

The invention of the electric cell by Volta in 1800 immediately resulted in many discoveries in chemistry. One of these discoveries was that electric cells could be used as an electric power source for electrolytic cells. Many natural substances, such as soda (sodium carbonate) and potash (potassium carbonate) that were thought to be elements, were shown to be composed of the previously unknown elements sodium and potassium (Figure 1). Industrial applications of electrolytic cells include the production of elements, the refining of metals, and the plating of metals onto the surface of an object. The study of electrolysis in industry reveals the strong relationship between science and technology.

Production of Elements

Most elements occur naturally combined with other elements in compounds. For example, ionic compounds of sodium, potassium, lithium, magnesium, calcium, and aluminum are abundant, but these reactive metals are not found uncombined in nature. The explanation is that the reduction potentials for these metals are very negative. Consequently, the metals are easily oxidized by practically all other substances. Even water has a more positive reduction potential than any of these metal ions, so if the metals did exist naturally, a spontaneous reaction would convert them into their ions (Figure 2).

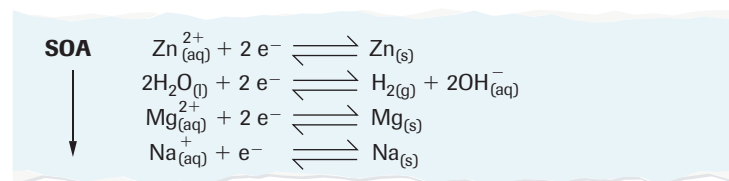


Figure 2

In an aqueous cell, metal cations can undergo a reduction to the metal as long as the metal cation is above water; i.e., when the metal cation is a stronger oxidizing agent. If you try to reduce active metal cations such as sodium and magnesium ions, water will react instead.

Many metals can be produced by electrolysis of solutions of their ionic compounds, but two difficulties arise. First, many naturally occurring ionic compounds have low solubility in water and second, water is a stronger oxidizing agent than active metal cations. To overcome these difficulties, a technological design in which water is not present can be used. Fortunately, ionic compounds can be melted. These molten ionic compounds are good electrical conductors and can function as the electrolyte in a cell. In the electrolysis of molten binary ionic compounds, only one oxidizing agent and one reducing agent are present. The production of active metals (strong reducing agents) from their minerals typically involves the electrolysis of molten compounds of the metal, a technology first used in the scientific work of Humphry Davy.

Strontium metal was one of many active metals discovered by Davy using the electrolysis of molten salts. Strontium chloride was first melted in an electrolytic cell with inert electrodes. In this cell, there are only two kinds of ions present, $\text{Sr}_{(\text{l})}^{2+}$ and $\text{Cl}_{(\text{l})}^-$. You may recall from the previous chapter that metal cations generally tend to undergo a reduction and nonmetal anions tend to undergo an oxidation. In this cell, there are no other competing substances. Therefore, the strontium ions will consume (gain) electrons at the cathode to form strontium metal.



Figure 1

In his youth, Sir Humphry Davy (1778–1829) worked as an assistant to a physician who was interested in the therapeutic properties of gases. Davy studied nitrous oxide (laughing gas) by conducting experiments on himself. He was eventually fired from his job, supposedly because of his liking for explosive chemical reactions. Davy's main fame came from his experiments with electricity. He constructed a voltaic pile with over 250 metal plates. He used this powerful cell to decompose stable compounds and discover the elements sodium, potassium, barium, strontium, calcium, and magnesium. Davy had many other scientific accomplishments; for example, he was the first to show that chlorine is an element and will support combustion, and that hydrogen is the key component of acids. Given his habit of tasting, inhaling, and exploding new chemicals, it is not surprising to learn that he was an invalid in his early thirties and died in middle age, probably of chemical poisoning.

LEARNING TIP

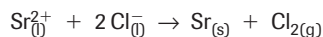
No reduction potentials can be listed for the electrolysis of a molten salt. The table of oxidizing and reducing agents in Appendix C11 lists only electric potentials for half-reactions in 1.0 mol/L aqueous solutions at SATP.



