ELECTRO CHEMISTRY

TOPIC-4
Faraday's laws of electrolysis and applications

VERY SHORT ANSWER QUESTIONS

1.Explain Faraday's First law of elelctrolysis?

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 = current in amperes × 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 elelctrolysis?**

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 coulomb, W becomes gram equivalent mass (E).

Thus, $E = Z \times 96500$

or $Z = E/96500$

$z_1/z_2 = E_1/E_2$

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 6.02×10^{23} ions.

Then,

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

For n = 1,

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

i.e., $96500/(6.02 \times 1023) = 1.6 \times 10^{-19}$ coulomb

or 1 coulomb*=6.24×10^{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-}

$= 3 \times 1.6 \times 10^{-19}$ coulomb

Thus, charge on one g-ion of N^{3-}

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

$= 2.89 \times 10^{5}$ 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

$Al^{3+} + 3e^{-} \rightarrow Al$

1 mole 3 mole

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

$Q = 3 \times F$

$= 3 \times 96500 = 289500$ coulomb

(b) The reduction is

$Mn_4^- + 8H + 5e^- \rightarrow MN^{2+} + 4H_2O$

1 mole 5 mole

$Q = 5 \times F$

$= 5 \times 96500 = 48500$ 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:

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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 = current in amperes × 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.

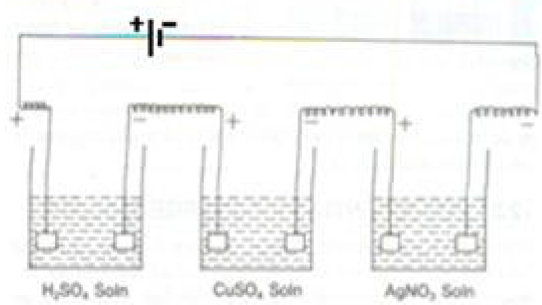

Fig. 12.1 Voltameters arranged in series

The law can be illustrated by passing same quantity of electric current through three voltametres containing solutions of H_2SO_4, $CuSO_4$ and $AgNO_3$ 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.

(Mass of hydrogen)/(Mass of copper) = (Equivalent mass of hydrogen)/
(Equivalent mass of copper)

or (Mass of copper)/(Mass of silver) = (Equivalent mass of copper)/
(Equivalent mass of silver)

or (Mass of silver)/(Mass of hydrogen) = (Equivalent mass of silver)/
(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

W_A/W_B = (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 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.

Fused electrolyte	**Metal isolated**
$NaCl + CaCl_2 + KF$	Na
$CaCl_2 + CaF_2$	Ca
Al_2O_3 + cryolite	Al
$MgCi_2$ (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 $KCIO_3$, white lead, $KMnO_4$, 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:

(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.

For electroplating	**Anode**	**Cathode**	**Electrolyte**
With copper	Cu	Object	$CuSo_4$ + dilute H_2So_4
With silver	Ag	Object	$KAg(CN)_2$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$KAu(CN)_2$
With zinc	Zn	Iron objects	$ZnSO_4$
With thin	Sn	Iron objects	$SnSO_4$

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) cm^3

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

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Thus, charge on one g-ion of N^{3-}

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

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Al^{3+} + $3e^{-}$ --> Al

1 mole 3 mole

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$Q = 3 \times F$

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(b) The reduction is

Mn_4^{-} + 8H + $5e^{-}$ --> MN^{2+} + $4H_2O$

1 mole 5 mole

$Q = 5 \times F$

$= 5 \times 96500 = 48500$ 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

$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^-$

1 mole 2 mole

$Q = 2 \times F$

$= 2 \times 96500 = 193000$ coulomb

(b) The oxidation reaction is

$FeO + 1/2\ H_2O \rightarrow Fe_2O_3 + H^+ + e^-$

$Q = F = 96500$ coulomb

Example 4 Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing AgNO3, second CuSO4 and third FeCl3 solution. How many gram of rach 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, Ag deposited = 108 × 0.4 = 43.2 g

Cu deposited = 63.5/2×0.4 = 12.7 g

and Fe deposited = 56/3×0.4 = 7.47 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

$2Cl^- \text{-->} \; Cl_2 \quad + 2e^-$

71.0 g 71.0 g 2 × 96500 coulomb

1 mole

Q = I × t = 100 × 5 × 600 coulomb

The amount of chlorine liberated by passing 100 × 5 × 60 × 60 coulomb of electric charge.

= 1/(2×96500)×100×5×60×60 = 9.3264 mole

Volume of Cl_2 liberated at NTP = 9.3264 × 22.4 = 208.91 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

Watt = ampere × volt

100 = ampere × 110

Ampere = 100/110

Quantity of charge = ampere × second

= 100/110×10×60×60 coulomb

The cathodic reaction is

$Cd^{2+} \quad + \quad 2e^- \quad \text{-->} \quad Cd$

112.4 g $\quad 2 \times 96500$ C

Mass of cadmium deposited by passing $100/110\times10\times60\times60$

Coulomb charge = $112.4/(2\times96500)\times100/110\times10\times60\times60 = 19.0598$ 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

(Mass of Au deposited)/(Mass f Cu deposited)=(Eq.mass of Au)/(Eq.Mass of Cu)

Eq. mass of Au = 197/3 ; Eq. mass of Cu 63.5/2

Mass of copper deposited

$= 9.85 \times 63.5/2\times3/197$ g = 4.7625 g

Let Z be the electrochemical equivalent of Cu.

$E = Z \times 96500$

or $Z = E/96500 = 63.5/(2\times96500)$

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

$T = 5$ hour $= 5 \times 3600$ second

$4.7625 = 63.5/(2\times96500) \times I \times 5 \times 3600$

or $I = (4.7625 \times 2 \times 96500)/(63.5 \times 5 \times 3600) = 0.0804$ 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 cm2 with 0.005 cm thick layer? Density of silver is 10.5 g/cm^3.

Solution: Mass of silver to be deposited

= Volume × density

= Area ×thickness × density

Given: Area = 80 cm^2, thickness = 0.0005 cm and density = 10.5 g/cm^3

Mass of silver to be deposited = $80 \times 0.0005 \times 10.5$

$= 0.42$ g

Applying to silver $E = Z \times 96500$

$Z = 108/96500$ g