THE ELECTROCHEMICAL SYNTHESIS OF $K_2S_2O_8$

Introduction

Electrochemical cells can be divided into two categories; galvanic cells and electrolytic cells. A galvanic cell is a cell in which a spontaneous oxidation-reduction reaction is used to produce electrical current; a galvanic cell is essentially a battery. An electrolytic cell, in contrast, is one in which electrical current is used to cause a nonspontaneous oxidation-reduction reaction to occur.

In an electrolytic cell electrical current is passed through a conducting solution via two electrodes, referred to as the *anode* and *cathode*. The conducting solution may be pure water, an aqueous solution, or even a molten salt. The electrodes may be composed of any conducting material, but inert electrodes are often required. In cases where inert electrodes are required, platinum is often used.

The Electrolysis of Pure Water

Let's start with the simplest case, the electrolysis of pure water using inert electrodes. In this case, hydrogen gas is evolved at one electrode and oxygen gas is observed at the other. The two half-reactions and the overall balanced reaction are shown below.

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	*Reduction reaction*
$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$	*Oxidation reaction*
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$	*Overall reaction*

Which gas is evolved at which electrode? By definition, the *anode* of an electrochemical cell is the electrode at which *oxidation* occurs and the *cathode* is the electrode at which *reduction* occurs. So, does the production of hydrogen gas from water involve oxidation or reduction? To answer this question, it may be helpful to review the rules for assigning oxidation numbers.

1. An element in elemental form has an oxidation state of zero

2. Oxygen always has an oxidation state of zero, unless it is a peroxide (O_2^{2-}) or superoxide (O_2^-)

3. Hydrogen always has an oxidation state of +1 unless it is a hydride, in which case it has an oxidation state of –1

4. The sum of the oxidation states for the atoms in a molecule must add to the charge on the molecule

From these rules, you should be able to see that in water the hydrogen has an oxidation state of +1 and the oxygen has an oxidation state of –2. Therefore the production of hydrogen from water is a reduction (from an oxidation state of +1 to 0) and occurs at the cathode, whereas the production of oxygen from water is an oxidation (from an oxidation state of –2 to 0) and occurs at the anode.

If you are setting up such an electrolysis cell, which electrode would you connect to the positive terminal of your power supply and which would you connect to the negative terminal? You can envision electricity as traveling from the negative to the positive terminals of a battery or power supply. Electrons enter the cell through the cathode (where the reduction reaction or "consumption" of electrons occurs), travel through the solution, and return through the anode (where the oxidation or "liberation" of electrons occurs). Therefore in an electrolysis cell the electrode connected to the negative terminal of the power supply is the cathode and is electrode connected to the positive terminal of the power supply is the anode.

Competing Reduction Reactions

Very often, electrolysis is performed on aqueous solutions contains dissolved salts. In such cases, the substance most easily reduced is produced at the cathode and the substance most easily oxidized is produced at the anode. Suppose, for example, that you are performing electrolysis on a solution of copper chloride. In this case there are two competing reduction reactions, reduction of water and reduction of the copper ion. Which of these two processes occur? To answer this question, we must consult a table of standard reduction potentials, which list the potentials associated with various half reactions.

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^o = -0.83V$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o = +0.43V$

The more positive the potential for a reaction, the greater the tendency for the reaction to occur as written. Therefore reduction of the copper will occur preferentially over the reduction of water; metallic copper will be plated onto the anode.

Now suppose that we wish to perform electrolysis on a solution containing the sodium ion, such as sodium chloride or sodium nitrate. Is it possible that the reduction of the sodium ion may compete with the reduction of the water? Again, the answer lies with standard reduction potentials for these two half-reactions.

$2H_2O(l) +2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^o = -0.83V$

$Na^+(aq) + e^- \rightarrow Na(s)$ $E^o = -2.71V$

Both of these reduction potentials are negative, but the reduction of sodium is far more negative. Therefore, the reduction of water occurs preferentially over the reduction of the sodium ion. In order to obtain sodium metal from an electrolysis cell, the competing reaction with water must be removed, and the only way to this is by performing electrolysis on a molten salt. Sodium metal is obtained by the electrolysis of molten sodium chloride. Generally, the more reactive metals such as Na, K, Mg, Ca, and Al cannot be obtained from the electrolysis of aqueous solution.