At the anode, chloride ions will give up (lose) electrons to form chlorine gas.



Electrons are balanced and adding the two equations gives the overall reaction in the cell.



This reaction would not be possible in an aqueous solution because water is a stronger oxidizing agent (i.e., has a more positive reduction potential) than aqueous strontium ions.

In molten-salt electrolysis, metal cations move to the cathode and are reduced to metals, and nonmetal anions move to the anode and are oxidized to nonmetals.

Production of Sodium

Electrolysis of molten ionic compounds is expensive; a significant quantity of energy must be used and the electrolysis cell must be specially designed to withstand the high temperatures involved. One common method to reduce the temperature is to add an inert compound to form a mixture that melts at a lower temperature. In general, the melting point of any substance is lowered by adding an impurity. (This is the reason people sprinkle salt on roads or sidewalks in winter to melt ice—adding salt lowers the melting point of ice.) Pure sodium chloride has a melting point of about 800°C, but when mixed with calcium chloride, the melting point is about 600°C. In such a cell, the potential difference that is applied to the mixture must be controlled to reduce sodium ions but not calcium ions (**Figure 3**). The electrolysis of molten sodium chloride in a Down's cell is the main source of sodium metal (**Figure 4**).



Figure 4

One of the uses of sodium metal is the production of sodium vapour lamps used for street lighting. Sodium lamps produce a yellow light that penetrates farther than white light and allows better vision in fog. Sodium lamps are also fifteen times more efficient than regular incandescent lamps.

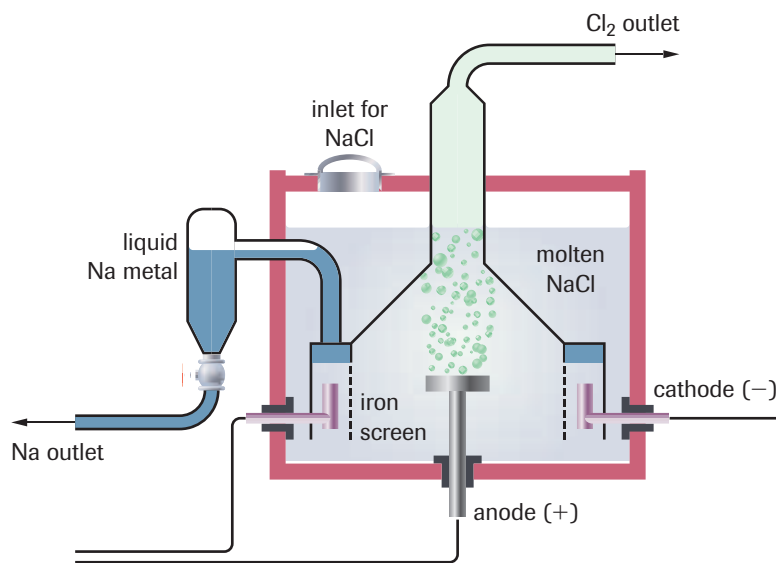
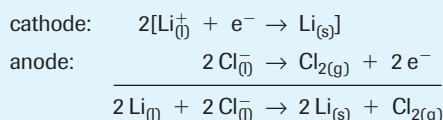


Figure 3

At the operating temperature of the cell (600°C), sodium is liquid because its melting point is only 98°C. Liquid sodium metal is formed at the cylindrical cathode and then floats to the top of the molten sodium chloride. Chlorine gas forms on the carbon anode and rises out of the cell.

