Education makes people easy to lead, but difficult to drive; easy to govern, but impossible to enslave.
--Henry, Baron Brougham

Electrolysis of Aqueous Solutions

You have seen that chemical reactions in solution can produce electricity. It might seem logical that electricity passed through a solution may result in a chemical reaction. In fact, many of you will have done this very thing before in another science class: the electrolysis of water to produce hydrogen and oxygen gas. For that process we might write:

$$\text{electrical energy} + H_2O(\ell) \rightarrow H_2(g) + \tfrac{1}{2}\, O_2(g)$$

It can be shown that this is a redox reaction by inspecting the changes in oxidation number. It should therefore be possible to write *half-reactions* for the processes which occur at each electrode, cathode and anode. We use these terms to mean the same thing in an *electrolytic* cell as they meant in a *galvanic* cell. One possible way to investigate these changes is with an acid/base indicator. Since water contains small amounts of H^+ and OH^-, it may be that these ions are involved in the breakdown of water into its elements. In other words, the *mechanism* for the reaction written above might involve these ions.

Reactions like this require some external source of electrons (we usually call that electricity!) in order to occur. A battery or power supply can act as the "electron pump". As you have noted in your experiments with galvanic cells (simple batteries) electrons emerge from the negative (-) electrode and return to the positive (+) electrode. Placing these electrodes into a solution makes the electrons available for redox reactions.

You may also remember that in order to electrolyze water, some electrolyte dissolved in the water was necessary. This is true since there are very few free ions in pure water, only about 2×10^{-7} M total (why?). Does the nature of the electrolyte affect the products of the electrolysis?

The questions posed above can be investigated in a series of simple experiments, but it would be wrong to surmise from this that electrode processes in such cells are simple. In fact just the opposite is true. A complete quantitative treatment of aqueous electrolytic cells is beyond the scope of this course. But the fundamentals--which you can investigate in the lab--are not.

Preparing to experiment

You will be provided with the following materials:

1. mini U-tube
2. power supply (set on 12 volts)
3. graphite electrodes
4. black/white cardboard
5. 0.1 M NaF solution
6. 0.1 M $CoCl_2$ solution
7. 0.1 M $CuBr_2$ solution
8. 0.1 M KI solution
9. bromthymol blue indicator (use 1 drop in each arm)
10. phenolphthalein indicator (use 1 drop in each arm)
11. starch solution (use 1 drop in each arm)
12. food coloring dye (use 1 drop ONLY in each arm)

Design an experiment using bromthymol blue indicator to investigate the changes in a sodium fluoride solution when electricity passes through it.

Design an experiment using food coloring dye to investigate the changes in $CoCl_2$ solution when electricity passes through it.

Design an experiment to investigate the changes in $CuBr_2$ solution when electricity passes through it.

Design an experiment using phenolphthalein indicator and starch solution to investigate the changes in a KI solution when electricity passes through it.

In each case be sure to note down all visual observations such as changes in color, gas formation and relative rates of gas formation if gases form at both electrodes.

Pre-lab take-home quiz

These questions should be answered on a separate sheet of paper to be turned in on the day you do this experiment.

1. Show, by assigning oxidation numbers, that the decomposition of water into hydrogen and oxygen is a redox reaction.

2. It is stated in the introduction that the total ionic concentration in pure water is about 2×10^{-7} M. Why is this?

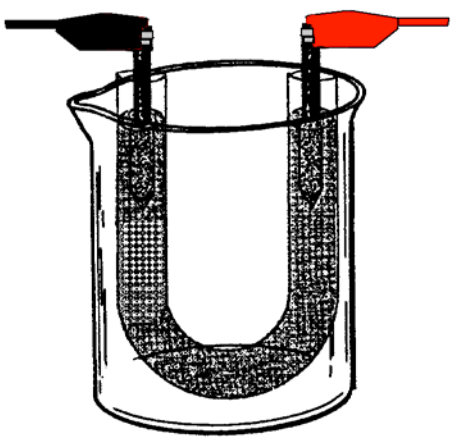
Technique

1. Using mini U-tubes as electrolysis cells

The mini U-tubes are designed to keep the electrode reactions more or less separate but still allow ions to migrate through the solution and carry the electricity. You can fill a tube directly from the squeeze bottles and add the indicators with the droppers provided. Then attach the graphite electrodes to the alligator clips from the power supply. Insert the electrodes into the arms of the U-tube and make your observations. Be careful not to touch the electrodes together or you could damage the power supply. You also might get a nasty shock if you are careless.

