

Electrochemistry: Electrolysis of Solutions

Teacher Activity

Pre-Lab Procedure

1. Prepare cotton cloth or filter paper strips (if strips are cut to more than 4 inches long, students can snip smaller strips for use with each pair of reacting wells; width of strips does not have to be greater than 1/4 inch).
2. Starch solution is the standard 3%; a quick alternative is to add starch from a spray can into a 250-cm³ beaker of distilled water.
3. If you do not have the clips that fit onto the two terminals of a 9-volt battery, they can be purchased from an electronics or home building supply store. You will need to purchase the smaller alligator clips to add to the leads on the battery clip. The lead wires can be soldered to the alligator clips. Otherwise, simply wrap the lead wires through the holes on the ends of the clips or use the small screws that may be present.
4. Prepare the 0.1 M solutions needed.
5. Wash bottles are needed to rinse off the pencil carbon electrodes in between each electrolysis. If some plating has occurred, gentle cleaning with a small piece of fine emery cloth will work. The pencil carbon will probably break if not held close to the point where it needs to be cleaned.

Procedure (see student version of lab exercise)

This activity should be done in groups of 3 or 4 students and will require two 45-minute periods to complete.

Student Skills Required

Students should have basic skills for working in the lab: reading and following directions carefully, making skilled observations, and taking good notes.

Before carrying out the activity students should

- Be able to skillfully manipulate basic lab equipment;
- Have a basic understanding of the principles behind oxidation and reduction; and
- Be able to write equations that describe the basic activity at each of the electrodes (anode and cathode).

Lesson Concepts

- For non-spontaneous redox reactions, energy in the form of an electric current is supplied to produce a redox reaction.
- If the electrolysis process is done with an aqueous solution of ions, products can be predicted based on a redox chart (oxidation or reduction potentials).
- If metal ions are in solution, electroplating is possible.
- Electrical setups for electrolysis or electroplating use a direct current with a negative pole (cathode) and a positive pole (anode).
- Electrolysis at the cathode is reduction, and at the anode, oxidation.
- Oxidation and reduction processes require the loss and gain of electrons, respectively.

Student Misconceptions

- Electrons can flow through a solution.
In conduction of electricity through solutions, electrons do not pass through the solution. In maintaining the balance of charge within a circuit that includes an ionic solution, the anions and cations move to the particular electrode where charge transfer can occur (the negative

electrode, or cathode, donates electrons to positively charged ions, and the positive electrode, or anode, accepts electrons from a negatively charged ion). The flow of electrons is between the power source, the electrodes, and the ions that are attracted to the electrodes. The demonstration to show the movement of the ions within the solution uses a solution of KNO_3 (potassium nitrate) in a U-tube with electrodes at each opening. A solution of $\text{Cu}(\text{MnO}_4)_2$ (copper II permanganate) is introduced at the bottom of the curved tube without mixing with the potassium nitrate solution. Use of an electric current will show the migration of the purple MnO_4^- ion to the anode and the hydrated blue copper (II) ion to the cathode.

Answers to Pre-Lab Questions

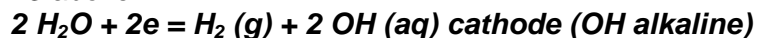
1. Does "pure water" (distilled) conduct electricity? Test this.
"Pure water" (distilled or deionized) does not conduct electricity because it lacks enough ions that migrate to electrodes to "complete" the circuit through the gain and loss of electrons.
2. Does a solution formed from the dissolving of sugar in water conduct electricity? Test the solution and explain your results in terms of Arrhenius's ideas.
Sugar, a molecular rather than an ionic solid, does not dissociate into ions when it dissolves. Rather the sugar conglomerate dissociates into individual molecules that do not possess any charge.
3. Does a solution formed from the dissolving of table salt in water conduct electricity? Test the solution and explain your results in terms of Arrhenius's ideas.
A solution of table salt will conduct electricity because the ionic solid will dissociate into individual ions that are needed for conduction.
4. Using equations, show why there is a difference in conductivity between the solution with the dissolved (dissociated) sugar and that with the dissolved table salt.
 **$(\text{C}_{12}\text{H}_{22}\text{O}_{11})_x (\text{s}) + \text{H}_2\text{O}(\text{l}) = x \text{C}_{12}\text{H}_{22}\text{O}_{11} (\text{aq})$
 $\text{NaCl} (\text{s}) + \text{H}_2\text{O} = \text{Na}^+(\text{aq}) + \text{Cl}^- (\text{aq})$**
5. If an ion loses electrons, is it oxidized or reduced?
The ion is oxidized.
6. If an ion gains electrons, is it oxidized or reduced?
The ion is reduced.

