1. Electrochemistry II: Electrolysis

Objective

Electrolysis is the use of an electrical current to force a chemical reaction to occur that would ordinarily not proceed spontaneously. When an electrical current is passed through a molten or dissolved electrolyte, between two physically separated electrodes, two chemical changes take place. At the positive electrode (also called the **anode**), an oxidation half-reaction takes place. At the negative electrode (referred to as the **cathode**) a reduction half-reaction takes place. Exactly what half-reaction occurs at each electrode is determined by the relative ease of oxidation/reduction of all the species present in the electrolysis cell. In this experiment you will study the electrolysis of water (Choice I), and the electrolysis of a salt solution (Choice II).

Choice I. Electrolysis of Water

Introduction

When an electrical current is passed through water, two electrochemical processes take place. At the anode, water molecules are *oxidized:*

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Gaseous elemental oxygen is produced at the anode and can be collected and tested. The solution in the immediate vicinity of the electrode becomes acidic as H^+ ions are released. At the cathode during the electrolysis of water, water molecules are *reduced*:

$$4e^- + 4H_2O \rightarrow 2H_2 + 4OH^-$$

Gaseous elemental hydrogen is produced at the cathode and may be collected and tested. The solution in the immediate vicinity of the electrode becomes basic as OH^- ions are released.

The two processes above are called **half-reactions**. It is the combination of the two half-reactions, which are taking place at the same time but in different locations, that constitutes the overall reaction in the electrolysis cell. The overall cell reaction that takes place is obtained by adding together the two half-reactions and canceling species common to either side:

$$6H_2O \rightarrow O_2 + 2H_2 + 4H^+ + 4OH^-$$

However, when the hydrogen ions and hydroxide ions migrate toward each other in the cell, they will react with each other,

$$H^+ + OH^- \rightarrow H_2O$$

resulting in the production of four water molecules. This leaves the final overall equation for what occurs in the cell as simply:

$$2H_2O \rightarrow O_2 + 2H_2$$

Note the *coefficients* in this final overall equation. Twice as many moles of elemental hydrogen gas are produced as elemental oxygen gas. If the gases produced are collected, then according to Avogadro's law, the volume of hydrogen collected should be twice the volume of oxygen collected.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times in the laboratory.**
- **A 9-volt transistor battery will be used as the source of electrical current. Be aware that even a small battery can cause an electrical shock if care is not exercised.**
- **Hydrogen gas is produced in the reaction. Hydrogen is flammable. Use caution during its generation and testing.**

Apparatus/Reagents Required

Electrolysis apparatus (9-volt battery and leads, graphite electrodes, two test tubes for collecting gases evolved), two rubber stoppers to fit the test tubes tightly, wood splints, ruler, 1 *M* sodium sulfate solution

Procedure

Record all data and observations directly in your notebook in ink.

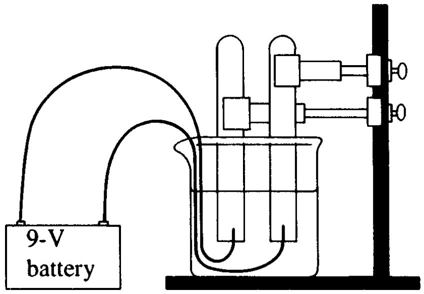
A. Electrolysis of Water

Place approximately 200 mL of distilled water in a 400-mL beaker. Add 2–3 mL of 1 *M* sodium sulfate to the water and stir. The sodium sulfate is added to help the electrical current pass more easily through the cell.

Arrange the dc power supply (9-volt battery) and graphite electrodes as indicated in Figure 1-1, using connecting wires terminating in alligator clips to make the connections. *Do not connect the battery at this point, however.* Make sure that the electrodes do not touch each other, and be certain that the electrodes are arranged in such a way that the test tubes can be inverted over them easily.

Fill each of the test tubes to be used for collecting gas with some of the water to be electrolyzed. Take one of the test tubes and place your finger over the mouth of the test tube to prevent loss of water.

FIGURE 1-1
Apparatus for electrolysis of water with collection of the evolved gases. Beware of electrical shock hazard.



Invert the test tube and lower the test tube into the water in the beaker. Remove your finger, and place the test tube over one of the electrodes so that the gas evolved at the electrode surface will be directed into the test tube.

If the liquid in the test tube is lost during this procedure, remove the test tube, refill with water, and repeat the transfer. Repeat the procedure with the other test tube and the remaining electrode.

Have the instructor check your set-up before continuing.

If the instructor approves, connect the battery to begin the electrolysis. Allow the electrolysis to continue until one of the test tubes is just filled with gas (hydrogen).

Disconnect the battery.

Stopper the test tubes while they are still *under the surface* of the water in the beaker and remove. One test tube should be filled with gas (hydrogen), while the other test tube should be only about half-filled with gas (oxygen), with the remainder of the test tube filled with water.

