Experiment 9B

FV 9/15/05

STUDYING THE DECOMPOSITION OF POTASSIUM CHLORATE

MATERIALS: Small test tube (20 x 150 mm), one-hole rubber stopper fitted with glass tube and rubber tubing, gas collecting tube, small plastic water basin, test tube holder, wooden splints, 600 mL beaker, 100 mL beaker, 100 mL graduated cylinder, large test tube (25 x 150 mm), 16 oz. glass collection bottle fitted with a two hole-rubber stopper with glass tubes and tubing, pinch clamp, pipet bulb, 2 clamps, 2 ring stands, Bunsen burner, weighing boats, glass wool, MnO_2, pure $KClO_3$, unknown mixture containing $KClO_3$ and an inert substance.

PURPOSE: The purpose of this experiment is to study the decomposition reaction of potassium chlorate. By collecting data on the reaction, the student will: 1) verify the identity of one of the products; 2) determine if the gas product obeys the ideal gas law; 3) determine the percent by mass of potassium chlorate in an unknown mixture.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Find the MSDS and/or Safety Card for a chemical species, and locate important information related to physical properties, reactivity, and appropriate handling protocols.
2. Perform simple tests to verify gas production in general, and oxygen gas in particular.
3. Explain the relationship between the mass of a substance and the number of moles of a substance.
4. Apply stoichiometric ratios between the moles of reactant(s) and product(s) in balanced chemical reactions.
5. Calculate the percent by mass of a compound in a mixture.
6. Determine if a gas obeys the ideal gas law.

PRE-LAB: Complete the pre-lab questions on page E9B-7 **before lab**.

DISCUSSION:

Material Safety Data Sheets and International Chemical Safety Cards. Any institution where chemicals are used is required to have copies of the material safety data sheets (MSDS) available for use. These sheets provide key information relating to health hazards, appropriate storage, handling and disposal arrangements, fire and explosive hazards, required control measures, physical/chemical properties, and reactivity data. In this experiment, the MSDS for potassium chlorate will be used to help guide the experimental study of its decomposition reactions. In general, prior to any chemical procedure, the relevant MSDS should be consulted to assure safe and proper procedures are followed. Another system which provides similar information is the International Chemical Safety Card system. Both MSDS and Safety Cards are available on-line through links found on the Plebe Chemistry homepage.

Relevant Naval Application. On submarines, oxygen for breathing is normally produced through electrolysis of water. Details relating to this process will be studied later in the course. In an emergency, a chemical process is used to produce oxygen gas for breathing, i.e., the decomposition of sodium chlorate at high temperature (i.e., above 300^oC), producing oxygen gas and sodium chloride. Unfortunately, there are several complications associated with this reaction which must be remedied if the production of oxygen gas for breathing is to be performed safely and efficiently.

First, though the decomposition reaction occurs at temperatures above 300^oC, it is extremely slow and therefore impractical for oxygen production. This is remedied by adding a *catalyst*, in this case manganese(IV) oxide, which significantly increases the rate of the reaction, without itself being consumed.

Second, the intense flame used to raise the temperature of the sodium chlorate above 300^oC is produced by a combustion reaction, which *consumes* large quantities of oxygen gas, whereas the purpose of the overall process is to *produce* oxygen gas. While this issue cannot be completely remedied, small amounts of iron metal are mixed in, reacting with some of the oxygen to produce iron oxide and releasing large quantities of energy which helps maintain the mixture above the 300^{o}C decomposition temperature. The oxygen-consuming flame used to initiate the decomposition reaction is replaced by this iron combustion process.

Third, while the desired decomposition reaction predominates, there is another decomposition reaction which produces toxic chlorine gas, oxygen gas and sodium oxide. This is remedied by including small amounts of barium peroxide in the mixture, which reacts with the toxic chlorine gas to produce barium chloride and oxygen gas.

In summary, the “chlorate” or “oxygen” candle used for emergency production of oxygen gas for breathing on submarines consists of a mixture of sodium chlorate, iron, a small amount of barium peroxide, and a fibrous binding material. In practice, each candle burns near 400^{o}C for 45-60 minutes, and produces approximately 115 SCF (standard cubic feet) of oxygen gas at 0.5 psig (pounds per square inch, gauge pressure), which is enough oxygen for about 100 people. The stored candles represent a significant fire hazard since they are self-sustaining in oxygen.

