FARADAY'S LAWS OF ELECTROLYSIS

Learning Objectives:

Students will be able to

1. define and explain Faraday's first law of electrolysis.
2. define and explain Faraday's second law of electrolysis.
3. solve the numerical problems related to Faraday's first and second laws of electrolysis.

Faraday's laws of Electrolysis

Michael Faraday, on the basis of his research, investigated electrolysis quantitatively. He found that, during electrolysis, the quantities of substances liberated at electrodes depend upon the following three factors.

i. The quantity of current passed.
ii. Time duration of passing the current at a uniform rate.
iii. Charge on the ions being deposited.

Faraday's First Law of Electrolysis

"The mass of an element liberated on an electrode during electrolysis is directly proportional to the quantity of electricity, Q, which passes through the solution of an electrolyte".

Explanation: If 'm' is the mass or amount of a substance deposited or liberated and 'I' is the current in amperes, which passes for 't' seconds, then according to the law:

$$m \propto I \times t$$

or

$$m = Z \times I \times t$$

Where 'Z' is a constant which is called '*Electrochemical equivalent* ' of the substance.

If one ampere of current is passed for one second, then m = Z. This means when 'one ampere' of current is passed for 'one second', then the mass or amount of the substance deposited or liberated is exactly equal to its 'electrochemical equivalent'.

The unit of the quantity of electricity is called *coulomb*. Coulomb is the quantity of electricity passed when one ampere current passes for one second. If 'Q' is the quantity of electricity then according to the Faraday's 1st law:

$$Q = I \times t$$

The larger unit of the quantity of electricity is called Faraday.

One Faraday = 96500 Coulombs

The quantity of a substance, which is deposited when one Faraday (96500 coulombs) of electricity is passed through an electrolyte is called one 'Gram Chemical Equivalent' of that substance.

Electrochemical equivalent:

Electrochemical equivalent of a substance may be defined as "*The amount (or weight) of the substance deposited or liberated, when one coulomb of electric charge is passed through an electrolyte*". It is denoted by 'Z' and in SI units it is expressed in Kg/Coulomb.

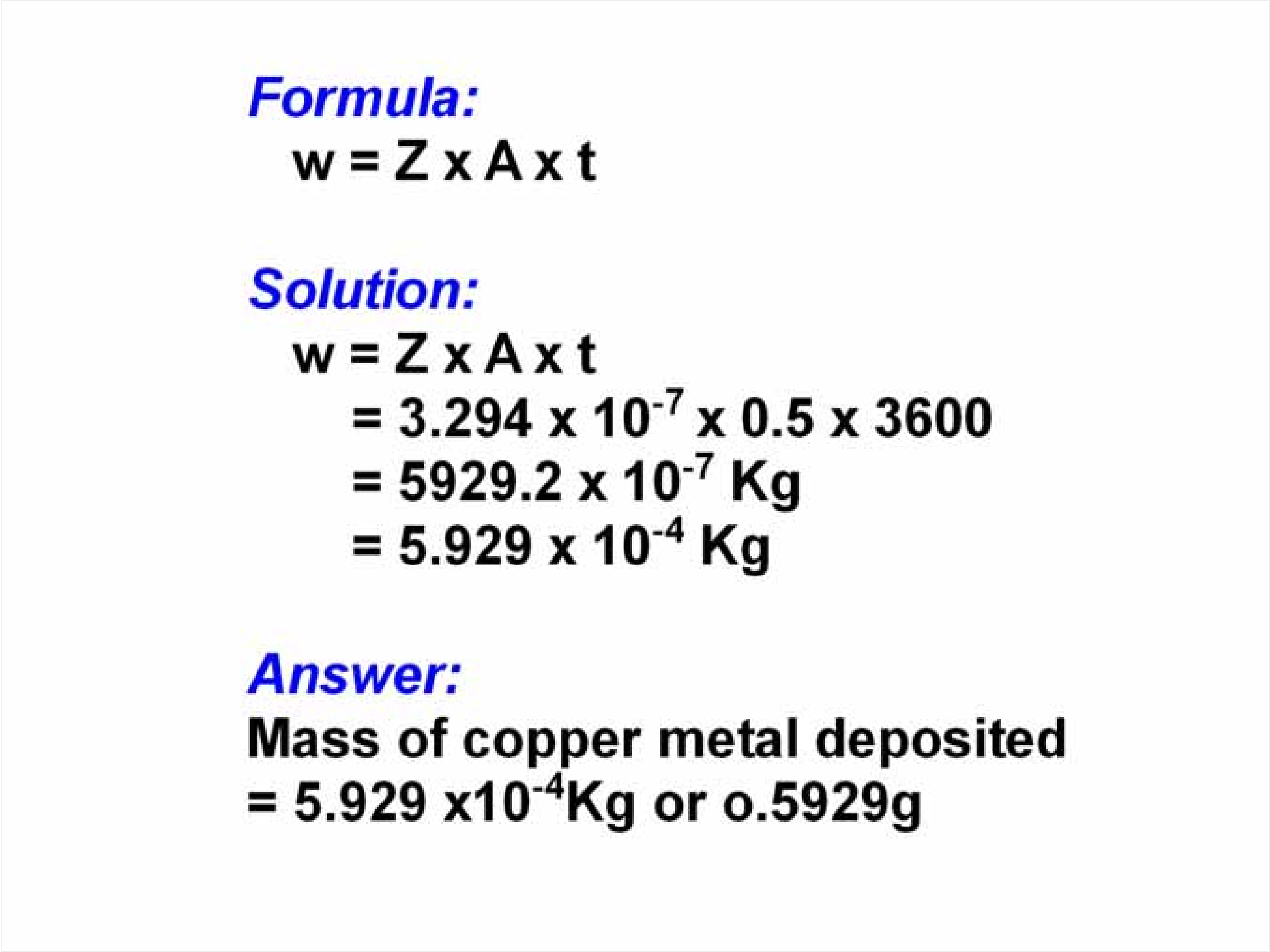
Example 1:

A current of 0.5 ampere was passed through a solution of $CuSO_4$ for one hour. Calculate the mass of copper metal deposited on the cathode.

Electrochemical equivalent of Cu=0.000329 g/C
$= 3.29 \times 10^{-4}$ g/C or 3.294×10^{-7} Kg/C

Data:

1. Current in ampere (A) = 0.5
2. Time in second (1 hour) = $1 \times 60 \times 60$
= 3600 s
3. Z for Cu metal = 3.294×10^{-4} g/C
= 3.294×10^{-7} Kg/C



Formula:

$w = Z \times A \times t$

Solution:

$$\begin{aligned} w &= Z \times A \times t \\ &= 3.294 \times 10^{-7} \times 0.5 \times 3600 \\ &= 5929.2 \times 10^{-7}\ \text{Kg} \\ &= 5.929 \times 10^{-4}\ \text{Kg} \end{aligned}$$

Answer:

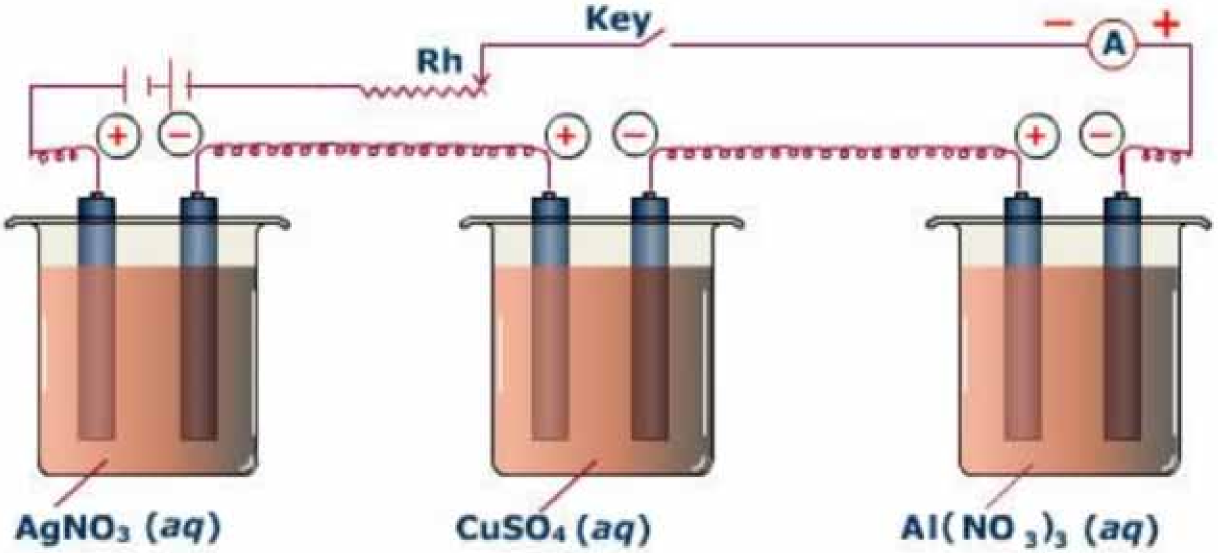
Mass of copper metal deposited
= 5.929×10^{-4}Kg or o.5929g

