Production of \(\ce{NaOH}\) is an important industrial process. Three different methods are employed, all of which involve the use of electricity. When calculating the price of sodium hydroxide a company has to charge in order to make a profit, the cost of electricity has to be factored in. To make a metric ton of \(\ce{NaOH}\), between \(3300\text{ - }5000 \text{kWh}\) (kilowatt hours) are required. Compare that with the power needed to run an average house. You could power a home for 6 - 10 months with the same amount of electricity.

Electrolysis of Molten Sodium Chloride

Molten (liquid) sodium chloride can be electrolyzed to produce sodium metal and chlorine gas. The electrolytic cell used in the process is called a Down's cell (see figure below).

In a Down's cell, the liquid sodium ions are reduced at the cathode to liquid sodium metal. At the anode, liquid chlorine ions are oxidized to chlorine gas. The reactions and cell potentials are shown below:

\[
\begin{array}{lll}
\text{oxidation (anode):} & 2 \ce{Cl^-} \rightarrow \ce{Cl_2} + 2 \ce{e^-} & E^0 = -1.36 \text{ V} \\
\text{reduction (cathode):} & \ce{Na^+} + \ce{e^-} \rightarrow \ce{Na} & E^0 = -2.71 \text{ V} \\
\hline
\text{overall reaction:} & 2 \ce{Na^+} + 2 \ce{Cl^-} \rightarrow 2 \ce{Na} + \ce{Cl_2} & E^0_{\text{cell}} = -4.07 \text{ V}
\end{array}
\]

The battery must supply over 4 volts to carry out this electrolysis. This reaction is a major source of production of chlorine gas and is the only way to obtain pure sodium metal. Chlorine gas is widely used in cleaning, disinfecting, and in swimming pools.

Electrolysis of Aqueous Sodium Chloride

It may be logical to assume that the electrolysis of aqueous sodium chloride, called brine, would yield the same result through the same reactions as the process in molten \(\ce{NaCl}\). However, the reduction reaction that occurs at the cathode does not produce sodium metal because the water is reduced instead. This is because the reduction potential for water is only \(-0.83 \text{ V}\) compared to \(-2.71 \text{ V}\) for the reduction of sodium ions. This makes the
reduction of water preferable because its reduction potential is less negative. Chlorine gas is still produced at the anode, just as in the electrolysis of molten NaCl.

\[
\begin{array}{lll}
\text{oxidation (anode):} & 2 \ce{Cl^-} (aq) \rightarrow \ce{Cl_2} (g) + 2 \ce{e^-} & E^0 = -1.36 \text{ V} \\
\text{reduction (cathode):} & 2 \ce{H_2O} (l) + 2 \ce{e^-} \rightarrow \ce{H_2} (g) + 2 \ce{OH^-} (aq) & E^0 = -0.83 \text{ V} \\
\hline
\text{overall reaction} & 2 \ce{Cl^-} (aq) + 2 \ce{H_2O} (l) \rightarrow \ce{Cl_2} (g) + \ce{H_2} (g) + 2 \ce{OH^-} (aq) & E^0_{\text{cell}} = -2.19 \text{ V}
\end{array}
\]

Since hydroxide ions are also a product of the net reaction, the important chemical sodium hydroxide NaOH is obtained from evaporation of the aqueous solution at the end of the hydrolysis.

Summary

- The reactions involving the electrolysis of molten NaCl are described.
- The reactions involving the electrolysis of brine are described.

Contributors and Attributions

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