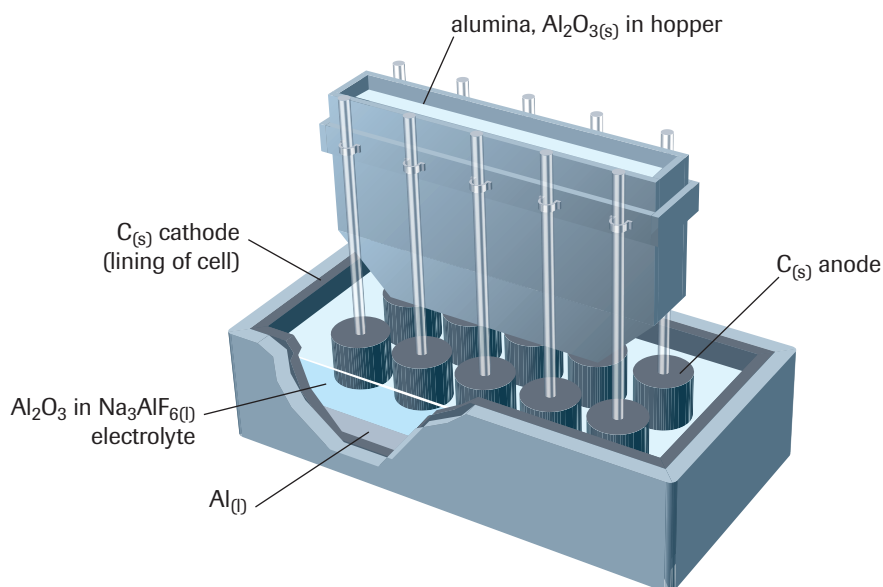
Example 1

Lithium is the least dense of all metals and is a very strong reducing agent; both qualities make it an excellent anode for batteries. Lithium can be produced by electrolysis of molten lithium chloride at a temperature greater than 605°C, the melting point of lithium chloride. Write the equations for the cathode and anode half-reactions, and the net cell reaction.

Solution**Production of Aluminum**

Aluminum is the third most abundant element on Earth. It was discovered in France in the early 1800s. At the time, aluminum was more expensive than gold. The wonderful properties of aluminum—shiny, light, strong, and corrosion resistant—made it ideal for jewellery and cutlery, so there was a high demand for the metal, especially among the aristocracy. However, the supply of aluminum was limited because the technology for producing aluminum was not yet practical or economically viable for mass production.

Initial efforts to produce aluminum by electrolysis were unproductive because its common ore, $\text{Al}_2\text{O}_{3(s)}$, has a high melting point, 2072°C. No material could be found to hold the molten compound. In 1886 two scientists, working independently and knowing nothing of each other's work, made the same discovery. Charles Martin Hall in the United States and Paul-Louis-Toussaint Héroult in France discovered that $\text{Al}_2\text{O}_{3(s)}$ dissolves in a molten mineral called cryolite, Na_3AlF_6 . In this design, the cryolite acts as an inert solvent for the electrolysis of aluminum oxide and forms a molten conducting mixture with a melting point around 1000°C. Aluminum (m.p. 660°C) can be produced electrolytically from this molten mixture (**Figure 5**). This discovery had an immediate effect on the supply and cost of aluminum. Around 1855, aluminum was sold for \$45,000 per kilogram; a few years after the Hall-Héroult invention, the cost was about 90 cents.

**DID YOU KNOW?****Aluminum Production in Canada**

The production of aluminum is important to Canada's economy, although Canada does not have large deposits of aluminum ore. Hydroelectric power is used to produce aluminum metal from concentrated, imported bauxite in an electrolytic cell. Recycling aluminum from soft drink and beer cans requires only 5% of the energy required to produce aluminum by electrolysis.

**Figure 5**

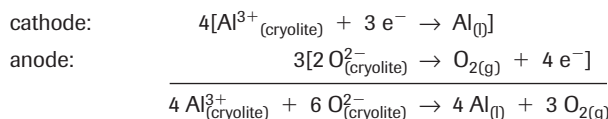
The Hall-Héroult cell for the production of aluminum. The cathode is the carbon lining of the steel cell. At the cathode, aluminum ions are reduced to produce liquid aluminum, which collects at the bottom of the cell and is periodically drained away. At the carbon anode, oxide ions are oxidized to produce oxygen gas. The oxygen produced at the anode reacts with the carbon electrodes, producing carbon dioxide, so these electrodes must be replaced frequently.