Figure 1. Examples of oxygen candles.

Various candle sizes are manufactured for different applications. While oxygen candles are most commonly used for emergency purposes on submarines, they are also used in spacecraft, refuge shelters in underground mines, and emergency shelters. One manufacturer claims that with a shelf life of 10 years, one oxygen candle produces enough O_2 to keep 15 people alive for 5.7 hours, assuming they are at rest (calculation based on 0.5 L per person per minute).

Use of potassium chlorate. In this experiment, potassium chlorate will be used instead of sodium chlorate. Analogous reactions occur with all of the same complications. The only remedy that will be applied here will be the inclusion of the manganese (IV) oxide catalyst. Since all of the procedures will be carried out in the fume hood, any toxic chlorine gas produced will be safely carried away in the ventilation system.

Potassium chlorate is a strong oxidizing agent and it reacts readily with easily oxidized substances such as oils, rubber, glycerin, and paper towels. These must never be mixed with potassium chlorate. Careless handling or improper disposal could possibly result in an explosion or fire. Consult the MSDS to review important safety and handling information.

PROCEDURE:

Part A: Verifying the Identity of the Gas Product

1. Observe the correct usage of the Bunsen burner, as demonstrated by your instructor. Make any special notes for future reference.
2. Obtain a small, dry test tube and connect the stopper assembly to it (stopper with single glass tube and tubing). Place the end of the tubing into a small plastic basin containing water. Heat the empty test tube for a few seconds, holding the tube with test tube holders. What do you observe right away? What gas is escaping from the tube? After heating, remove the stopper to prevent water from being pulled into the cooling test tube.
3. With a weighing boat, add about 0.3 g of potassium chlorate to a small, dry test tube (use the tube from step 2 when it is cooled). With a spatula, add a small amount of the catalyst manganese (IV) oxide to the tube (about the size of a "pinch of salt" or fraction of the tip of the spatula). Be careful since MnO_2 stains hands and clothing. Though no exact mass of catalyst is required, the mixture should appear *light grey* after gently tapping the test tube to mix the contents uniformly. Add a small, loose layer of glass wool to the top of the tube which will allow gases to escape but keep solids from splattering onto the stopper. Add the stopper assembly.
4. Devise a way to collect the nearly-pure gas product in a gas collecting tube (hint: water displacement). Implement a chemical test to verify that the main collected gas is oxygen gas. Your instructor will provide important safety information regarding this chemical test. As the decomposition reaction occurs, observe the changes to the material upon heating and the rate of gas evolution. Remember that you want to collect the decomposition gas product so make sure the decomposition has started before you collect the gas.

Part B: Quantitative Study of the Decomposition Reaction

1. Fill a 600 mL beaker ½ full with distilled water.
2. Fill the large gas collection bottle about ¾ full with distilled water. With the stopper inserted, the water level should be slightly below the short tube inside the bottle (the long tube will be immersed). Clamp the bottle to a ring stand. Place the long tubing end (not the one with the stopper) into the beaker of water. Do not attach the pinch clamp yet. See Figure 2 for the initial setup.

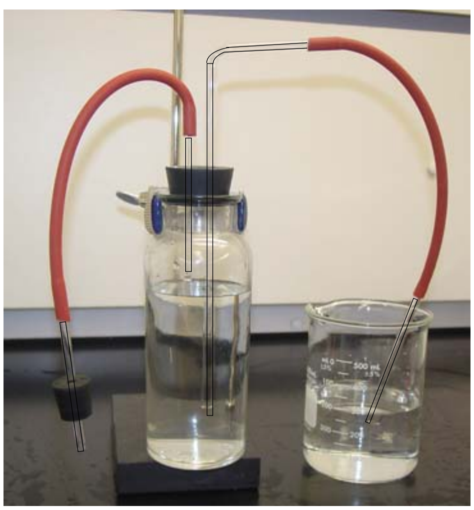
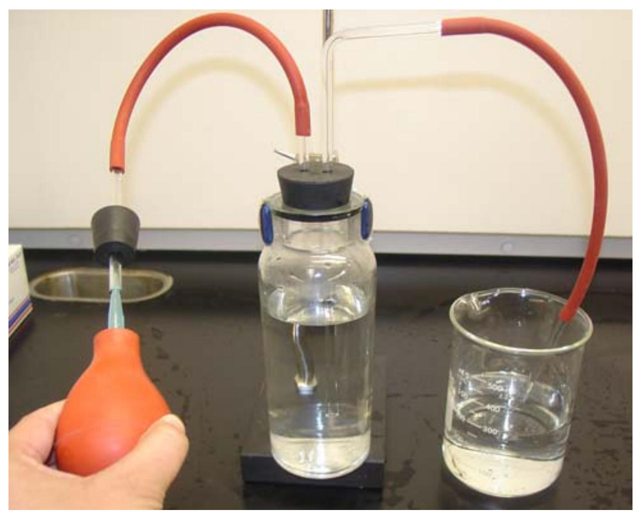