Faraday's Second Law of Electrolysis

Faraday's laws are very useful for the determination of chemical equivalents of different electrolytes. Its usefulness is evident from 2nd law.

According to the 2nd law of Faraday, "The masses of different substances deposited or liberated, when same quantity of electricity is passed through different electrolytes, connected in series are proportional to their '*chemical equivalent masses*'.

Consider three different electrolytes, $AgNO_3$, $CuSO_4$ and $Al(NO_3)_3$ in their aqueous solutions, connected in series.


Key
Rh
A
−
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AgNO₃ (aq)
CuSO₄ (aq)
Al(NO₃)₃ (aq)

Same quantity of electricity is passed through them, then the masses of Ag, Cu and Al, deposited on their respective electrodes would be directly proportional to their chemical equivalent masses.

According to Faraday, if exactly 96500 coulombs of electric charge is passed then the mass of Ag deposited would be equal to 108g (108/1), that of copper is 31.75 g (63.5/2) and Al is 9g (27/3), which are their equivalent masss of an element.

$$\text{Eq. Mass of an element} = \frac{\text{Atomic mass of an element}}{\text{valency of the element}}$$

The current of 96500 coulombs is called one Faraday (F) charge after the name of scientist. Thus, Faraday is defined as the quantity of charge which deposits or liberates exactly one gram equivalent of a substance.

Example:

When an aqueous solution of copper sulphate is electrolysed, copper is deposited at the cathode.

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)} \quad \text{(at cathode)}$$

If a constant current was passed for 5 hours and 404 mg of Cu was deposited. Calculate the current passed through $CuSO_4$.

Solution:

Amount of Cu deposited = 404 mg =0.404 g
Gain of $2e^{-}$ means 2 F electric charge
Atomic mass of Cu = 63.5 a.m.u.

According to cathode reaction.
63.5 g of Cu is deposited by 2 F electric charge
0.404g of Cu is deposited by $2 \div 63.5 \times 0.404$
$= 0.0127$ F

We know,
1F = 96,500 coulomb
0.0127 F = $0.0127 \times 96{,}500 = 1225.6$ C

Coulomb = Ampere x time (sec) (time = 5 hours)
Ampere = Coulomb (C) / time (t)
$= 1225.6 \div 5 \times 60 \times 60 = 0.0680$
$= 6.80 \times 10^{-2}$ ampere

Numericals related to Faraday's laws

Problem 1:

When one Faraday or 96500 coulombs of elecricity is passsed through silver nitrate solution, 108 gms of silver are deposited. Calculate the electrochemical equivalent of silver.