DID YOU KNOW?

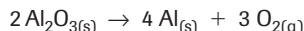
Overpotential

There are many variables that affect an electrolytic cell, such as concentration gradients within the electrolyte, internal resistance of the cell, temperature, nature of the electrodes, and current density. Like other chemical processes, a half-cell reaction at an electrode has an activation energy that varies for different half-reactions and conditions. Therefore, the actual reduction potential required for a particular half-reaction and the reported half-reaction reduction potential may be quite different. This difference is known as the half-cell overpotential and is generally much greater for the production of oxygen than chlorine.

Aluminum oxide is obtained from bauxite, an aluminum ore. Once the ore is purified, the aluminum oxide is dissolved in molten cryolite and it dissociates into individual ions. The reactions occurring at the electrodes in a Hall-Héroult cell are summarized below.

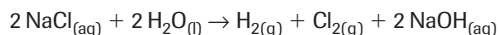


The overall cell reaction is a decomposition of aluminum oxide.



The Chlor-Alkali Process

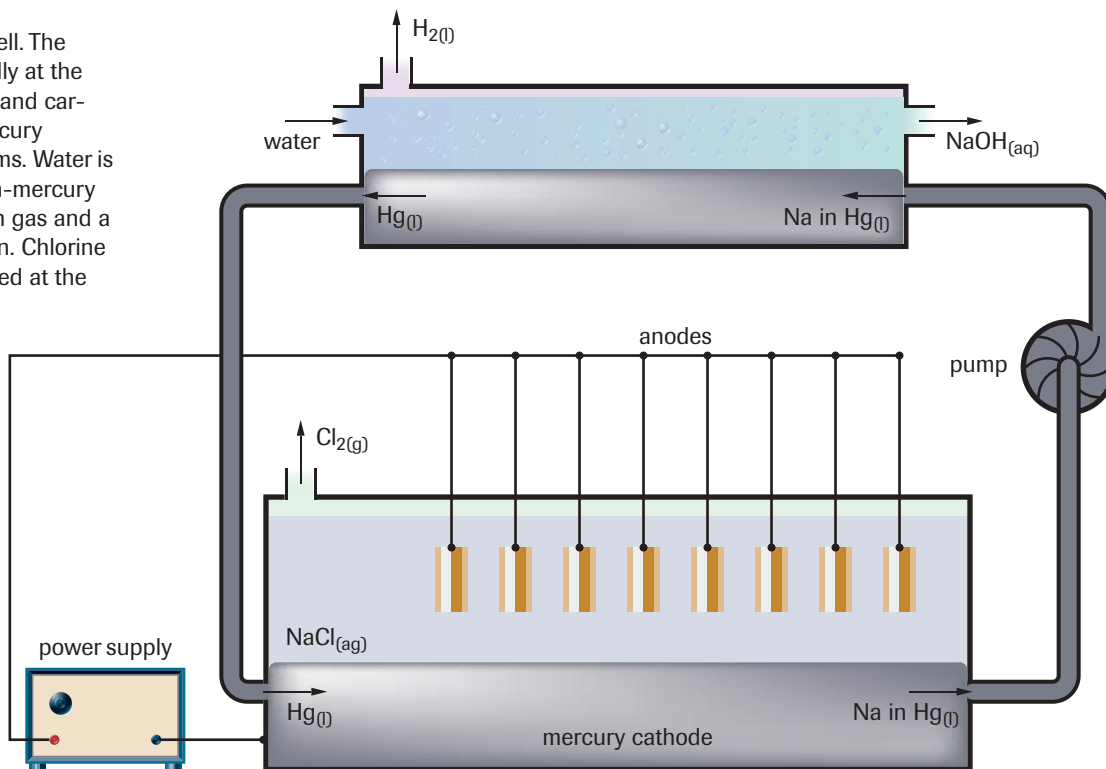
Instead of eliminating or replacing water as a solvent in the electrolytic production of elements, another design overcomes the difficulty of producing active metals by simply “overpowering” the reduction of the water. A high voltage leads to the reduction of metal ions rather than water because the reduction of water is a relatively slow reaction. Aqueous sodium chloride can be electrolyzed in this manner to produce chlorine, hydrogen, and sodium hydroxide, all very important industrial chemicals.