Answers to Post-Lab Questions

1. How do you explain the results in your first electrolysis using distilled water? What does this tell you about the presence or absence of ions in "pure" water?
Distilled water does not contain enough ions (10^{-7} M each for H^+ and OH^-) for conduction of an electric current.
2. What happens when you add drops of sodium sulfate (Na_2SO_4) to the distilled water? By adding the sodium sulfate solution, what has changed in the water?
Adding Na_2SO_4 , an ionic solution, provides enough ions for conduction of an electric current, which in turn provides for electrolysis of the water. The sodium sulfate does not undergo electrolysis (see redox or reduction potential charts).
3. Observation of bubbles would indicate the presence of a gas. What gases could be produced from the breakup ("lysis") of water, assuming sodium sulfate in solution is not changed?
The electrolysis of water produces hydrogen gas at the cathode (negative electrode) and oxygen gas at the anode (positive electrode).
4. What pH category (acidic, basic) is shown by color changes for the universal indicator in each of the reacting wells containing water?

Knowing that water contains hydrogen (H^+) and hydroxide (OH^-) ions in equal numbers when neutral ($pH = 7$), what must have happened in each of the reacting wells to have produced the particular pH changes noted through the color changes of the universal indicator? Identify each pH change (acidic, basic) with each type of electrode (positive, negative). In the electrolysis of water the production of hydrogen gas at the cathode (negative electrode) leaves an excess of hydroxide ions (OH^-), greater than $10^{-7} M$ of neutral water. The indicator changes color to reflect a change in pH to the alkaline range (> 7). At the anode (positive electrode) production of oxygen gas from the electrolysis leaves an excess of hydrogen ion (H^+), greater than $10^{-7} M$, changing the pH to the acidic range (< 7).

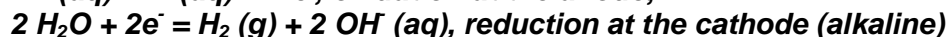
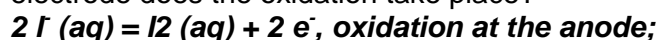
5. Consult a redox chart (oxidation or reduction potential) to find the half-reaction equations associated with the redox (by electrolysis) of water. Relate each of the half-reaction products to your observations in #3 above.



6. From #5, relate the products of each half reaction to the pH changes noted in #4.

See answer #5.

7. Explain your observations for the electrolysis of KI solution. Note that based on redox potentials for K^+ , I^- , and H_2O , potassium ions are not reduced. That leaves iodide ions and water to react. Write a half reaction equation for the oxidation of iodide ions. Does the product match your observations? At which electrode does the oxidation take place?



8. Using the information in question #5 above for the half reactions of water electrolysis, how do you account for the pH change at the negative electrode (cathode)? Write the appropriate half reaction and circle the product in the equation responsible for the pH change.

(See second equation in #7.) Production of hydroxide ions (OH^-) produces an alkaline condition, $pH > 7$.

9. What does the starch react with in the KI electrolysis? Write the chemical formula for the substance that starch reacts with.

The starch reacts with the iodine (I_2) formed from electrolysis, producing a dark blue black color.

