Quantitative Aspects of Electrolytic Reactions

The principal cost in the electrolytic preparation of metals is the cost of electricity, therefore it is important to know how much electricity is needed to produce a certain amount of metal.

The quantity of product that results from electrolysis will depend upon the magnitude of the current and the time for which the current flows.

Metallic silver is produced at the cathode in the electrolysis of aqueous AgNO3, the reaction being:

$$Ag^{+1}_{(aq)} + e^{-1} \longrightarrow Ag_{(s)}$$

One mol of electrons is required to produce 1 mol of silver from 1 mol of silver ions. In contrast, 2 mol of electrons is required to produce 1 mol of copper:

$$Cu^{+2}_{(aq)} + 2e^{-1} \longrightarrow Cu_{(s)}$$

It follows that, if the number of moles of electrons flowing through the electrolysis cell could be measured, the number of moles of silver or copper produced could be calculated. Conversely, if the amount of silver or copper produced is known, then the number of moles of electrons used could be calculated.

The number of moles of electrons consumed or produced in an electron transfer reaction is usually obtained by measuring the current flowing in the external electric circuit in a given time.

The **current** flowing in an electric circuit is the amount of charge (in units of coulombs) passed per unit time, and the usual unit for current is the **ampere.**

$$\text{Current, I (amps)} = \frac{\text{electric charge (Coulomb, C)}}{\text{Time (seconds, s)}}$$

Michael Faraday (1791-1867) first explored the quantitative aspects of electricity. In his honour scientists have defined the **Faraday constant, 96 485.31 C/mol**, as **the charge carried by one mole of electrons**.

(Note: the charge on one electron is 1.602×10^{-19}, thus, the charge on one mole of electrons = $6.02\times10^{23} \times 1.602\times10^{-19}$ = 96485 C/mol = Faraday Constant, F).

Faraday's Laws:

1. In an electrolysis, the amount of product produced or reactant consumed is directly proportional to the length of time that a constant current is passed through a circuit.

2. To produce one mole of product, or consume one mole of reactant requires $9.65 \times 10^4 \times n$ coulombs of charge, where 'n' is the number of moles of electrons gained or lost per mole of reactant. (Or: moles of electrons $= \frac{C}{F}$)

The current passing through an electrochemical cell, and the time the current flowed, are easily measured with modern instruments. The charge that passed through the cell can therefore by obtained by multiplying the current (in amperes) by the time (in seconds).

Electric charge, Coulombs, C = Current, I (Amps) x time, t (s)

Knowing the charge, and using the Faraday constant as a conversion factor, the number of moles of electrons that passed through an electrochemical cell can be calculated.

Number of moles of e^{-1} = quantity of charge passed, C÷ Faraday = $\frac{C}{F}$

Example 1

A current of 1.50 amp is passed through a solution containing silver ions for 15.0 min. The voltage is such that silver deposited at the cathode. What mass of silver, in grams, is deposited?

$$Ag^{+1}_{(aq)} + e^{-1} \longrightarrow Ag_{(s)}$$

From the half-reaction we know that if 1 mol of electrons passed through the cell, then 1 mol of silver was deposited.
To find the number of moles of electrons, we need to know the total electric charge passed through the cell.
The charge can be calculated from experimental measurements of the current (in amps) and the time the current flowed.
Thus, the *logic of the calculation* is:

Time(s) x current (A) ⟶ charge (C) ⟶ Mol e^{-1} —— Mol Ag ⟶ Mass Ag

Steps to Solving Electrochemical Stoichiometry Problems

1. Quantity of Charge in Coulombs, C = current (A) x time (s)
2. Moles of e^{-1} = C ÷ F
3. Moles of e^{-1} from equation
4. Moles to grams

Solution to Example 1

1. Calculate the quantity of charge (number of coulombs) passed in 15.0 min.
   = 1.50 amps (15.0 min)(60.0 s/min)
   = 1.35×10^3 C

2. Calculate the number of moles of electrons...
   1.35×10^3 C = 1 mol e^{-1} / 9.65×10^4 C =1.40×10^{-2} mol e^{-1}

3. Calculate the number of moles of silver that passed through the cell and then the mass of silver deposited.
   = 1.40×10^{-2} mol e^{-1} (1 mol Ag/ 1 mol e^{-1})(107.9g Ag / 1 mol Ag)
   = 1.51 g

Example 2

What mass of copper can be produced by the electrolysis of $CuSO_{4(aq)}$ for 1.00 hour at a current of 100 A? $Cu^{+2}{}_{(aq)} + 2e^{-1} \longrightarrow Cu_{(s)}$ (119 g)

Example 3

In the electrolysis of molten $MgCl_{2(l)}$, what mass of Mg metal is deposited by a current of 16.0 amperes run for 100 minutes?

$Mg^{+2}{}_{(l)} + 2e^{-1} \longrightarrow Mg(s)$ (12.2 g)

Example 4

How long does it take a current of 2 amperes to deposit 81 g of silver?

$Ag^{+1} + e^{-1}$ ______ Ag (10 hours)

Example 5

What current is used to liberate 213 g of chlorine, $Cl_{2(g)}$ from a solution of NaCl if it take 2 hours? $2Cl^{-1} \longrightarrow Cl_{2(g)} + 2e^{-1}$ (80.4 A)

Example 6

What mass of Al will be deposited in 1.00 hr by the electrolysis of molten $AlCl_3$, using a current of 10.0A? $Al^{+3}{}_{(l)} + 3e^{-1} \longrightarrow Al_{(s)}$ (3.36 g)

Example 7

What volume of $Cl_{2(g)}$ at STP is produced when a current of 20 A is passed through molten $NaCl_{(l)}$ for 2.0 hours? $2Cl^{-1} \longrightarrow Cl_{2(g)} + 2e^{-1}$ (16.7 L)