Section 17.7 Electrolysis

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Learning Objectives

- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrolysis

- Electrolysis is a process where *an external circuit does work on a redox system by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction*
  - Recharging a battery
  - Refinement of metallic ores
  - Manufacture of commodity chemicals,
  - Electroplating of metallic coatings on various products

NaCl Electrolysis

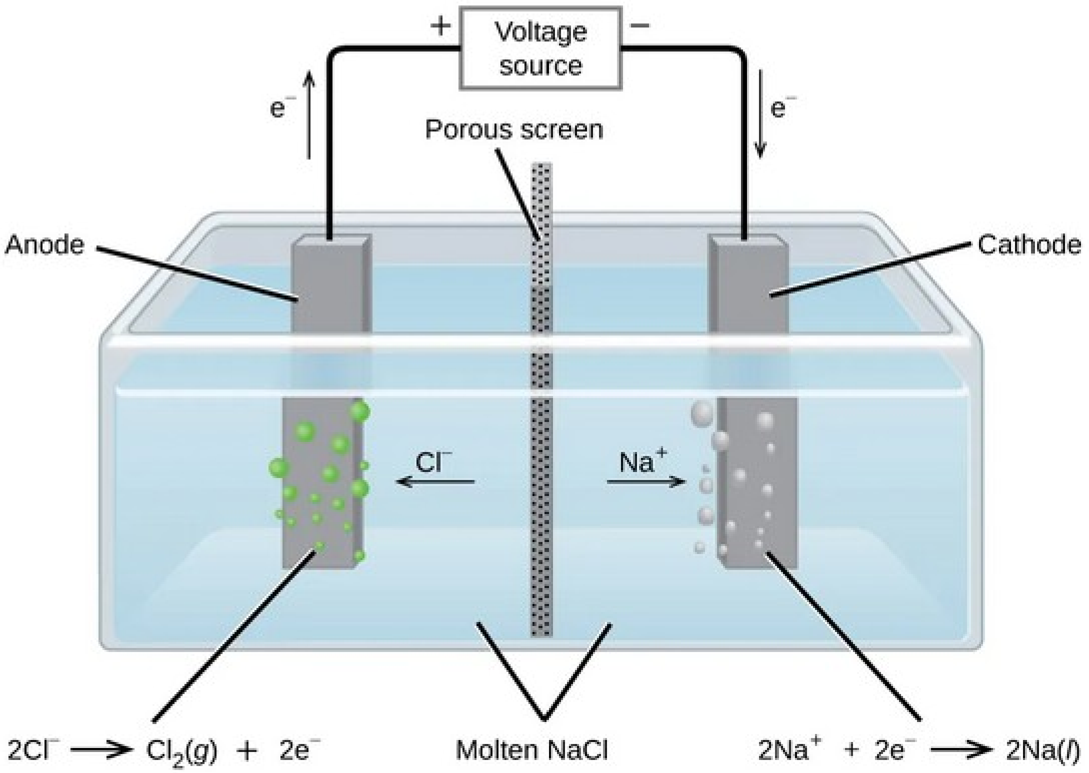
- Metallic sodium, Na, and chlorine gas, Cl_2, are used in numerous applications
- Their industrial production relies on the large-scale electrolysis of molten sodium chloride, NaCl

$$\begin{array}{lrcl} \text{anode:} & 2Cl^-(l) & \longrightarrow & Cl_2(g) + 2e^- \\ \text{cathode:} & Na^+(l) + e^- & \longrightarrow & Na(l) \\ \hline \text{cell:} & 2Na^+(l) + 2Cl^-(l) & \longrightarrow & 2Na(l) + Cl_2(g) \end{array}$$

- To force this reaction, *a positive potential of magnitude greater than the negative cell potential must be applied to the cell*.

Downs Cell

- The industrial process typically uses a *Downs Cell*



Water Electrolysis

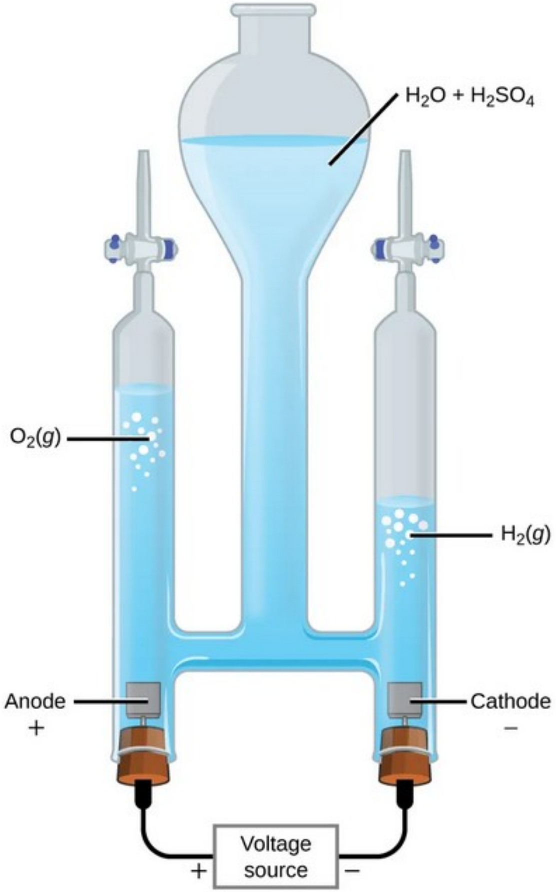
- The redox processes associated with the electrolysis of water are:

$$
\begin{array}{llll}
\text{anode:} & 2\mathrm{H_2O}(l) \longrightarrow \mathrm{O_2}(g) + 4\mathrm{H^+}(aq) + 4\mathrm{e^-} & E^\circ_{\text{anode}} = & +1.229\ \mathrm{V} \\
\text{cathode:} & 2\mathrm{H^+}(aq) + 2\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) & E^\circ_{\text{cathode}} = & 0\ \mathrm{V} \\
\hline
\text{cell:} & 2\mathrm{H_2O}(l) \longrightarrow 2\mathrm{H_2}(g) + \mathrm{O_2}(g) & E^\circ_{\text{cell}} = & -1.229\ \mathrm{V}
\end{array}
$$

- To improve electrical conductivity without introducing a different redox species, strong acid is usually added.