Competing Oxidation Reactions

Just as certain reactions may compete with the reduction of water, certain reactions may also compete with the oxidation of water. Under standard conditions, the oxidation of water has a potential of –1.23 V.

$O_2(g) + 4H^+ + 4e^- \rightarrow H_2O$ $\quad E^o = +1.23$ V

Note that the above reaction is written as reduction, not an oxidation. It was decided, by convention, that potentials would be listed as reductions rather than oxidations. When a reaction is reversed, the sign is changed. Therefore as a reduction this reaction has a potential of +1.23V. When reversed it has a potential of –1.23V.

If a solution contains an ion that is fairly easily oxidized, the oxidation of the ion may compete with the oxidation of water. The most common examples are halide ions, which can be oxidized to the corresponding halogen.

$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	$E^o = +2.87$ V
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	$E^o = +1.36$V
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	$E^o = +1.07$ V
$I_2(g) + 2e^- \rightarrow 2I^-(aq)$	$E^o = +0.53$ V

When reversed, the signs are changed, so that the oxidation of the fluoride ion is least favorable and the oxidation of the iodide ion is most favorable. Going strictly by these standard potentials, only the oxidation of bromide and iodide ions can compete with the oxidation of water. In reality, this is not entirely true. The potentials listed above are standard potentials, which means they were measured under standard conditions. Increasing the concentration of the ions decreases the potential, so that the oxidation of the chloride ion can compete with the oxidation of water.

Competing oxidation reactions may also arise if the electrodes are not inert. Suppose, for example, that we attempted to perform the electrolysis of pure water using copper electrodes. In this case, the reduction of water to hydrogen gas would occur as before. However, the oxidation reaction would be different. The copper ion is more easily oxidized than water and would instead. Therefore our reactions would be as shown below.

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	*Reduction reaction*
$Cu \rightarrow Cu^{2+} + 2e^-$	*Oxidation reaction*
$2H_2O + Cu \rightarrow 2H_2 + 2OH^- + Cu^{2+}$	*Overall reaction*

Faraday's Law

It would obviously be very useful to be able to calculate the amount of product formed in an electrochemical process. Suppose, for example, that a mole of sodium is to be produced by the electrolysis of molten sodium chloride. Since sodium forms a +1 ion, one mole of electrons is required to produce one mole of sodium. But how long would it take to pass a mole of electrons though the cell? The answer to this question depends upon the **electrical current** passing though the cell.

Electrical current is measured in **amperes**, where an ampere is defined as one coulomb per second. A coulomb is a physical quantity of charge in much the same way as a mole is a physical number of atoms or molecules. A mole of electrons has a charge of 96,500 coulombs, a quantity of charge known as a **Faraday.** To produce a mole of sodium 96,500 coulombs of charge must be used.

From this point, determining the time required to produce the mole of sodium is a matter of simple division. Suppose that an electrical current of one ampere is used. Since an ampere is equivalent to one coulomb of charge per second, it will take 96,500 seconds, or 26.8 hours, for a mole of electrons to pass through the cell. The time required is decreased as the electrical current is increased. If a current of two amperes were used, the same quantity of sodium would be produced in half the time.

Note two or even three moles of electrons might be needed to produce a mole of a given product. For example, if magnesium were being produced, two moles of electrons would be required for every mole of magnesium produced. If aluminum were being produced, three moles of electrons would be required for every moles of aluminum produced.

The Experiment

In this experiment, we will produce potassium peroxydisulfate ($K_2S_2O_8$) by performing electrolysis on a saturated solution of $KHSO_4$. Our cell will consist of a platinum anode and a copper cathode. The associated half-reactions are shown below.