Solution:

Problem 2:

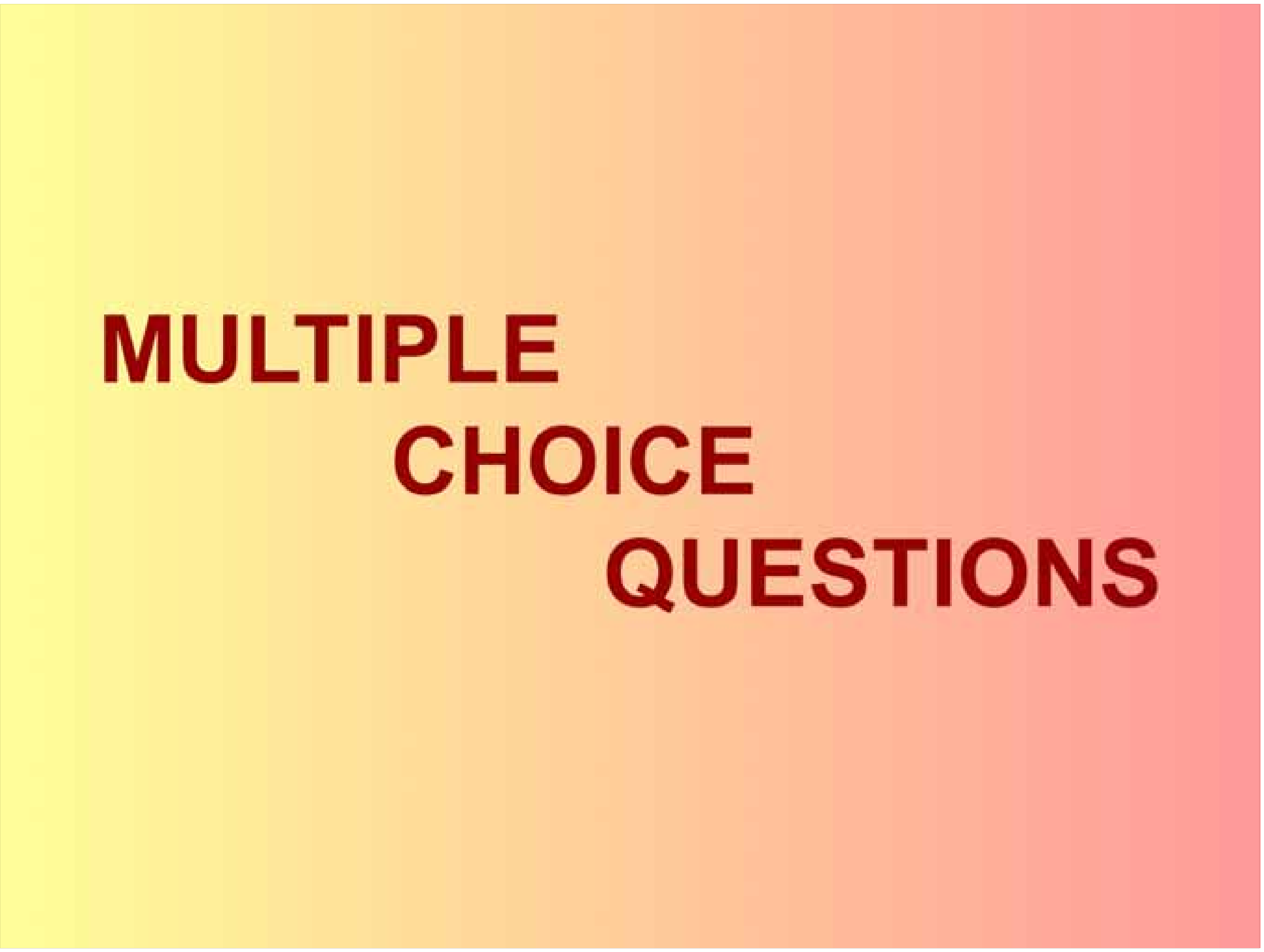
How many grams of oxygen is liberated by the electrolysis of water after passing 0.0565 ampere for 185 sec.

Solution:

Problem 3

0.1978g of copper is obtained on electrolyzing copper salt solution for 5 minutes using 2 ampere current. Calculate the electrochemical equivalent of copper.

Solution:



MULTIPLE
CHOICE
QUESTIONS

1. A compound whose aqueous solution is decomposed into its components when electricity is passed through it is called

A. non-electrolyte.
B. electrolyte.
C. acid.
D. salt.

2. The unit used for the quantity of electricity, in SI system, is

A. ohm.
B. ampere.
C. coulomb.
D. gram/equivalent.

3. What mass of calcium is collected on cathode when 1F of electricity is passed through its solution?

A. 40g
B. 20g
C. 10g
D. 5g