr>
<td>CaCl₂ + CaF₂</td>
<td>Ca</td>
</tr>
<tr>
<td>Al₂O₃ + cryolite</td>
<td>Al</td>
</tr>
<tr>
<td>MgCl₂ (35%) + NaCl (50%) + CaCl₂ (15%)</td>
<td>Mg</td>
</tr>
<tr>
<td>NaOH</td>
<td>Na</td>
</tr>
<tr>
<td>KCl + CaCl₂</td>
<td>K</td>
</tr>
</tbody>
</table>

(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, Na₂CO₃, KClO₃, white lead, KMnO₄, 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:

(i) To prevent the inferior metal from corrosion.

(ii) 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. The following are the requirements for fine coating:

(i) The surface of the article should be free from greasy matter and its oxide layer. The surface is cleaned with chromic acid or detergents.

(ii) The surface of the article should be rough so that the metal deposited sticks permanently.

(iii) The concentration of the electrolyte should be so adjusted as to get smooth coating.

(iv) Current density must be the same throughout.

<table>
<thead>
<tr>
<th>For electroplating</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>With copper</td>
<td>Cu</td>
<td>Object</td>
<td>CuSO₄ + dilute H₂SO₄</td>
</tr>
<tr>
<td>With silver</td>
<td>Ag</td>
<td>Object</td>
<td>KAg(CN)₂</td>
</tr>
<tr>
<td>With nickel</td>
<td>Ni</td>
<td>Object</td>
<td>Nickel ammonium sulphate</td>
</tr>
<tr>
<td>With gold</td>
<td>Au</td>
<td>Object</td>
<td>KAu(CN)₂</td>
</tr>
<tr>
<td>With zinc</td>
<td>Zn</td>
<td>Iron objects</td>
<td>ZnSO₄</td>
</tr>
<tr>
<td>With thin</td>
<td>Sn</td>
<td>Iron objects</td>
<td>SnSO₄</td>
</tr>
</tbody>
</table>

**Thickness of coated layer**

Let the dimensions of metal sheet to be coated be (a cm × b cm).

Thickness of coated layer = c cm

Volume of coated layer = (a × b × c) cm³

Mass of the deposited substance = Volume × density
\[
= (a \times b \times c) \times d \ g
\]

=>

\[
(a \times b \times c) \times d = (I \times t \times E)/96500
\]

Using above relation we may calculate the thickness of coated layer.

**Solved Examples on Faraday’s Laws of Electrolysis**

**Some Solved Examples**

**Example 1.** Find the charge in coulomb on 1 g-ion of

**Solution:** Charge on one ion of N\(^{3-}\):

\[
= 3 \times 1.6 \times 10^{-19} \text{ coulomb}
\]

Thus, charge on one g-ion of N\(^{3-}\):

\[
= 3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23}
\]

\[
= 2.89 \times 10^5 \text{ coulomb}
\]

**Example 2.** How much charge is required to reduce (a) 1 mole of Al\(^{3+}\) to Al and (b) 1 mole of \(\text{Mn}^{4-}\) to \(\text{Mn}^{2+}\)?

**Solution:** (a) The reduction reaction is

\[
\text{Al}^{3+} + 3e^- \rightarrow \text{Al}
\]

1 mole 3 mole

Thus, 3 mole of electrons are needed to reduce 1 mole of Al\(^{3+}\).

\[
Q = 3 \times F
\]

\[
= 3 \times 96500 = 289500 \text{ coulomb}
\]

(b) The reduction is

\[
\text{Mn}^{4-} + 8H^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4H_2O
\]

1 mole 5 mole

\[
Q = 5 \times F
\]

\[
= 5 \times 96500 = 48500 \text{ coulomb}
\]
Example 3. How much electric charge is required to oxidise (a) 1 mole of $H_2O$ to $O_2$ and (b) 1 mole of $FeO$ to $Fe_2O_3$?