$2H^+(aq)\ 2e^- \rightarrow H_2(g)$ *reduction, cathode reaction*

$2HSO_4^-(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-$ *oxidation, anode reaction*

The oxidation reaction has a large negative potential (-2.05 volts) and theoretically cannot compete with the oxidation of water (-1.23 volts). However, we will employ a high concentration of HSO_4^- (a saturated solution) to make this reaction less unfavorable. Furthermore, we will keep the cell immersed in an ice bath so that the $S_2O_8^{2-}$ is precipitated out as $K_2S_2O_8$ as it is formed.

In the last week of the experiment, we will employ a starch-iodine titration to determine the purity of our $K_2S_2O_8$. The peroxydisulfate ion is a strong oxidizing agent, and is capable of oxidizing the iodide ion to molecular iodine.

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

A standard method of determining iodine is reduction to the iodide ion using sodium thiosulfate.

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$

In such titrations soluble starch functions as an indicator because it forms an intensely colored blue-black complex with molecular iodine. As the thiosulfate is added, the iodine is reduced to the iodide ion, and the blue-black color disappears once all of the iodine has reacted.

Our method for determining the purity of the synthesized potassium peroxydisulfate will be to allow a measured quantity to react with an excess of potassium iodide, producing molecular iodine. This will then be titrated with sodium thiosulfate using starch as an indicator.

A Sample Calculation

Let's work an example of the type of calculation you will be performing in lab. Suppose that a 0.25-gram sample of $K_2S_2O_8$ is titrated according to the procedure described above. If 12.50 mL of 0.10 M $Na_2S_2O_3$ are required to reach the end point, determine the purity of the sample.

According to the stoichiometry of the reaction, one mole of persulfate ions oxidizes two moles of iodide ions to one mole of molecular iodine. This one mole of molecular iodine reacts with two moles of sodium thiosulfate. Ultimately, therefore, *one* mole of persulfate ions reacts with *two* moles of thiosulfate ions.

The number of moles of thiosulfate ion added can be determined from the volume and concentration of the solution:

0.0125 liters x 0.10 moles/liter = 0.00125 moles

Now apply the reaction stoichiometry; two moles of thiosulfate ion are required to react with one mole of persulfate ion. Therefore, the number of moles of persulfate ion in the sample is half this number.

Number of moles of $S_2O_8^{2-}$ = 0.00125/2 = 0.000625 moles

Now multiply this number of moles by the molar mass of potassium persulfate:

0.000625 moles x 270 grams/mole = 0.17 grams

Finally, express this as a percentage of the original mass:

(0.17 grams / 0.25 grams) x 100 = 68%

Procedure

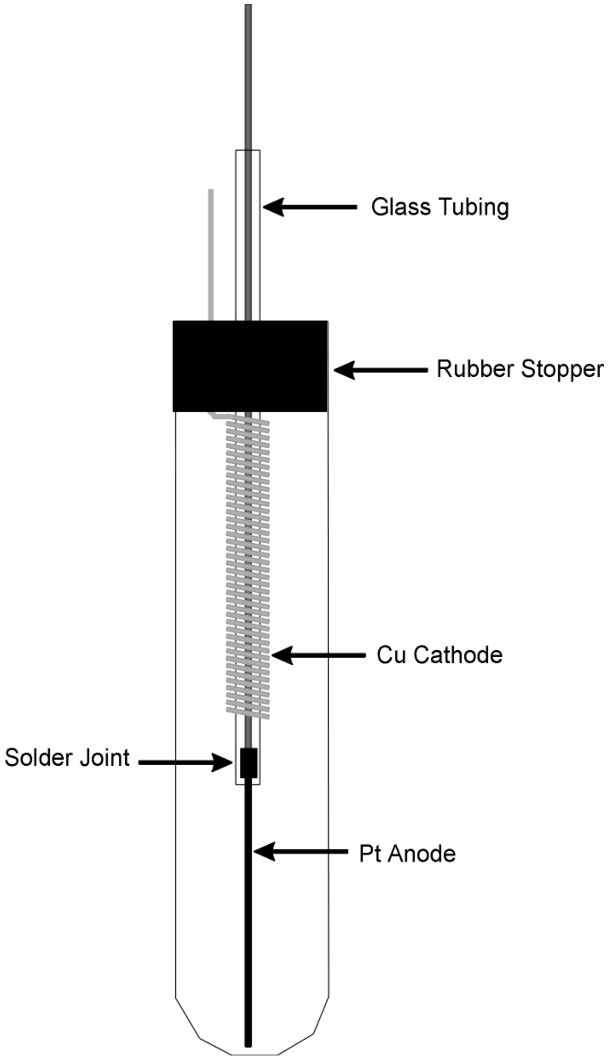
Week 1 –Synthesis of Saturated $KHSO_4$

Add approximately 150 mL of water to a 600-mL or 800-mL beaker. Carefully add 60 mL concentrated sulfuric acid. *(Caution: this reaction is very exothermic and must be done slowly. When diluting acids, always add acid to water and not the other way around!)* Heat the solution to a temperature of approximately 60°C (no warmer) and add K_2SO_4 until no further K_2SO_4 will dissolve. Cool the solution in an ice bath until a temperature of 15°C or less is obtained. Filter the solution through a Buchner funnel and dispose of the solid in the appropriate waste container. Transfer the solution to a 125-mL Erlenmeyer flask, cover with Parafilm, and store in your drawer until the following week.

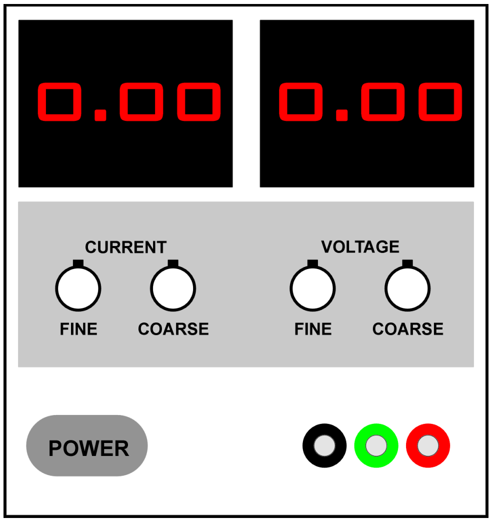
Week 2- Electrochemical Synthesis of $K_2S_2O_8$

The electrolysis cell you will be using is constructed as shown on the right. It will consist of a glass tube mounted through a large rubber stopper. Platinum wire functions as the anode and runs through the glass tube; however to minimize the amount of platinum used it is soldered to a copper wire inside the glass tubing so that it is copper as it emerges from the top. Copper wire functions as the cathode and is wrapped around the outside of the glass tube. The entire assembly is mounted inside a large test tube.

Fill the test tube nearly full of your saturated $KHSO_4$ solution (it should be as full as possible without overflowing when the rubber stopper is inserted. Fill a 1000-mL beaker with ice to serve as an ice bath, and clamp your tube in the ice. As much of the tube as possible should be immersed in the ice bath. Attach the wires as previously described, and have your instructor check the equipment before beginning.



The power supplies you will use (right) have knobs for fine and coarse adjustment of the voltage and current. They can be run in constant current or constant voltage mode; in this lab we will use the constant current mode, where the power supply automatically adjusts the voltage as needed to maintain a set current. To operate the power supply in constant current mode, turn both the fine and coarse voltage knobs all the way to the right, then adjust the current knobs until the desired current is obtained.



The cell should be operated for 30-45 minutes. At the end of this time, filter the contents of your cell through a Buchner funnel. Wash the product with a small quantity (approximately 20 mL) of ethanol or acetone. Obtain the mass of the product, and calculate the percent yield. Transfer the solid to a sample vial and store it in your drawer until the following laboratory period.

Week 3 – Titration of $K_2S_2O_8$

Obtain three 125-mL Erlenmeyer flasks. To each flask, add 3-4 grams of solid KI, 25 mL of 3.0 M NH_4Cl (the NH_4Cl is a catalyst that aids in the oxidation of the iodide), and 0.20–0.50 grams of commercial $K_2S_2O_8$ (it is a good idea to use a different mass of $K_2S_2O_8$ for each titration). Heat the flasks to a temperature of 40^{o}C for a period of 15 minutes. The flasks must be heated because the oxidation of iodide ion to molecular iodide occurs slowly. Do not overheat the flasks, as iodine is volatile and can easily be driven off. While some hotplates display a temperature, they are very inaccurate and you should use a thermometer to monitor your temperature. The solutions should slowly turn to orange-brown as the I_2 is formed.