This process, called the *chlor-alkali process*, is electrolysis of a concentrated sodium chloride solution. One common design (Figure 6) uses high voltages to force the reduction of aqueous sodium ions to sodium metal. The sodium metal is then reacted with water to produce hydrogen gas and sodium hydroxide. Chlorine is preferentially produced at the anode instead of oxygen, in spite of its more favourable position in the redox table. There are several factors that contribute to this effect.

Figure 6

Design of a chlor-alkali cell. The sodium metal forms rapidly at the cathode and is dissolved and carried away by a liquid mercury cathode as soon as it forms. Water is later added to the sodium-mercury solution to form hydrogen gas and a sodium hydroxide solution. Chlorine gas is formed and collected at the anodes.



The chlor-alkali technology requires large quantities of electrical energy and, in the past, employed mercury as the cathode. The extreme toxicity of mercury endangered the safety of workers and the environment. Newer chlor-alkali plants now use a process that relies on an ion-exchange membrane to separate the sodium and chloride ions during electrolysis. This new technology not only eliminates mercury but is also less expensive. For all chlor-alkali processes, the overall reaction is still the same.

Hydrogen gas is used to make ammonia, hydrogen peroxide, and margarine, and to crack petroleum. It may also be used on site as a fuel to produce electricity. Chlorine is used as a disinfectant for drinking water and to manufacture bleach (sodium hypochlorite), plastics, pesticides, and solvents. Sodium hydroxide is used on a large scale in industry to make cellophane, pulp and paper, aluminum, and detergents.

Practice

Understanding Concepts

- (a) Describe two difficulties associated with the electrolysis of aqueous ionic compounds in the production of active metals.
(b) What two designs can be used to offset these difficulties?
- Scandium is a metal with a low density and a melting point that is higher than that of aluminum. These properties are of interest to engineers who design space vehicles. Scandium metal is produced by electrolysis of molten scandium chloride. List all ions present in the electrolysis cell, and write the equations for the reactions that occur at the cathode and anode and the net cell reaction.
- The following statements summarize the steps in the chemical technology of obtaining magnesium from seawater. Write a balanced equation to represent each reaction.
 - Slaked lime (solid calcium hydroxide) is added to seawater (ignore all solutes except $\text{MgCl}_{2(\text{aq})}$) in a double displacement reaction to precipitate magnesium hydroxide.
 - Hydrochloric acid is added to the magnesium hydroxide precipitate.
 - After the magnesium chloride product is separated and dried, it is melted in preparation for electrolysis. List all ions present in the electrolysis, and write the equations for the reactions that occur at the cathode and anode and the net cell reaction.
 - An alternative process produces magnesium from dolomite, a mineral containing CaCO_3 and MgCO_3 . Suggest some technological advantages and disadvantages of the dolomite process compared with the seawater process.

Making Connections

- What products in your home may have originated from substances produced in the chlor-alkali process?
- Why should we recycle metals such as aluminum? State several arguments that you might use in a debate.
- Research and describe some of the variety of uses of aluminum summarized in the exhibition, "Aluminum by Design: Jewellery to Jets."



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Extension

- Research and describe the newer, ion-exchange membrane cell design for the chlor-alkali process. Include a labelled cell diagram and the function of the membrane. Why is it superior to other designs?



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DID YOU KNOW?