10. If the chloride ion of NaCl reacts in the same manner as the iodide ion of KI because they are from the same family, write a half-reaction equation for the change that occurs to the chloride ion (Cl^-) during electrolysis. At which electrode did this change take place? What is your evidence from your observations?

$2 Cl^- (aq) = Cl_2 (g) + 2 e^-$ anode; chlorine gas is produced, which may be detectable by its odor and possibly by a slight yellow color.

11. As with the KI electrolysis, water electrolysis takes place in the NaCl solution rather than sodium electrolysis. Write the appropriate half reaction for water electrolysis, based on the information from question #5. Does this correlate with the pH change observed at the negative electrode (cathode)?

$2 H_2O + 2e^- = H_2 (g) + 2 OH^- (aq)$ cathode; there should be a change in pH to the alkaline range (>7).

12. As with KI and NaCl electrolysis, the electrolysis of KBr produces similar results. Write the half-reaction equations for the electrolysis of Br^- and H_2O . What is your evidence for the formation of Br_2 and the electrolysis of water?



$2 H_2O + 2 e^- = H_2 (g) + 2 OH^- (aq)$ cathode; indicator change is to the alkaline range (>7) because of excess hydroxide ion produced. Bubbling is from the hydrogen gas produced.

13. What changes did you observe when you did electrolysis of the copper sulfate (CuSO_4) solution? Relate each change to a particular electrode (positive, negative).
A brownish orange deposit occurred at the cathode. Bubbling and a change in pH to the acidic range (<7) occurred at the anode.
14. Write half-reaction equations for each observation in #13. Relate each change to a specific electrode. Remember to relate any pH changes to your observations. Assume electrolysis of water took place at one of the electrodes and not that of the sulfate (SO_4^{2-}) ion.
 ***$\text{Cu}^{+2}(\text{aq}) + 2\text{e}^- = \text{Cu}(\text{s})$ cathode (solid copper deposited on electrode);
 $\text{H}_2\text{O} = \frac{1}{2} \text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$ anode (excess hydrogen ions, acidic)***

Assessment

1. The topic of electrochemistry has an extensive and interesting history, starting with Alessandro Volta's design of a battery called an "electric pile." It was this electric pile that allowed such early investigators as Humphry Davy and Jöns Jakob Berzelius to do electrolysis and the isolation of a number of elemental metals, including potassium, calcium, strontium, and barium (isolated by Davy) and cerium, selenium, and thorium. The separation and identification of these elements was necessary for determining the chemical and physical properties that would later prove useful for establishing the periodic table. Students can do a lot of biographical research into the lives of these chemistry giants as well as other pioneers in the field. Later extensions in the use of electrolysis for industrial extraction purposes continues to this day (aluminum and other metals from ores [Hall and Heroult]; halogens from brine [Dow]).
2. Students could be asked to perform other electrolysis operations using the microscale setups, while being expected to predict from reduction or oxidation potential charts what products are formed, using the pH test (and other qualitative tests of the products if appropriate) to determine whether H_2O is electrolyzed and which half reaction occurs. Nitrate compounds are good choices. Copper chloride solution also gives good results.
3. Students could compare the difference in electrolysis using nonreactive electrodes (carbon pencil "lead") and reactive electrodes for the same ionic solution, copper sulfate. Observations alone will show the difference. Products can be determined from observation (pH change, color change on an electrode) or consulting the redox charts.
4. Students could run micro-electroplating devices using the pencil carbon for nonreacting electrodes and identifying the metal products based on the starting solution's metallic compound. Some of the solutions for this experiment include lead nitrate, copper nitrate, and zinc nitrate, where the nitrate is not involved but water is at the anode (positive pH test for acidity).
5. Students can investigate the chemistry behind an important industrial process that is done with electrolysis. This process that produces sodium hydroxide and chlorine gas, two of the more important chemicals for the manufacturing industry (paper and textiles), is known as the chloralkali process, which was begun by Herbert Dow. This process nicely illustrates the workings of electrolysis as well as spontaneous redox reactions.