Figure 2. Initial setup.



attach pinch clamp here

Figure 3. Expelling air from exit tubing.

3. With a pipet bulb, slowly blow air into the stopper end of the tubing until the water fills the long glass tube and tubing at the other end (no bubbles left in the exit tube or tubing) making sure the tubing end remains under the beaker water level. Attach the pinch clamp to the tubing as close to the beaker as possible. Make sure the bottle is still more than ½ filled with water. See Figure 3.
4. Obtain your potassium chlorate unknown (mix of $KClO_3$ and an inert material) and record its unknown code.

5. Obtain a large, dry test tube and measure its mass using an analytical balance. To weigh a test tube, use a small beaker to hold it up on the balance. Add 0.3 +/- 0.05 g of your unknown to a weighing boat (using a top-loading balance for this "pre-weight" is fine). Transfer the unknown to your test tube. Use an analytical balance to obtain the mass of the test tube containing the unknown to the nearest 0.0001 g.
6. Add a small amount of MnO_2 to form a light grey uniform mixture after mixing. Add a small, loose layer of glass wool to the test tube.
7. Weigh the test tube and its contents to the nearest 0.0001 g. This will be your mass before heating.
8. Attach the test tube to the stopper end of the tubing using a slight twisting motion to ensure a good seal. Clamp the test tube at the top of the test tube with the tube at about a 30° angle. Make sure all of the solid is at the bottom of the test tube.
9. Check the system for leaks by removing the pinch clamp. Make sure the exit tube stays below the beaker water level. If no water flows, continue; otherwise find out where the leaks are.
10. With the pinch clamp off and the exit tube under the beaker water level, equalize the pressure inside the bottle to atmospheric pressure by raising or lowering the beaker until the water levels in the beaker and bottle are the same. Once level, attach the pinch clamp to the tubing closest to the beaker. See Figure 4. Why is this equalizing step necessary? Relate this to an open-end manometer.

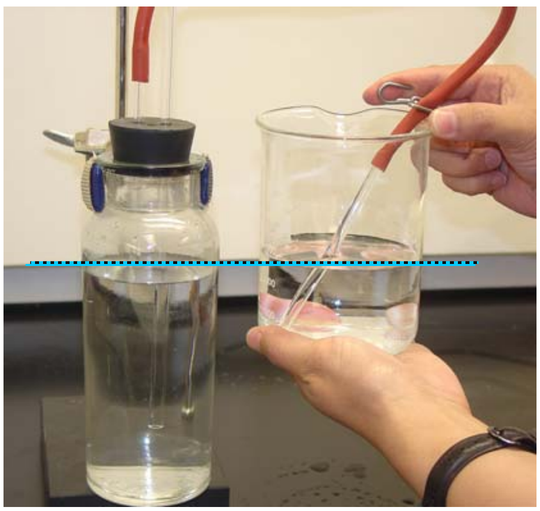


Figure 4. Equalizing pressure.