The Pidgeon Process

Lloyd Pidgeon (1903–1999) was born in Markham, Ontario, studied undergraduate chemistry at the University of Manitoba, and obtained his Ph.D. from McGill University in 1929. Later, while working at the National Research Council in Ottawa, Pidgeon developed the first process for producing high-quality magnesium metal from dolomite (calcium magnesium carbonate). This led to the formation of Dominion Magnesium Ltd. using dolomite mined at Hale in the Ottawa Valley. The Pidgeon Process is still used in many countries to produce magnesium.

► EXPLORE an issue

Take a Stand: The Case For and Against Chlorine

Chlorine is a controversial chemical. There is no doubt that chlorine and products made from chlorine have been very beneficial to society, but there are concerns. Should the production or use of chlorine be limited to certain essential uses?

- (a) Research the production, storage, transportation, and uses of chlorine and assess one environmental, health, or safety issue.

Decision-Making Skills

- Define the Issue
- Analyze the Issue
- Research
- Defend the Position
- Identify Alternatives
- Evaluate

- (b) What is the best resolution of the issue you assessed? Present your solution in a way designed to influence decision makers. Include an outline of your findings in your presentation.



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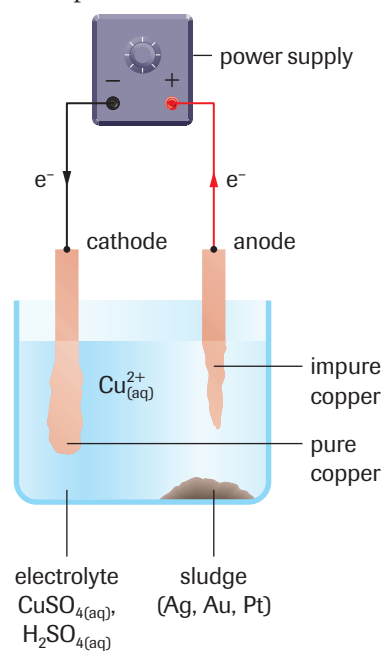
electrorefining production of a pure metal at the cathode of an electrolytic cell using impure metal at the anode

Figure 7

When the electrolytic cell is operated at a carefully controlled voltage, only copper and metals more easily oxidized than copper, such as iron and zinc, are oxidized to ions and dissolve at the anode. Only copper is reduced at the cathode. Other impurities in the anode, such as silver, gold, and platinum, do not react; these fall to the bottom of the cell as a sludge called anode mud. Removed from the cell periodically, the anode mud undergoes further processing to extract valuable metals.

Refining of Metals

In the production of metals, the initial product is usually an impure metal. Impurities are often other metals that come from various compounds in the original ore. To purify or refine a metal, a variety of methods are used. However, a common method, known as **electrorefining**, uses an electrolytic cell to obtain high-grade metals at the cathode from an impure metal at the anode.



A good example is the electrorefining of copper. The presence of impurities in copper lowers its electrical conductivity, not a desirable property considering that one of the most common uses of copper is in electrical wiring. The initial smelting process produces copper that is about 99% pure, containing some silver, gold, platinum, iron, and zinc. These valuable impurities can be recovered and sold to help pay for the process. As shown in **Figure 7**, a slab of impure copper is the anode of an electrolytic cell that contains copper(II) sulfate dissolved in sulfuric acid. The cathode is a thin sheet of very pure copper. As the cell operates, copper and some of the other metals in the anode are oxidized, but only copper is reduced at the cathode. An understanding of oxidation, reduction, and reduction potentials allows precise control over what is oxidized and what is reduced, so that after electrorefining, the copper is about 99.98% pure (**Figure 8**). The half-reactions are:

cathode: reduction of copper
 anode: oxidation of copper
 oxidation of zinc
 oxidation of iron

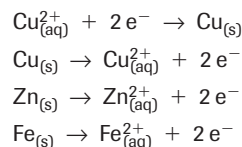
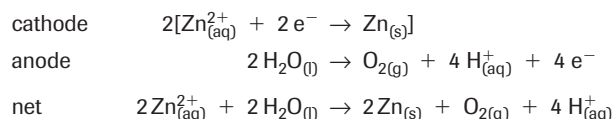


Figure 8

A bundle of cathodes shows the corrugation of alternating cathodes that helps ensure more efficient subsequent melting.

