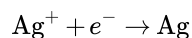


17.7: Quantitative Aspects of Electrolysis

Michael Faraday discovered in 1833 that there is always a simple relationship between the amount of substance produced or consumed at an electrode during **electrolysis** and the quantity of electrical charge Q which passes through the cell. For example, the half-equation



tells us that when 1 mol Ag^+ is plated out as 1 mol Ag , 1 mol e^- must be supplied from the cathode. Since the negative charge on a single electron is known to be 1.6022×10^{-19} C, we can multiply by the Avogadro constant to obtain the charge per mole of electrons. This quantity is called the **Faraday constant**, symbol F :

$$F = 1.6022 \times 10^{-19} \text{ C} \times 6.0221 \times 10^{23} \text{ mol}^{-1} = 9.649 \times 10^4 \text{ C mol}^{-1}$$

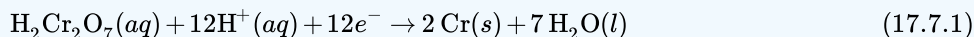
Thus in the case of Eq. (1), 96 490 C would have to pass through the cathode in order to deposit 1 mol Ag . For any electrolysis the electrical charge Q passing through an electrode is related to the amount of electrons n_{e^-} by

$$F = \frac{Q}{n_{e^-}}$$

Thus F serves as a conversion factor between n_{e^-} and Q .

✓ Example 17.7.1: Electrical Charge

Calculate the quantity of electrical charge needed to plate 1.386 mol Cr from an acidic solution of $\text{K}_2\text{Cr}_2\text{O}_7$ according to half-equation



Solution

According to Eq. 17.7.1, 12 mol e^- is required to plate 2 mol Cr , giving us a stoichiometric ratio $S(e^-/\text{Cr})$. Then the Faraday constant can be used to find the quantity of charge. In road-map form

$$n_{\text{Cr}} \xrightarrow{S(e^-/\text{Cr})} n_{e^-} \xrightarrow{F} Q$$

$$Q = 1.386 \text{ mol Cr} \times \frac{12 \text{ mol } e^-}{2 \text{ mol Cr}} \times \frac{9.649 \times 10^4 \text{ C}}{1 \text{ mol } e^-} = 8.024 \times 10^5 \text{ C}$$

Often the electrical current rather than the quantity of electrical charge is measured in an electrolysis experiment. Since a **coulomb** is defined as the quantity of charge which passes a fixed point in an electrical circuit when a current of one ampere flows for one second, the charge in coulombs can be calculated by multiplying the measured current (in amperes) by the time (in seconds) during which it flows:

$$Q = It$$

In this equation I represents current and t represents time. If you remember that

$$\text{coulomb} = 1 \text{ ampere} \times 1 \text{ second} \quad 1 \text{ C} = 1 \text{ A s}$$

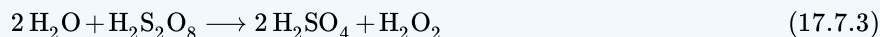
you can adjust the time units to obtain the correct result.

✓ Example 17.7.2 : Mass of Hydrogen Peroxide

Hydrogen peroxide, H_2O_2 , can be manufactured by electrolysis of cold concentrated sulfuric acid. The reaction at the anode is



When the resultant peroxydisulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$, is boiled at reduced pressure, it decomposes:



Calculate the mass of hydrogen peroxide produced if a current of 0.893 flows for 1 h.

Solution

he product of current and time gives us the quantity of electricity, Q . Knowing this we easily calculate the amount of electrons, n_{e^-} . From half-equation 17.7.2 we can then find the amount of peroxydisulfuric acid. Equation 17.7.3 then leads to $n_{H_2O_2}$ and finally to $m_{H_2O_2}$. The road map to describe this logic is as follows:

$$I \xrightarrow{t} Q \xrightarrow{F} n_{e^-} \xrightarrow{S_e} n_{H_2S_2O_8} \xrightarrow{S} n_{H_2O_2} \xrightarrow{M} m_{H_2O_2}$$

so that

$$\begin{aligned} m_{H_2O_2} &= 0.893 \text{ A} \times 3600 \text{ s} \times \frac{1 \text{ mol } e^-}{96\,490 \text{ C}} \times \frac{1 \text{ mol } H_2S_2O_8}{2 \text{ mol } e^-} \\ &= \frac{1 \text{ mol } H_2O_2}{1 \text{ mol } H_2S_2O_8} \times \frac{34.01 \text{ g } H_2O_2}{1 \text{ mol } H_2O_2} \end{aligned}$$

$$= 0.5666 \frac{\text{A s}}{\text{C}} \times \text{g } H_2O_2 = 0.5666 \text{ g } H_2O_2$$

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