B. Testing of the Gases Evolved

With a ruler, measure the approximate height of gas contained in each test tube as an index of the volume of gas that was generated. Do the relative amounts of hydrogen and oxygen generated seem to correspond to the stoichiometry of the reaction?

Ignite a wooden splint. Using a clamp or test tube holder to protect your hands, hold the test tube containing the hydrogen gas upside down (hydrogen is lighter than air) and remove the stopper. Bring the flame near the open mouth of the test tube. Describe what happens to the hydrogen when ignited.

Obtain a wooden splint. Ignite the splint in a burner flame or match; then *blow out* the splint quickly so that the wood is still glowing. Remove the stopper from the oxygen test tube and insert the splint. Describe what happens to the splint.

Choice II. Electrolysis of Potassium Iodide Solution

Introduction

The reactions that take place in an electrolysis cell are always those that require the least expenditure of energy. In Choice I of this experiment, you electrolyzed water. Since water was the only reagent present in any quantity, water was both oxidized at the anode and reduced at the cathode. In this option, you will electrolyze a solution of the salt potassium iodide, KI.

Two possible oxidation half-reactions must be considered. Depending on which species present in the solution is more easily oxidized, one of these half-reactions will represent what actually occurs in the cell:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$2I^- \rightarrow I_2(s) + 2e^-$$

In the first half-reaction, *water* is being oxidized. This half-reaction would generate elemental oxygen gas, whose presence can be detected with a glowing splint as in Choice I. In addition, the pH of the solution in the region of the anode would be expected to decrease as hydrogen ion is generated by the electrode process. An indicator might be added to determine if the pH changes in the region of the anode. In the second possible half-reaction, elemental *iodine* is generated. Elemental iodine is slightly soluble in water, producing a brown solution. If this is the correct oxidation half-reaction, you would notice the solution surrounding the anode in the cell becoming progressively more brown as the electrolysis occurs. You might also notice that the anode becomes coated with dark crystals of solid iodine as the electrolysis continues.

The reduction half-reaction that takes place at the cathode in this experiment could be either of two processes, again depending on which reduction requires a lower expenditure of energy:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$K^+ + e^- \rightarrow K(s)$$

If the reduction of *water* is the actual half-reaction, as in the first example, hydrogen gas will be generated at the cathode and can be collected and tested for its flammability. Notice that hydroxide ion is also produced. Hydroxide ion will make the solution basic in the region of the cathode. As before, an indicator might be added to detect this change in pH in the region of the cathode. If the actual reduction, on the other hand, is that of *potassium ion,* the cathode would be expected to increase in size (and mass) as potassium metal is plated out on the surface of the cathode.

By careful observation in this experiment, you should be able to determine which oxidation and which reduction of those suggested actually take place in the cell.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **A 9-volt transistor battery will be used as the source of electrical current for the electrolysis. Be aware that even a small battery can cause an electrical shock if care is not exercised.**
- **Potassium iodide may be irritating to the skin. Avoid contact.**
- **Elemental iodine will stain the skin. The staining is generally not harmful unless a person is hypersensitive to iodine, but the stain will take 2–3 days to wear off.**
- **Hydrogen gas is flammable. Exercise caution during its generation and testing.**

Apparatus/Reagents Required

Electrolysis apparatus (9-volt battery and leads, graphite electrodes, and connecting wires), two test tubes and tightly fitting stoppers for isolation of the products, potassium iodide, sodium thiosulfate, Universal indicator solution and color chart, starch solution

Procedure

Record all data and observations directly in your notebook in ink.

Weigh out approximately 2.5 g of potassium iodide and dissolve in 150 mL of distilled water. This results in an approximately 0.1 *M* KI solution.

The KI solution should be *colorless.* If the solution is brown at this point, some of the iodide ion present has been oxidized. If this has happened, add a *single* crystal of sodium thiosulfate and stir. If the brown color does not fade, add more single crystals of sodium thiosulfate until the potassium iodide solution is colorless.

Add 4–5 drops of Universal indicator solution to the beaker and stir. Record the color and pH of the solution. Keep handy the color chart provided with the indicator.

Arrange the dc power supply (9-volt battery) and graphite electrodes as indicated in Figure 1-1 (Choice I), but *do not connect the battery yet.* Make sure that the electrodes do not touch each other and that the electrodes are arranged in such a way that the test tubes can be inverted over them easily.

Fill each of the test tubes with some of the KI solution to be electrolyzed. Take one of the test tubes and place your finger over its mouth to prevent loss of solution.

Invert the test tube and lower the test tube into the solution in the beaker. Remove your finger, and place the test tube over one of the electrodes so that the substances evolved at the electrode surface will be directed into the test tube.

If the liquid in the test tube is lost during this procedure, remove the test tube, refill with solution, and repeat the transfer. Repeat the procedure with the other test tube and the remaining electrode.

Wash your hands at this point to remove potassium iodide.

Have the instructor check your set-up before continuing.