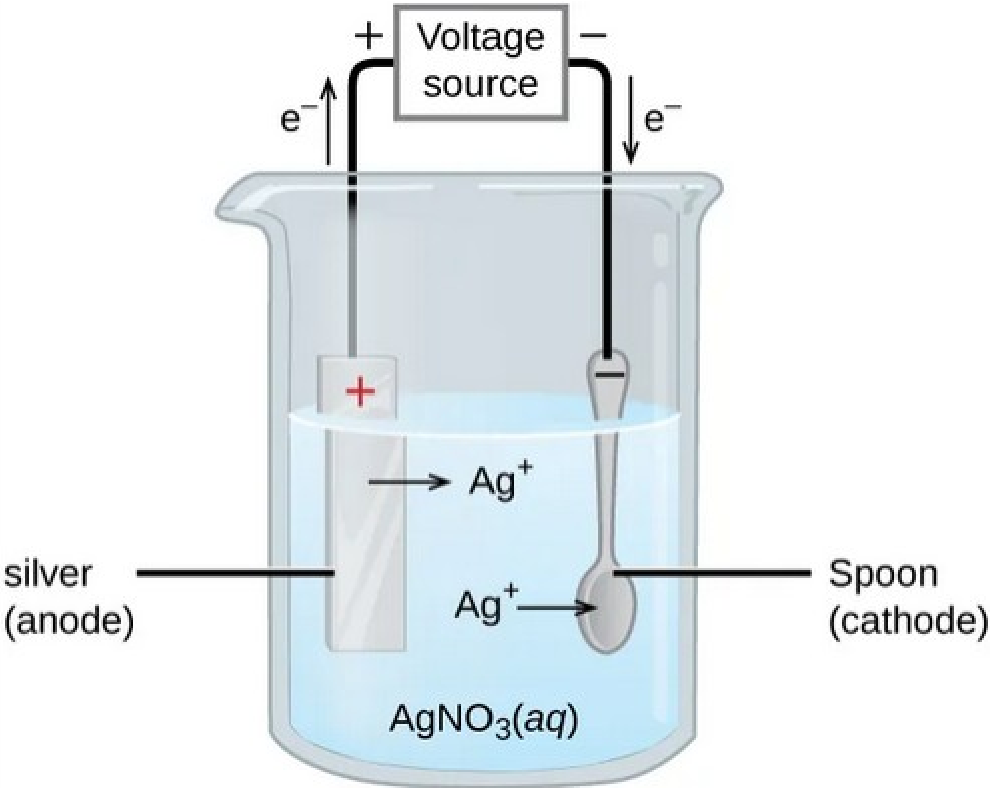
Hoffman Apparatus

- Under standard conditions the reaction must be driven by imposing a cell voltage greater than +1.229 V.
- Keep in mind that under nonstandard conditions the required voltage will vary.



Electroplating

- **Electroplating** results in a thin coating of one metal on top of a conducting surface.
  - Used to make objects more corrosion resistant
  - Strengthen surfaces against abrasion
  - Produce attractive finishes
  - Purifying metal



Calculating Current

- Electrical current is defined as the rate of flow for any charged species.
  - Current is measured in a composite unit called an ampere defined as one coulomb per second, A = 1 C/s.
- The charge transferred, *Q*, by passage of a constant current, *I*, over a specified time interval, *t*, is

$$Q = It$$

Stoichiometry of Electron Transfer

- When electrons are transferred during a redox process, the stoichiometry of the reaction may be used to derive the total amount of (electronic) charge involved.

$$\mathrm{M}^{\mathrm{n}+}(aq) + \mathrm{ne}^{-} \longrightarrow \mathrm{M}(s)$$

$$Q = nF$$

- Where F is Faraday's constant, the charge in coulombs for one mole of electrons.

Example Problem

- While electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour.
  - How many moles of electrons passed through the cell?
  - What mass of silver was deposited at the cathode from the silver nitrate solution?

$$n = \frac{Q}{F} = \frac{it}{F}$$

$$= \frac{10.23\ \frac{\mathrm{C}}{\mathrm{s}} \times 3600\,\mathrm{s}}{96,485\ \frac{\mathrm{C}}{\mathrm{mol\ e^-}}} = 0.3817\,\mathrm{mol\ e^-}$$

Stoichiometry

- Mols of electrons can be treated using stoichiometric ratios just like chemical species.

$$\mathrm{Ag^{+}}\ (aq) + \mathrm{e^{-}} \longrightarrow \mathrm{Ag}\ (s)$$

$$\text{mole Ag}\ (s) = 0.3817\,\text{mol e}^{-}\left(\frac{1\,\text{mol Ag}}{1\,\text{mol e}^{-}}\right) = 0.3817\,\text{mol Ag}$$

$$0.3817\,\text{mol Ag}\left(\frac{107.9\,\text{g Ag}}{1\,\text{mol Ag}}\right) = 41.19\,\text{g Ag}$$