# Stoichiometric Relationships in Electrolysis

## Background

Electrolytes are substances that conduct electricity when dissolved in water. The fact that a solution of an electrolyte conducts electricity doesn't mean that free electrons travel through the solution. An electrolyte solution conducts electricity because of ion movements, and the loss and gain of electrons at the electrodes. The terms *electrode* and *electrolyte* were invented by the Michael Faraday (1791-1867).

Faraday's most significant contributions to the field of electrochemistry was to connect the concepts of stoichiometry and electrochemistry.

We know that a balanced equation represents relationships between the quantities of reactants and products. For a reaction to take place in a cell, stoichiometric calculations can also include the quantity of electricity produced or consumed.

First, we need to understand how electricity is measured. We know that:

- The flow of electrons through an external circuit is called the *electric current*
  - It is measured in a unit called *ampere* (symbol 'A')

The **quantity of electricity**, also known as **electric charge**, is the product of the current flowing through a circuit and the time for which it flows.

- The quantity of electricity is measured in a unit called the *coulomb* (symbol 'C')

The ampere and the coulomb are related, in that:

- *1 coulomb is the quantity of electricity that flows through a circuit in 1 second if the current is 1 ampere*

Mathematically:

$$\text{charge (in coulombs)} = \text{current (in amperes)} \times \text{time (in seconds)}$$

## Example

Suppose a current of 2.00 A flows for 5.00 min. Calculate the quantity of electricity.

**<u>Given</u>**
(t) Time → 5.00 min = 300 s
(I) Current → 2.00 A
(Q) Quantity of Electricity → ?

$$Q = I \times t$$
$$Q = 2.00\ \text{A} \times 300\ \text{s}$$
$$Q = 600\ \text{A} \cdot \text{s} = 600\ \text{C} = 6.00 \times 10^2\ \text{C}$$

For stoichiometric calculations, you also need to know the electric charge on a mole of electrons. This charge can be calculated by:

- multiplying the charge on one electron and the number of electrons in one mole (Avogadro's number)

The charge on a mole of electrons is known as one faraday (1 F), named after Michael Faraday.

$$\begin{aligned}\text{Charge on one mole of electrons} &= \frac{1.602 \times 10^{-19}\ \text{C}}{1\cancel{e^-}} \times \frac{6.022 \times 10^{23}\ \cancel{e^-}}{1\ \text{mol}} \\ &= 9.647 \times 10^{4}\ \text{C/mol}\end{aligned}$$

## Sample Problem: Calculating the Mass of an Electrolysis Product

### Problem

Calculate the mass of aluminum produced by the electrolysis of molten aluminum chloride ($AlCl_3$), if a current of 500 mA passes for 1.50 h.

### What is Required?

You need to calculate the mass of aluminum product.

### What is Given?

Electrolyte: $AlCl_{3(l)}$

Current: 500 mA

Time: 1.50 h

### Steps

| | **Description** |
|---|---|
| Step 1 | Use the current and the time to find the quantity of electricity used |
| Step 2 | From the quantity of electricity, find the amount of electrons that passed through the circuit |
| Step 3 | Use the stoichiometry of the relevant half-reaction to relate the amount of electrons to the amount of aluminum produced |
| Step 4 | Use the molar mass of aluminum to convert the amount of aluminum to a mass |

**Step 1**

To calculate the quantity of electricity in coulombs, work in amperes and seconds.

$$500 \text{ mA} = 500 \cancel{\text{mA}} \times \frac{1 \text{ A}}{1000 \cancel{\text{mA}}} = 0.500 \text{ A}$$

$$1.50 \text{ h} = 1.50 \cancel{\text{h}} \times \frac{60 \cancel{\text{min}}}{1 \cancel{\text{h}}} \times \frac{60 \text{ s}}{1 \cancel{\text{min}}} = 5400 \text{ s}$$

Quantity of electricity → $Q = I \times t = 0.500 \text{ A} \times 5400 \text{ s} = 2700 \text{ C}$

**Step 2**

Find the amount of electrons. One mole of electrons has a charge of 1 F ($9.65 \times 10^4$ C/mol)

Amount of electrons → $n_{e^-} = \frac{\text{Quantity of Electricity}}{\text{Faraday's Number}} = \frac{2700 \text{ C}}{9.65 \times 10^4 \text{ C/mol}} = 0.028\, mol\, e^-$

**Step 3**

The half-reaction for the reduction of aluminum ions to aluminum is:

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

Amount of aluminum formed $= 0.028 \cancel{\text{mol e}^-} \times \frac{1 \text{ mol Al}}{3 \cancel{\text{mol e}^-}} = 0.00933 \text{ mol Al}$

**Step 4**

Convert the amount of aluminum to a mass

Mass of Al formed $= 0.00933 \text{ mol Al} \times \frac{27.0 \text{ g Al}}{1 \text{ mol Al}} = 0.252 \text{ g}$

∴About 0.252g of Aluminum is formed in the electrolysis of molten aluminum chloride.