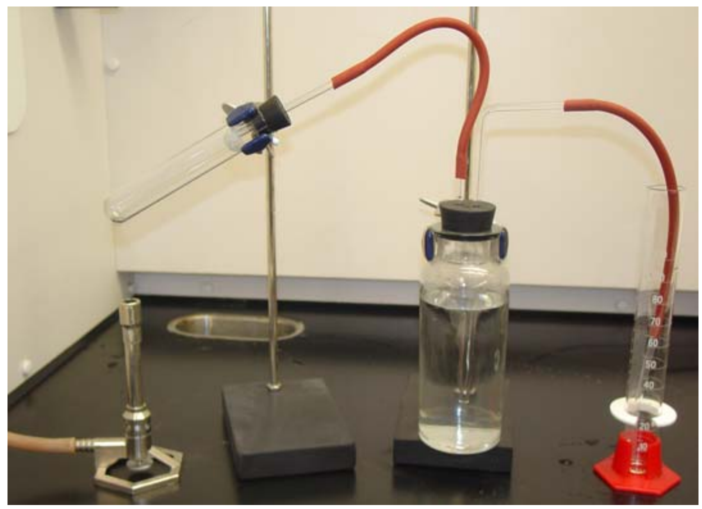


Figure 5. Setup before heating.

11. Without draining the water from the end of the exit tube, carefully replace the beaker with an empty 100 mL graduated cylinder while removing the pinch clamp. If some water from the tube drains into the graduated cylinder that is fine as long as there isn't a continuous flow. Make sure the exit tube is down inside the graduated cylinder. Your setup should look like Figure 5. Have your instructor check your setup.

12. With a Bunsen burner, gently heat the test tube contents. Once the solid begins to melt, the reaction will be quite vigorous, so control the heating by continuously moving the flame. Do not apply heat near the clamp or stopper as they will melt. If the reaction is too vigorous, remove the flame for a few seconds. You should see the liquid level in the graduated cylinder increase as gas is produced and water displaced. Once the bubbling has subsided, apply high heat to the test tube for 8-10 minutes to ensure the decomposition is complete and no more gas is produced. Note that O_2 is still produced at a slower rate even when the bubbling has stopped as evidenced by the water level rising.

13. Allow the test tube to cool leaving the apparatus alone (no pinch clamp, tubing left inside the graduated cylinder under the water level). This should require 8-10 minutes to completely reach room temperature. Do you notice that the liquid level in the graduated cylinder changes upon cooling? Why?

14. Obtain the barometric pressure in the room.

15. When the test tube is cool, slowly raise or lower the graduated cylinder (keeping the tubing under water) until the water levels in the cylinder and bottle are equal. If needed, you may have to raise the bottle instead by carefully lifting the ring stand assembly. Once the levels are equal, clamp the tubing with the pinch clamp. The mixture of gases in the bottle and test tube are now at the room's atmospheric pressure.

16. Carefully remove the tubing from the graduated cylinder so that the water inside the tube does not drain out. Determine the water level in the graduated cylinder, reporting the value with the correct number of significant figures. Measure the temperature of the water. At this temperature, obtain the vapor pressure of water from a reference.

17. Carefully remove the test tube from the clamp and weigh it on the analytical balance.

18. Before leaving lab, make sure you have recorded all the necessary experimental information to answer the questions in the Data Analysis section. Show your data to your instructor.

19. If time permits or as directed by your instructor, perform a second trial or start your data analysis.

Clean Up:

1. Disassemble the gas collection apparatus, draining all glassware and tubing.
2. Place all used test tubes, including their contents, in the designated solid waste container in the laboratory. Any extra or unreacted $KClO_3$ must be disposed in the designated waste container, not in the trash can.
3. Return all glassware and equipment to the bins or drawers where they were originally obtained.

Data Analysis:

1. Based on your experimental data, determine the mass % of $KClO_3$ in your unknown sample.
2. Based on your experimental data (i.e., volume and mass of gas produced, etc.), determine if the collected gas product obeys the ideal gas law by determining the value for the ideal gas constant, R. You will not need to use your mass % $KClO_3$ value from step #1. Compare your experimental value of R with the theoretical value by calculating the % difference. Does the gas behave ideally?
3. Other than human error, what errors could affect your %$KClO_3$ and R values?