Extension Activities

1. Either as lab activities, demonstrations, or student projects, there is much to explore under basic spontaneous redox reactions (done on the microscale with metals and their metallic solutions). And the whole business of voltaic cells (electrochemical cells or "batteries") is fundamental redox chemistry that can be investigated and quantified (voltage readings in the cells). Depending on their background, students could write the two half reactions, the net equation, and the predicted voltage of the cell (1 M solutions).

2. Students can research both the history of developing voltaic cells (in the parlance, “batteries”), current ideas about battery designs (and why different applications require different types of batteries), making batteries from polymers (plastics), fuel-cell chemistry, and the future of what are known as lithium batteries for powering rechargeable automobiles.

Additional Teacher Resources

1. An interesting read about two important industrial processes, the Solvay process and the chloralkali process (involves electrolysis), is found in the chemistry textbook *Chemistry in Context* (American Chemical Society; published by Wm. C. Brown, 1994, ISBN: 0697219488, Chap. 7, 181–201). This reading includes environmental issues and how they have been solved relative to the manufacturing processes.
2. Production of aluminum (historical) is nicely described at <http://acswebcontent.acs.org/landmarks/landmarks/cmh/index.html> and <http://acswebcontent.acs.org/landmarks/landmarks/al/index.html>.
3. A general reference on the history of chemistry is *Creations of Fire* (Cobb and Goldwhite; published by Plenum Publishers, 1995, ISBN 0-306-45087-9). Specific pages for the history of famous chemists involved in electrochemistry are pp. 179–206.
4. The basics of oxidation-reduction with good diagrams for electrolysis setups are provided at <http://library.thinkquest.org/3659/electrochem/redox.html>.
5. There is a reference in which a virtual electrolysis setup can be used for a variety of electrode metal–ionic solution combinations. Changes in the mass of the electrodes are displayed, and visuals show both electron and atom-ion changes at each electrode. http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem/electrolysis1_0.html.
6. A completely documented and illustrated student project on electrolysis of water, using a solar photovoltaic cell as the source of electricity is given at http://www.nmsea.org/Curriculum/7_12/electrolysis/electrolysis.htm.
7. A student project on electroplating is well explained and illustrated at <http://www.finishing.com/faqs/howworks.html>.

Additional Teacher Notes

Students can make a conductivity device indicator that can also be used as a 9-volt DC current for electrolysis and electroplating. The following is what is needed to construct the device:

- a 9-volt battery and battery snap connector with black and red leads,
- one LED (light-emitting diode),
- one 1-K ohm 1/4 watt resistor,
- two alligator clips, and
- a film canister.

Connections between wire leads and the resistor or LED are made mechanically (twisting two wire ends), then soldered with tape solder that is melted with a match or candle flame.

The circuit is made with the battery snap connector, its black and red leads, and the resistor and LED. Starting with what will be the positive (+) side of the connector (fits on the positive side of the 9-volt battery), mechanically wrap the red lead of the connector to one end of the 1-K ohm resistor to make a connection.

Next, identify the *longer* lead of the LED. Connect this lead to the free end of the resistor. Connect a mini-alligator clip to the free end (the shorter end) of the LED. These steps complete the positive lead (red) after you solder each connection between wires.

Next, take the black lead (-) of the battery connector and connect it to another mini-alligator clip. Solder the mechanical connection. These steps complete the conductivity device.

Test the circuitry by attaching the snap connector onto the positive and negative terminals of the battery. If you touch the two alligator clips together, the LED should light.

Now you are ready to put the battery into a film canister so that it will stand on the lab bench while you do electrolysis activities. The fact that the light is on while touching the alligator clips (with pencil carbon electrodes) to two microplate wells with an ionic solution shows that a current is flowing. The device can also be used in other activities such as determining the conductivity of various materials.