Be sure to note which electrode (+ or -) is in which arm when you record your observations. Not all the reactions happen equally fast. Be sure to give enough time to see any changes before you move on.

The diagram below is provided for your reference. You will probably find it easier to support the U-tube in a 50 mL beaker while working. The white/black cardboard provided can be used behind it in order to better observe changes.



2. Using starch to test for I_2

Starch (ordinary clothes starch or even cornstarch would work just fine) provides a sensitive test for I_2 in solution that is used often in the lab. It forms an intense blue complex molecule (sometimes appearing almost black or dark purple) in the presence of I_2. Otherwise it is colorless.

Analysis

1. Recall the colors of bromthymol blue in various solutions:

acid	yellow
neutral	green
base	blue

According to this, what ions must be produced at the + and - electrodes during the electrolysis of an aqueous solution of NaF (along with the hydrogen and oxygen gas)? Why does the indicator start out *blue* or *bluish green* in the NaF solution? (*hint:* what acid and base form NaF?)

2. Which gas (H_2 or O_2) was produced at which electrode (+ or -) in the sodium fluoride cell? Based on your visual observations at each electrode, HOW CAN YOU TELL?

3. Find the appropriate half-reactions for this process in the Standard reduction potential table in your text (hint: they are found at -0.83 v and +1.23 v). Combine them to give the overall reaction you observed (you will have to reverse one).

a. What is the net cell voltage?
b. Which electrode reaction occurs at the anode?
Which electrode reaction occurs at the cathode?
c. Generalize a rule for the location of anodes and cathodes in the table for an *electrolytic* cell
d. Why doesn't the sodium fluoride solution electrolyze spontaneously?
e. Since sodium and fluoride ions do not appear in the reaction, what function do they serve?

4. In order for the reaction to occur, the net cell voltage must be positive. You added +12 v to the sodium fluoride cell. Does that result in a net positive voltage?

5. Use your results for the electrolysis of $CuBr_2$ solution to determine the following:

a. the half-cell reactions at each electrode
b. the net cell reaction
c. the cell voltage

[refer to the Standard reduction potential table in your text]

6. Which gas (H_2 or O_2) is produced in the KI cell? [*hint:* at which electrodes were these gases produced in earlier cells?]

7. Considering your answer to #6, use your results for the electrolysis of KI solution to determine the following:

a. the half-reactions at each electrode
b. the net cell reaction
c. the cell voltage

[refer to the Standard reduction potential table in your text]

8. Why isn't potassium metal a product of this electrolysis?

9. Generalize a rule for "guessing" which of two competing electrode processes (for example, the reduction of water to produce hydrogen gas or the reduction of Co^{2+} to produce cobalt metal) will occur in the electrolysis of an aqueous solution. [note: this "rule" will only be correct in dilute solutions such as the ones you used in this experiment; in concentrated solutions all bets are off]

10. Why do you think cobalt metal is produced instead of hydrogen gas in the electrolysis of $CoCl_2$ solution? [hint: compare the voltages in the table].

11. What gas do you think was produced at the other electrode? HOW CAN YOU TELL? [hint: what does chlorine do to dyes?]. How does this fit in with your generalization given in #9? Explain.

12. Use your results for the electrolysis of $CoCl_2$ solution to determine the following:

a. the half-reactions at each electrode
b. the net cell reaction
c. the cell voltage

[refer to the Standard reduction potential table in your text]