Questions for Consideration:

1. a. Ignoring any side reactions and assuming the reaction occurs completely, how large (in kg) an oxygen candle ($KClO_3$) would be needed to supply 8 people with enough oxygen for 24 hours on a small submarine? Although this depends on the size of the person and their respiration rate (activity), according to NASA[1], an average person needs about 0.84 kg of O_2 per day.

   b. How much air (in liters) contains 0.84 kg of O_2 if air consists of 21% by mass of oxygen, 78% by mass of nitrogen, and other minor gas components. Assume 760 mm Hg and 25°C conditions. Convert your answer from liters to cubic feet (cf) and compare it to the capacity of a basketball (~2.1 cf).

2. Assuming all of the analogous reactions occur, why would lithium chlorate be a more practical choice for the "chlorate candle" than either sodium or potassium chlorate?

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[1]Wieland, P.O., Designing for Human Presence in Space: An Introduction to Environment Control and Life Support Systems, NASA Reference Publication 1324, 1994, pp. 6, 183-262.

3. a. Explain why it is necessary to expel air from the glass tube and exit tubing in step 3 of Part B?

   b. If the water levels in the bottle and graduated cylinder were not equalized in step 15 of Part B, say for example the level in the bottle was much higher than in the graduated cylinder, how would this affect the calculated value of R?

4. During an emergency on a submarine, in addition to providing oxygen for the crew, what other safety measures must be taken in terms of maintaining the submarine atmosphere?

5. Starting with 100.0 g of potassium chlorate, and assuming that 95% decomposes into potassium chloride/oxygen and 5% decomposes into potassium oxide/chlorine/oxygen, how many grams of residue would remain after complete reaction? If the investigator had assumed that only the potassium chloride/oxygen reaction was taking place, what would he find for a mole ratio of oxygen gas: potassium chlorate?

6. In practice, rather than using a Bunsen burner to maintain the heat needed for this reaction, a small amount of iron metal is introduced into the mixture. Write the balanced reaction with oxygen, if iron(II) oxide is the product. Explain why this reaction is only useful if it produces large quantities of energy.

7. When used for producing oxygen, the small percentage of decomposition which follows a second pathway produces hazardous chemicals. In practice, small amounts of barium peroxide are introduced to react with these products, as described in the Discussion section above. Balance this reaction.

8. What would have been the expected mass of residue if the potassium chlorate reaction produced potassium hypochlorite instead of potassium chloride, assuming no alternate decomposition pathways? Determine the oxygen to potassium chlorate mole ratio for this scenario.

9. Will a 50.00 mL gas collection tube be large enough to hold all of the Cl_2 gas generated from 4.91 g of HCl, in aqueous solution, which reacts with an excess of $KMnO_4$ according to the following equation? The system is maintained at 44.0°C and 778 mm Hg. The vapor pressure of water at 44°C is 61.9 torr. Support your answer.

$$2\,KMnO_4\,(s) + 16\,HCl\,(aq) \rightarrow 8\,H_2O\,(l) + 2\,KCl\,(aq) + 2\,MnCl_2\,(aq) + 5\,Cl_2\,(g)$$

Name ______________________________ Section ___________________________

PRE-LAB QUESTIONS
Experiment 9B

Complete these questions <u>before</u> lab.

1. Write out the balanced reaction for the decomposition of potassium chlorate solid. One of the products is a gas and the other is potassium chloride solid.

   How is this type of reaction utilized on Navy submarines?

2. Find the MSDS for potassium chlorate. Determine if there are any health hazards and what conditions produce these hazards. Under what conditions does it produce fire or explosion hazards? What are the measures that should be taken to assure safe handling? Since this experiment involves high temperatures, what are the melting point and decomposition temperatures for potassium chlorate? Based on these values, what will you see happening to the potassium chlorate solid as you begin heating it to high temperatures?

3. What is the purpose of MnO_2 in this experiment?

4. If 0.500 g of $KClO_3$ is heated to complete decomposition and the gas is collected <u>over water</u>, how many milliliters of oxygen gas will be produced at 22.0°C and 765.00 mm Hg atmospheric pressure. The vapor pressure of water at 22.0°C is 19.83 torr.

5. An open-end manometer is used for measuring pressure in a gas-filled bulb. What is the pressure (in torr) inside a bulb of gas connected to a mercury-filled, open-end manometer when the level in the arm connected to the bulb is 122 mm lower than the level in the arm open to the atmosphere. The atmospheric pressure outside the apparatus is 754 torr. The principles of a manometer and equalizing pressure will be applied in this experiment.