Another related method of purifying metals is to reduce metal cations from a molten or aqueous electrolyte at the cathode of an electrolytic cell, much like the production of elements discussed previously. This method, which uses a molten salt, is known as *electrowinning*. It is the only way to obtain some active metals, such as those in Group 1. Many other metals, such as zinc, can be produced by electrowinning an aqueous solution. For example, Cominco's operation at Trail, BC uses the electrolysis of an acidic zinc sulfate solution with a specially treated lead anode to deposit very pure zinc metal at the cathode.



Electroplating

Several metals, such as silver, gold, zinc, and chromium, are valuable because of their resistance to corrosion. However, products made from these metals in their pure form are either too expensive or they lack suitable mechanical properties, such as strength and hardness. To achieve the best compromise among price, mechanical properties, appearance, and corrosion resistance, utensils or jewellery may be made of a relatively inexpensive, yet strong, alloy such as steel, and then coated (plated) with another metal or alloy to improve appearance or corrosion resistance. Plating of a metal at the cathode of an electrolytic cell is called **electroplating** and is a common technology that is used to cover the surface of an object with a thin layer of metal. The design of a process for plating metals is obtained by systematic trial and error, involving the careful manipulation of one possible variable at a time. In this situation, a scientific perspective helps identify variables but cannot usually provide successful predictions.

As mentioned earlier, the development and use of electric cells preceded scientific understanding of the processes involved. Today, we still have examples of technological processes that are not fully understood, such as chromium plating (**Figure 9**) and silver plating. For example, there is no satisfactory explanation for why silver deposited in an electrolysis of a silver nitrate solution does not adhere well to any surface, whereas silver plated from silver cyanide solution does.

SUMMARY

Applications of Electrolytic Cells

- In molten-salt electrolysis, metal cations are reduced to metal atoms at the cathode and nonmetal anions are oxidized at the anode.
- Mixtures of salts are used to lower the melting point for a more practical and economical molten-salt electrolysis.
- The use of high voltages favours the reduction of active metal cations over the reduction of water.
- Electrorefining is a process used to obtain high-grade metals at the cathode from an impure metal at the anode.
- Electroplating is a process in which a metal is deposited on the surface of an object placed at the cathode of an electrolytic cell.

DID YOU KNOW?

A Spinoff of the Voltaic Cell

Electroplating was discovered in 1802 by one of Volta's students.

electroplating depositing a layer of metal onto another object at the cathode of an electrolytic cell



Figure 9

Chromium is best plated from a solution of chromic acid. A thin layer of chromium metal is very shiny and, like aluminum, protects itself from corrosion by forming a tough oxide layer.

DID YOU KNOW?

Other Methods of Plating

Electroplating is only one method used to cover the surface of an object with a metal. Two other methods are vapour deposition, in which metal vapour is condensed on the surface, and dipping, in which an object is dipped into a molten metal that solidifies on the surface. Zinc-plated nails for exterior use are made by dipping.

Answer

9. (b) 0 V

DID YOU KNOW?

Dow Chemical Company

Herbert Dow (1866–1930) was born in Belleville, Ontario, but grew up in Cleveland, Ohio. The first of his 107 patents was the electrolytic production of bromine. Based on this process, he formed the Midland Chemical Co. When his financial backers refused to fund his invention of the chlor-alkali process, he formed the Dow Chemical Company, now one of the world's largest chemical producers.