If the instructor approves, connect the 9-volt battery to begin the electrolysis. Examine the electrodes for evolution of gas, or deposition of a solid. Allow the electrolysis to continue for several minutes. (If a gas is generated in the cell reaction, stop the electrolysis when the test tube above the electrode is filled with the gas.)

Observe and record the color changes that take place in the solution in the region of the electrodes. Be careful to distinguish between color changes associated with the indicator and the possible production of elemental iodine (brown color). By reference to the color chart provided with the indicator, determine what pH changes (if any) have occurred near the electrodes.

While still under the surface of the solution in the beaker, stopper the test tubes, and remove them from the solution in the beaker.

The possible oxidation and reduction half-reactions for this system were listed in the introduction to this choice. By testing the contents of the two test tubes, determine which half-reactions actually occurred.

If a gas is present in either test tube, use a clamp to hold the test tube and test the gas with a glowing wood splint. If you suspect the gas is hydrogen, invert the test tube (hydrogen is lighter than air), remove the stopper, and bring the wood splint near the mouth of the test tube. Hydrogen will explode with a loud pop. If you suspect the gas is oxygen, hold the test tube upright with the clamp, remove the stopper, and insert the glowing splint. Oxygen will cause the splint to burst into full flame.

If elemental iodine were produced, one of the test tubes would contain a brown solution. Confirm the presence of iodine by addition of a few drops of starch (blue/black color). If iodine were produced, the electrode at which the oxidation occurred would probably be coated with a thin layer of gray-black iodine crystals.

If metallic potassium were produced, it would have plated out as a thin gray-white coating on one of the electrodes.

After determining what oxidation and what reduction have actually occurred in the electrolysis cell, combine the appropriate half-reactions into the overall cell reaction for the electrolysis.

Electrochemistry II: Electrolysis

Date:	....	Student name:	....
Course:	....	Team members:	....
Section:	....		....
Instructor:	....		....

Prelaboratory Questions

Choice I. Electrolysis of Water

1. In this experiment we collect the gases produced by the electrolysis of water and measure their volumes to see if the volumes correspond to the stoichiometry of the reaction. Look up the solubilities of gaseous hydrogen and gaseous oxygen in a handbook to see if there will be any problem with one gas dissolving more than the other as it is generated, thereby affecting the volumes of gases measured. Write what you find.

2. Suppose 25 mL of gaseous hydrogen is collected through the electrolysis of water. What volume of gaseous oxygen should also be collected? Why?

3. Describe the qualitative tests for oxygen gas and for hydrogen gas.

Choice II. Electrolysis of Potassium Iodide Solution

1. When the electrolysis of an aqueous solution of an ionic salt is undertaken, very often the half-reactions that actually occur involve *water* molecules rather than the ions of the salt. Consult your textbook for information as to how you can predict what half-reactions are most likely to occur in an electrolysis experiment. Summarize your findings.

2. Suppose an aqueous solution of sodium fluoride were to be electrolyzed. What are the *possible* half-reactions that might take place in the system? Which are the *most likely* half-reactions? Why?

Electrochemistry II: Electrolysis

Date: .... Student name: ....
Course: .... Team members: ....
Section: ....
Instructor: ....

Results/Observations

Choice I. Electrolysis of Water

Observations on electrolysis

Approximately how long did it take to fill the test tube with H_2?

Height of gas in O_2 tube .... in H_2 tube ....

Ratio of H_2/O_2 heights .... error ....

Observation on testing H_2 with flame

Observation on testing O_2 with wood splint

Questions

1. How could the speed of an electrolysis such as you performed be increased?

2. Why was sodium sulfate added to the water to be electrolyzed? Was there any particular reason sodium sulfate, rather than some other salt, was used?

3. In order for an electrolysis to take place, the current used must be of sufficient voltage. Use your textbook to determine the minimum voltage current needed to electrolyze water.

Electrochemistry II: Electrolysis

Date:	....	Student name:	....
Course:	....	Team members:	....
Section:	....		....
Instructor:	....		....

Results/Observations

Choice II. Electrolysis of Potassium Iodide Solution

Was it necessary to add crystals of sodium thiosulfate to the potassium iodide solution? If so, how many crystals did you add?

Color and pH of KI solution before electrolysis ....

Color and pH of KI solution in region of the anode ....

Color and pH of KI solution in region of the cathode ....

What gas(es) were evolved during the electrolysis? At which electrode? How did the gas(es) respond when tested with the glowing wood splint?

Was elemental iodine produced? How was this confirmed?

Was elemental potassium produced? How was this confirmed?

Appearance of cathode after electrolysis

Appearance of anode after electrolysis

What half-reactions occurred in the electrolysis of aqueous KI?

What is the overall cell reaction?

Questions

1. Why were you advised to add a crystal of sodium thiosulfate to your potassium iodide solution if it had been brown when prepared? Write a balanced equation for the iodine/thiosulfate reaction.

2. If you had electrolyzed a potassium bromide solution, instead of potassium iodide, what would the likely half-reactions have been?