Fill a buret with 0.10 M $Na_2S_2O_3$ and titrate the samples. With each sample, titrate until the color lightens to a pale yellow; then add 5 mL of the starch indicator and titrate until the solution from blue-black to colorless. If the solution does not turn blue-black when the starch indicator is added then you have already overshot the endpoint and will have to re-run that trial. Based upon the amount of NaS_2O_3 added, determine the amount of $K_2S_2O_8$ in your sample and calculate the purity of your sample.

After titration, you may see a flask turn from colorless back to blue-black. This may happen if you did not heat the flask long enough or hot enough, and occurs because the oxidation of iodine ion to molecular iodine is still occurring. If this happens, simply continue the titration until the solution turns colorless again.

Repeat the above procedure on three samples of your synthesized $K_2S_2O_8$ solution.

The Electrochemical Synthesis of $K_2S_2O_8$ **Pre-Laboratory Week 1**	**Name:**

Look up the chemical properties and any hazards associated with each of the following reagents:

a. Concentrated Sulfuric Acid

b. Potassium Sulfate

The Electrochemical Synthesis of $K_2S_2O_8$ **In-Laboratory Week 1**	**Name:**

Briefly outline the procedure that you used to synthesis the saturated $KHSO_4$ solution. Include observations, quantities of reagents used, and so forth.

The Electrochemical Synthesis of $K_2S_2O_8$ **Pre-Laboratory Week 2**	**Name:**

1. Define the terms *anode* and *cathode*. Which process (oxidation or reduction) occurs at each?

2. Suppose that you run a current of 1.0 amperes through your cell for a period of 90 minutes. Calculate the theoretical amount of $K_2S_2O_8$ that would be produced.

3. Explain why we must use platinum wire (not copper) for our anode. What would happen if we did use copper?

The Electrochemical Synthesis of $K_2S_2O_8$ **In-Laboratory Week 2**	**Name:**

Describe the procedure that you used to synthesize the $K_2S_2O_8$. Include any observations that you have made.

Record the mass of $K_2S_2O_8$ that you obtained. Based upon the length of time that the cell was operated and the current used, calculate the theoretical yield of $K_2S_2O_8$.

Calculate the percent yield of $K_2S_2O_8$. Suggest some reasons why your yield might be less that 100%.

The Electrochemical Synthesis of $K_2S_2O_8$ **Pre-Laboratory Week 3**	**Name:**

1. Look up the chemical properties and any hazards associated with each of the following reagents:

a. Sodium Thiosulfate

b. Sodium Iodide

c. Ammonium chloride

2. Calculate the quantity of 0.10 M sodium thiosulfate that would be required to completely react with 0.25 grams of potassium peroxydisulfate.

The Electrochemical Synthesis of $K_2S_2O_8$ **In-Laboratory Week 3**	**Name:**

Titration of Synthesized $K_2S_20_8$

	Trial 1	Trial 2	Trial 3
Mass of $K_2S_2O_8$			
Starting Buret Volume			
Final Buret Volume			
Volume of $Na_2S_2O_3$ Dispensed			
Moles of $Na_2S_2O_3$ Dispensed			
Moles of $K_2S_2O_8$ in sample			
Mass of $K_2S_2O_8$ in sample			
Mass Percent of $K_2S_2O_8$ in sample			

The Electrochemical Synthesis of $K_2S_2O_8$ **In-Laboratory Week 3**	**Name:**

Titration of Commercial $K_2S_20_8$

	Trial 1	Trial 2	Trial 3
Mass of $K_2S_2O_8$			
Starting Buret Volume			
Final Buret Volume			
Volume of $Na_2S_2O_3$ Dispensed			
Moles of $Na_2S_2O_3$ Dispensed			
Moles of $K_2S_2O_8$ in sample			
Mass of $K_2S_2O_8$ in sample			
Mass Percent of $K_2S_2O_8$ in sample			