



FARADAY'S LAWS OF ELECTROLYSIS AND ITS APPLICATION IN DETERMINING THE CORROSION RATE

The classical electrochemical work conducted by Michael Faraday in the nineteenth century produced two laws published in 1833 and 1834 named after him. The two laws can be summarized below

The First Law:

The mass of primary products formed at an electrode by electrolysis is directly proportional to the quantity of electricity passed. Thus:

$$m \propto It \text{ or } m = ZIt$$

where

I= current in amperes

t = time in seconds

m = mass of the primary product in grams

Z = constant of proportionality (electrochemical equivalent). It is the mass of a substance

liberated by 1 ampere-second of a current (1 coulomb)



The Second Law:

The masses of different primary products formed by equal amounts of electricity are proportional to the ratio of molar mass to the number of electrons involved with a particular reaction:

$$m_1 \propto \frac{M_1}{n_1} \propto Z_1 \quad \text{.....2}$$

$$m_2 \propto \frac{M_2}{n_2} \propto Z_2 \quad \text{.....3}$$

where

m_1, m_2 = masses of primary product in grams

M_1, M_2 = molar masses (g.mol^{-1})

n_1, n_2 = number of electrons

Z_1, Z_2 = electrochemical equivalent

Combining the first law and the second law, as in equation:

$$m = k \frac{M}{n} It \quad \text{.....4}$$

$$m = \frac{1}{F} \cdot \frac{M}{n} It \quad \text{.....5}$$



where F = Faraday's constant. It is the quantity of electricity required to deposit the ratio of mass to the valency of any substance and expressed in coulombs per mole (C (g equiv.)⁻¹). It has a value of 96 485 coulombs per gram equivalent. This is sometimes written as 96 485 coulombs per mole of electrons



Applications of Faraday's Laws in Determination of Corrosion Rates of Metals & Alloys

Corrosion rate has dimensions of mass x reciprocal of time:

$$(g \cdot y^{-1} \text{ or } kg \cdot s^{-1})$$

In terms of loss of weight of a metal with time, from equation (5), we get:

$$\frac{dw}{dt} = \frac{MI}{nF} \quad (I = \text{current}) \quad \text{.....6}$$

The rate of corrosion is proportional to the current passed and to the molar mass. Dividing equation (5) by the exposed area of the metal in the alloy, we get

$$\frac{w}{At} = \frac{MI}{nFA} \quad \text{..... 7}$$

But, $\frac{I}{A} = \text{current density } (i)$. Then:

$$\frac{w}{At} = \frac{Mi}{nF} \quad (i = \text{current density})$$



The above equation has been successfully used to determine the rates of corrosion.

A very useful practical unit for representing the corrosion rate is milligrams per decimeter square per day (mg.dm⁻².day⁻¹) or mdd. Other practical units are millimeter per year (mm y⁻¹) and mils per year (mpy).

Below are some examples showing how Faraday's laws are used to determine the corrosion rate.

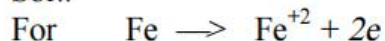
Example 1

Steel corrodes in an aqueous solution, the corrosion current is measured as 0.1 mA cm⁻². Calculate the rate of weight loss per unit area in units of mdd.

$$\frac{w}{At} = 2.897 \times 10^{-8} \text{ g cm}^{-2} \text{ s}^{-1}$$

Now converting g to mg (×103), cm⁻² to dm⁻², s to d

Sol.:



$$\frac{w}{At} = \frac{Mi}{nF} = 2.897 \times 10^{-5} \frac{\text{mg}}{\text{cm}^2 \text{ s}} * \frac{100 \text{ cm}^2}{\text{dm}^2} * \frac{3600 \text{ s}}{\text{h}} * \frac{24 \text{ h}}{\text{day}} = 250.3 \text{ mdd}$$

Where:

$$M = 55.9 \text{ g.mol}^{-1}$$

$$i = 0.1 \text{ mA.cm}^{-2}$$

$$n = 2$$



Example 2

Iron is corroding in seawater at a current density of $1.69 \times 10^{-4} \text{ A/cm}^2$. Determine the corrosion rate in

- (a) mdd (milligrams per decimeter²) mdd
- (b) ipy (inches per year)



(a) Apply Faraday's law as before



Example 4

Determine the corrosion rate of AISI 316 steel corresponding to $1 \mu\text{A}/\text{cm}^2$

Ni = 10%

Mo = 3%

Mn = 2%

Fe = balance, 67%

Cr = 18%

$$\begin{aligned} \text{Sol.: } 1 \mu\text{A}/\text{cm}^2 &= 0.128 \left[\frac{52.3}{(1)(7.19)} \right] 0.18 + 0.128 \left[\frac{54.94}{(2)(7.45)} \right] 0.02 + 0.128 \left[\frac{95.95}{(2)(10.1)} \right] 0.03 \\ &+ 0.128 \left[\frac{55.65}{(2)(7.86)} \right] 0.07 \text{ mpy} = 0.514587 \text{ mpy} \end{aligned}$$

Example 5

A sample of zinc corrodes uniformly with a current density of $4.2 \times 10^{-6} \text{ A}/\text{cm}^2$ in an aqueous .

(a) What is the corrosion rate of zinc in $\text{mg}/\text{dm}^2 \text{ /day}$?

(b) What is the corrosion rate of zinc in mm/year ?