Practice

Understanding Concepts

- When refining metals in an electrolytic cell, why must the metal product form at the cathode?
- High-purity copper metal is produced using electrorefining.
 - At which electrode is the impure copper placed? Why?
 - What is the minimum electric potential difference required for this cell?
 - Why is it unlikely that your answer to (b) is what is used? Discuss briefly.
- How can you predict which metals might be refined from an aqueous solution?
- List some reasons for, and examples of, electroplating.

Applying Inquiry Skills

- Suppose you want to set up an electrolytic cell to electroplate some metal spoons with a thin layer of silver.
 - As part of the experimental design, draw the cell and label the electrodes, power supply, electrolyte, and the directions of electron and ion movement.
 - What variables do you need to consider when planning the electrolysis?

Making Connections

- There are companies that specialize in bronzing baby booties, sports equipment, and keepsakes. Find one and research the service it offers.
 - How does it make a nonconductor like a shoe into an electrode? Which electrode?
 - Briefly describe the process and the approximate costs for typical items.



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- Electroplating industries produce considerable waste that is expensive to manage and an environmental hazard if not treated properly. List four different types of electroplating waste, including potential hazards. Describe some ways companies reduce, recover, and treat electroplating wastes.



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- Aluminum cans are widely used for beverages. Write a short report about the production of aluminum cans, including how the can is made, how the top is attached to the can, how the construction of the can has changed since the first model, and the advantages of using recycled aluminum instead of new aluminum.



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Section 10.2 Questions

Understanding Concepts

1. List three uses of electrolytic cells in industry.
2. Why were many metals discovered only after the invention of the electric cell?
3. How does the occurrence of metals in nature relate to the redox table of relative strengths of oxidizing and reducing agents?
4. How is the problem of solids with high melting points solved in industrial electrolysis? Provide some examples.
5. If ionic compounds can be electrolyzed in the aqueous and molten states, why can this not be done in their solid state?
6. Draw and label a simple cell for the electrolysis of molten potassium iodide (m.p. 682°C). Label electrodes and power supply, directions of electron and ion flow, and write half-reaction and net equations.
7. An electrolytic cell is set up to produce pure tin using tin(II) sulfate solution as the electrolyte. One electrode is a thin strip of pure tin and the other electrode is a large piece of impure tin containing silver and copper.
 - (a) Which metal piece should be the cathode and which the anode? Explain briefly.
 - (b) Draw a diagram of the cell and label the electrodes, electrolyte, power supply, including polarity, and the directions of ion and electron movement.
 - (c) What will be reduced and at which electrode? Write equations for the half-reaction(s).
 - (d) What will be oxidized and at which electrode? Write equations for the half-reaction(s).
 - (e) What is the range of potential difference that can be applied to a cell to obtain pure tin at the cathode? Justify your answer.
 - (f) Assuming that the cell operates as planned, what happens to the impurities?

Applying Inquiry Skills

8. Design a cell to electroplate zinc onto an iron spoon. In your cell diagram, include:
 - ions in the solution
 - substances used for the electrodes
 - anode and cathode labels
 - power supply, showing signs and connections
 - direction of ion and electron flow

9. Suppose you work for a mining company and you are given a job to design a process that will recover nickel metal from a waste solution containing nickel(II) ions.
 - (a) Propose an experimental design involving electrolysis that could be tested in the laboratory on a small scale.
 - (b) What are some possible complications or factors that need to be considered? List these as questions to be answered.

Making Connections

10. Describe how electrolytic processes are involved in the production of zinc metal and in the production of galvanized (zinc-plated) objects.

11. The loonie (Figure 10) replaced the one-dollar bill, which typically wore out in the space of a few months. The Royal Canadian Mint wanted to produce a dollar coin with a richer sheen than the shiny metals used in coins of lower value. Sherritt Gordon of Fort Saskatchewan, AB developed a unique process for plating the loonie coin.



Figure 10

The production line for the Canadian loonie

- (a) Research the production and composition of the loonie.
- (b) What is the golden “aureate” finish on the loonie? Describe the materials and process for producing this finish.
- (c) Why did the coin end up with a loon stamped on it?



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