

## Faraday's laws of electrolysis.

The laws which govern the deposition of substances (In the form of ions) on electrodes during the process of electrolysis is called **Faraday's laws of electrolysis**. These laws given by **Michael Faraday in 1833**.

(1) **Faraday's first law:** It states that,

"The mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed."

$$\text{i.e. } W \propto Q$$

Where,  $W$  = Mass of ions liberated in gm,

$Q$  = Quantity of electricity passed in Coulombs = Current in Amperes (I)  $\times$  Time in second (t)

$$\therefore \boxed{W \propto I \times t \text{ or } W = Z \times I \times t}$$

In case current efficiency ( $\eta$ ) is given, then

$$\boxed{W = Z \times I \times t \times \frac{\eta}{100}}$$

Where,  $Z$  = constant, known as **electrochemical equivalent** (ECE) of the ion deposited.

When a current of 1 Ampere is passed for 1 second (i.e.,  $Q = 1$ ), then,  $W = Z$

Thus, **electrochemical equivalent** (ECE) may be defined as "the mass of the ion deposited by passing a current of one Ampere for one second (i.e., by passing Coulomb of electricity)". Its unit is gram per Coulomb. The ECE values of some common elements are:

Element	Hydrogen	Oxygen	Copper	Silver	Iodine	Mercury
$Z, g C^{-1}$	$1.045 \times 10^{-5}$	$8.29 \times 10^{-5}$	$3.294 \times 10^{-4}$	$1.18 \times 10^{-3}$	$1.315 \times 10^{-3}$	$1.039 \times 10^{-3}$

Note: Coulomb is the smallest unit of electricity.

$$96500 \text{ Coulombs} = 6.023 \times 10^{23} \text{ electrons.}$$

$$1 \text{ Coulomb} = \frac{6.023 \times 10^{23}}{96500} = 6.28 \times 10^{18} \text{ electrons, or 1 electronic charge} = 1.6 \times 10^{-19} \text{ Coulomb.}$$

(2) **Faraday's second law:** It states that,

"When the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (Equivalent weights)." i.e.

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \quad \text{or} \quad \frac{Z_1 It}{Z_2 It} = \frac{E_1}{E_2} \quad \text{or} \quad \frac{Z_1}{Z_2} = \frac{E_1}{E_2} \quad (\because W = Zit)$$

Thus the electrochemical equivalent (Z) of an element is directly proportional to its equivalent weight (E), i.e.

$$E \propto Z \quad \text{or} \quad E = FZ \quad \text{or} \quad E = 96500 \times Z$$

Where,  $F$  = Faraday constant =  $96500 \text{ C mol}^{-1}$

So, 1 Faraday = 1F = Electrical charge carried out by one mole of electrons.

1F = Charge on an electron  $\times$  Avogadro's number.

$$1F = e^- \times N = (1.602 \times 10^{-19} \text{ C}) \times (6.023 \times 10^{23} \text{ mol}^{-1}).$$

$$\text{Number of Faraday} = \frac{\text{Number of electrons passed}}{6.023 \times 10^{23}}$$

(3) **Faraday's law for gaseous electrolytic product:** For the gases, we use

$$V = \frac{It V_e}{96500}$$

Where,  $V$  = Volume of gas evolved at S.T.P. at an electrode

$V_e$  = Equivalent volume = Volume of gas evolved at an electrode at S.T.P. by 1 Faraday charge

Examples: (a)  $O_2$  :  $M = 32, E = 8$  ;  $32 \text{ g } O_2 \equiv 22.4 \text{ L}$  at S.T.P.

[M = Molecular mass, E = Equivalent mass]

$8 \text{ g } O_2 \equiv 5.6 \text{ L}$  At S.T.P.; Thus  $V_e$  of  $O_2 = 5.6 \text{ L}$ .

(b)  $H_2$  :  $M = 2, E = 1$  ;  $2 \text{ g } H_2 \equiv 22.4 \text{ L}$  at S.T.P.

$1 \text{ g } H_2 \equiv 11.2 \text{ L}$  At S.T.P.

Thus  $V_e$  of  $H_2 = 11.2 \text{ L}$ .

(c)  $Cl_2$  :  $M = 71, E = 35.5$  ;  $71 \text{ g } Cl_2 \equiv 22.4 \text{ L}$  at S.T.P.

$$35.5 \text{ g } Cl_2 \equiv 11.2 \text{ L At S.T.P.}$$

$$\text{Thus } V_e \text{ of } Cl_2 = 11.2 \text{ L.}$$

(4) **Quantitative aspects of electrolysis:** We know that, one Faraday (1F) of electricity is equal to the charge carried by one mole ( $6.023 \times 10^{23}$ ) of electrons. So, in any reaction, if one mole of electrons are involved, then that reaction would consume or produce 1F of electricity. Since 1F is equal to 96,500 Coulombs, hence 96,500 Coulombs of electricity would cause a reaction involving one mole of electrons.

If in any reaction, n moles of electrons are involved, then the total electricity (Q) involved in the reaction is given by,  $Q = nF = n \times 96,500 \text{ C}$

Thus, the amount of electricity involved in any reaction is related to:

- (i) The number of moles of electrons involved in the reaction.
- (ii) The amount of any substance involved in the reaction.

Therefore, 1 Faraday or 96,500 C or 1 mole of electrons will reduce,

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|---|--|
| (a) 1 mole of monovalent cation,            | (b) $\frac{1}{2}$ mole of divalent cation, |
| (c) $\frac{1}{3}$ Mole of trivalent cation, | (d) $\frac{1}{n}$ mole of n valet cations. |