Solution: (a) The oxidation reaction is

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

1 mole 2 mole

$$Q = 2 \times F$$

$$= 2 \times 96500 = 193000 \text{ coulomb}$$

(b) The oxidation reaction is

$$FeO + \frac{1}{2}H_2O \rightarrow Fe_2O_3 + H^+ + e^-$$

$$Q = F = 96500 \text{ coulomb}$$

Example 4. Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing $AgNO_3$, second $CuSO_4$ and third $FeCl_3$ solution. How many gram of each metal will be deposited assuming only cathodic reaction in each cell?

Solution: The cathodic reactions in the cells are respectively.

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

1 mole 1 mole

108 g 1 F

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

1 mole 2 mole

63.5 g 2 F

and $$Fe^{3+} + 3e^- \rightarrow Fe$$

1 mole 3 mole

56 g 3 F
Hence, \(\text{Ag deposited} = 108 \times 0.4 = 43.2 \text{ g}\)

\(\text{Cu deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}\)

and \(\text{Fe deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}\)

**Example 5**  
An electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.

**Solution:**  
The reaction taking place at anode is

\[2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-\]

71.0 g 71.0 g \(2 \times 96500 \text{ coulomb}\)

\[\begin{align*}
1 \text{ mole} \\
Q &= I \times t = 100 \times 5 \times 600 \text{ coulomb}
\end{align*}\]

The amount of chlorine liberated by passing \(100 \times 5 \times 60 \times 60 \text{ coulomb}\) of electric charge.

\[\begin{align*}
&= \frac{1}{(2 \times 96500)} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}
\end{align*}\]

Volume of \(\text{Cl}_2\) liberated at NTP = 9.3264 \(\times 22.4 = 208.91 \text{ L}\)

**Example 6.**  
A 100 watt, 100 volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for 10 hours?

**Solution:**  
We know that

\[\text{Watt} = \text{ampere} \times \text{volt}\]

100 = \(\text{ampere} \times 110\)

Ampere = \(\frac{100}{110}\)

Quantity of charge = \(\text{ampere} \times \text{second}\)

\[= \frac{100}{110} \times 10 \times 60 \times 60 \text{ coulomb}\]

The cathodic reaction is

\[\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}\]
112.4 g  $2 \times 96500$ C

Mass of cadmium deposited by passing $\frac{100}{110} \times 10 \times 60 \times 60$ Coulomb charge = $\frac{112.4}{2 \times 96500} \times \frac{100}{110} \times 10 \times 60 \times 60 = 19.0598$ g

**Example 7.** In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution gold salt and the second cell contains copper sulphate solution. 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 in the second cell. Also calculate the magnitude of the current in ampere.

**Solution:** We know that

$$\frac{\text{Mass of Au deposited}}{\text{Mass of Cu deposited}} = \frac{\text{Eq. mass of Au}}{\text{Eq. Mass of Cu}}$$

Eq. mass of Au = $\frac{197}{3}$ ; Eq. mass of Cu $\frac{63.5}{2}$

Mass of copper deposited

$$= 9.85 \times \frac{63.5}{2} \times \frac{2}{197} g = 4.7625 g$$

Let $Z$ be the electrochemical equivalent of Cu.

$$E = Z \times 96500$$

or $$Z = \frac{E}{96500} = \frac{63.5}{(2 \times 96500)}$$

Applying $W = Z \times I \times t$

$$T = 5 \text{ hour} = 5 \times 3600 \text{ second}$$

$$4.7625 = \frac{63.5}{(2 \times 96500)} \times I \times 5 \times 3600$$

or $$I = \frac{4.7625 \times 2 \times 96500}{63.5 \times 5 \times 3600} = 0.0804 \text{ ampere}$$

**Example 8.** How long has a current of 3 ampere to be applied through a solution of silver nitrate to coat a metal surface of 80 cm$^2$ with 0.005 cm thick layer? Density of silver is 10.5 g/cm$^3$.

**Solution:** Mass of silver to be deposited

$$= \text{Volume} \times \text{density}$$

$$= \text{Area} \times \text{thickness} \times \text{density}$$
Given: Area = 80 cm², thickness = 0.0005 cm and density = 10.5 g/cm³

Mass of silver to be deposited = 80 × 0.0005 × 10.5

= 0.42 g

Applying to silver E = Z × 96500

Z = \frac{108}{96500} g