Skills to Develop

- Identify natural sources of representative metals
- Describe electrolytic and chemical reduction processes used to prepare these elements from natural sources

Because of their reactivity, we do not find most representative metals as free elements in nature. However, compounds that contain ions of most representative metals are abundant. In this section, we will consider the two common techniques used to isolate the metals from these compounds—electrolysis and chemical reduction. These metals primarily occur in minerals, with lithium found in silicate or phosphate minerals, and sodium and potassium found in salt deposits from evaporation of ancient seas and in silicates.

Ions of metals in of groups 1 and 2, along with aluminum, are very difficult to reduce; therefore, it is necessary to prepare these elements by electrolysis, an important process discussed in the chapter on electrochemistry. Briefly, electrolysis involves using electrical energy to drive unfavorable chemical reactions to completion; it is useful in the isolation of reactive metals in their pure forms. Sodium, aluminum, and magnesium are typical examples.

Electrometallurgy is a common extraction process for the more reactive metals, e.g., for aluminum and metals above it in the electrochemical series. It is one method of extracting copper and in the purification of copper. During electrolysis, electrons are being added directly to the metal ions at the cathode (the negative electrode). The downside (particularly in the aluminum case) is the cost of the electricity. An advantage is that it can produce very pure metals.

The Preparation of Sodium

The most important method for the production of sodium is the electrolysis of molten sodium chloride; the set-up is a Downs cell, shown in Figure \(\PageIndex{1}\). The reaction involved in this process is:

\[
\ce{2NaCl(l)} \underset{600\:^\circ\mathrm{C}}{\xrightarrow{electrolysis}} \ce{2Na(l)} + \ce{Cl2(g)}
\]

The electrolysis cell contains molten sodium chloride (melting point 801 °C), to which calcium chloride has been added to lower the melting point to 600 °C (a colligative effect). The passage of a direct current through the cell causes the sodium ions to migrate to the negatively charged cathode and pick up electrons, reducing the ions to sodium metal. Chloride ions migrate to the positively charged anode, lose electrons, and undergo oxidation to chlorine gas. The overall cell reaction comes from adding the following reactions:

\[
\begin{align}
\text{at the cathode: } & \ce{2Na+} + \ce{2e-} \rightarrow \ce{2Na(l)} \\
\text{at the anode: } & \ce{2Cl-} \rightarrow \ce{Cl2(g)} + \ce{2e-} \\
\text{overall change: } & \ce{2Na+} + \ce{2Cl-} \rightarrow \ce{2Na(l)} + \ce{Cl2(g)}
\end{align}
\]

Separation of the molten sodium and chlorine prevents recombination. The liquid sodium, which is less dense than molten sodium chloride, floats to the surface and flows into a collector. The gaseous chlorine goes to storage tanks. Chlorine is also a valuable product.
Pure sodium metal is isolated by electrolysis of molten sodium chloride using a Downs cell. It is not possible to isolate sodium by electrolysis of aqueous solutions of sodium salts because hydrogen ions are more easily reduced than are sodium ions; as a result, hydrogen gas forms at the cathode instead of the desired sodium metal. The high temperature required to melt NaCl means that liquid sodium metal forms.

The Preparation of Aluminum

The preparation of aluminum utilizes a process invented in 1886 by Charles M. Hall, who began to work on the problem while a student at Oberlin College in Ohio. Paul L. T. Héroult discovered the process independently a month or two later in France. In honor to the two inventors, this electrolysis cell is known as the Hall–Héroult cell. The Hall–Héroult cell is an electrolysis cell for the production of aluminum. Figure 1 illustrates the Hall–Héroult cell.

The production of aluminum begins with the purification of bauxite, the most common source of aluminum. The reaction of bauxite, AlO(OH), with hot sodium hydroxide forms soluble sodium aluminate, while clay and other impurities remain undissolved:

\[
\text{AlO(OH)}(s) + \text{NaOH}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{Na}[\text{Al(OH)}_4](aq)
\]

After the removal of the impurities by filtration, the addition of acid to the aluminate leads to the reprecipitation of aluminum hydroxide:

\[
\text{Na}[\text{Al(OH)}_4](aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{Al(OH)}_3(s) + \text{Na}^+(aq) + 2\text{H}_2\text{O}(l)
\]

The next step is to remove the precipitated aluminum hydroxide by filtration. Heating the hydroxide produces aluminum oxide, Al\(_2\)O\(_3\), which dissolves in a molten mixture of cryolite, Na\(_3\)AlF\(_6\), and calcium fluoride, CaF\(_2\). Electrolysis of this solution takes place in a cell like that shown in Figure 2. Reduction of aluminum ions to the metal occurs at the cathode, while oxygen, carbon monoxide, and carbon dioxide form at the anode.
Figure \(\PageIndex{2}\): An electrolytic cell is used for the production of aluminum. The electrolysis of a solution of cryolite and calcium fluoride results in aluminum metal at the cathode, and oxygen, carbon monoxide, and carbon dioxide at the anode.

The Preparation of Magnesium

Magnesium is the other metal that is isolated in large quantities by electrolysis. Seawater, which contains approximately 0.5% magnesium chloride, serves as the major source of magnesium. Addition of calcium hydroxide to seawater precipitates magnesium hydroxide. The addition of hydrochloric acid to magnesium hydroxide, followed by evaporation of the resultant aqueous solution, leaves pure magnesium chloride. The electrolysis of molten magnesium chloride forms liquid magnesium and chlorine gas:

\[
\ce{MgCl2}(aq)+\ce{Ca(OH)2}(aq)\rightarrow \ce{Mg(OH)2}(s)+\ce{CaCl2}(aq)
\]

\[
\ce{Mg(OH)2}(s)+\ce{2HCl}(aq)\rightarrow \ce{MgCl2}(aq)+\ce{2H2O}(l)
\]

\[
\ce{MgCl2}(l)\rightarrow \ce{Mg}(l)+\ce{Cl2}(g)
\]

Some production facilities have moved away from electrolysis completely.

Key Concepts and Summary

Because of their chemical reactivity, it is necessary to produce the representative metals in their pure forms by reduction from naturally occurring compounds. Electrolysis is important in the production of sodium, potassium, and aluminum. Chemical reduction is the primary method for the isolation of magnesium, zinc, and tin. Similar procedures are important for the other representative metals. A Downs cell is used to produce sodium metal from a mixture of salts, and the Hall–Héroult process is used to produce aluminum commercially.

Glossary

**chemical reduction**
method of preparing a representative metal using a reducing agent
**Downs cell**
electrochemical cell used for the commercial preparation of metallic sodium (and chlorine) from molten sodium chloride

**Hall–Héroult cell**
electrolysis apparatus used to isolate pure aluminum metal from a solution of alumina in molten cryolite

**Pidgeon process**
chemical reduction process used to produce magnesium through the thermal reaction of magnesium oxide with silicon

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