9/5/18

THE DECOMPOSITION OF POTASSIUM CHLORATE

MATERIALS: Two test tubes: (18x150), clamp, ring stand, Bunsen burner, weighing boat, glass wool, pure $KClO_3$, unknown mixture containing $KClO_3$ and inert substance, MnO_2

PURPOSE: The purpose of this experiment is to study the decomposition of potassium chlorate by quantitatively determining the correct stoichiometry, and to use that result to assess the purity of an unknown potassium chlorate mixture.

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

1. Explain the relationship between the mass of a substance and the number of moles of a substance.
2. Apply stoichiometric ratios between the moles of reactant(s) and product(s) in balanced chemical equations.
3. Calculate the percent by mass of a compound in a mixture.
4. Explain the purpose of a catalyst.

DISCUSSION:

Stoichiometry. Chemistry is making and breaking bonds. Because no atoms are created or destroyed, only the connecting bonds change in a chemical reaction. As such, it is imperative to know the correct formulas for all reactants and products involved in the reaction, as well as the relative molar amounts of each. Nature constrains us to having the same number and type of atoms before and after the reaction, a balanced chemical equation, but how do we know how the atoms are arranged—what compounds are the reactants and products? Where does *that* information come from? The answer is that reactions are determined by experiment.

Care and thought in measurements are fundamental to science, and mass measurements and physical and/or chemical tests allow one to deduce the proper reaction. Only when it is realized that better measurements make a reaction understood, can one start to consider useful applications of the reaction. Consider the title reaction, the thermal decomposition of potassium chlorate. When $KClO_3$ is heated strongly, it breaks down, releasing oxygen gas and leaving behind a thermally stable (i.e., heat-insensitive) solid residue of an ionic potassium compound.

$$\text{solid potassium chlorate} \rightarrow \text{oxygen gas + solid residue}$$

There are at least three plausible reactions one can write for the process, but only one occurs to any significant extent. Which one of the three is actually observed can only be determined by experiments, such as those conducted here. By measuring the amount of oxygen lost when a sample of potassium chlorate is heated, we will be able to determine the stoichiometric coefficients of $KClO_3$ and O_2 in the reaction, and thus determine the correct reaction.

Relevant Naval Application. On submarines, oxygen for breathing is normally produced by the electrical decomposition of an aqueous solution. Details relating to this electrolysis process will be studied later in the course. In case of problems with the electrolytic oxygen generators, a secondary supply source is also available to produce oxygen gas for breathing. This is a chemical process, directly analogous to your experiment: the decomposition of sodium chlorate ($NaClO_3$) at high temperature (above 300ºC) in a canister called a "chlorate candle. Unfortunately, there are a few complications associated with this reaction which must be remedied if the production of oxygen gas for breathing is to be performed safely and efficiently in this practical application.

First, the intense flame used to raise the temperature of the sodium chlorate above 300ºC is produced by a combustion reaction, which *consumes* 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 300ºC decomposition temperature. After the candle is ignited, the oxygen-consuming flame used to initiate the decomposition reaction is replaced by this iron combustion process, making it more self-sustaining.

Second, though the decomposition reaction occurs at temperatures above 300ºC, the direct reaction is still extremely slow and therefore impractical for oxygen production in bulk. This is remedied by adding a *catalyst*, in this case a small amount of manganese(IV) oxide, MnO_2, which significantly increases the rate of the reaction, without itself being consumed.

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 (BaO_2) 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 in production of oxygen gas for breathing on submarines consists of a mixture of $NaClO_3$, MnO_2, iron, a small amount of BaO_2, and a fibrous binding material. In practice, each candle burns near 400ºC 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. As you might suspect, since they are self-sustaining in oxygen, the stored candles represent a significant fire hazard.

Figure 1. Examples of chlorate (oxygen) candles.

Various candle sizes are manufactured for different applications. While oxygen candles are most commonly used for back-up purposes on submarines, they are also used in spacecraft, refuge shelters in underground mines, and emergency shelters. One manufacturer claims that 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). It has a shelf life of 10 years, so long-term storage for emergency use is practical.

Use of potassium chlorate. In this experiment, potassium chlorate will be used instead of the sodium chlorate employed commercially (see Figure 1). As you should suspect, 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. Why is $NaClO_3$ used commercially, rather than $KClO_3$? The principal reason is cost; sodium salts are typically much less expensive than their potassium counterparts. Also, because of the lower molar mass, there is a slightly higher mass percentage of oxygen in the sodium compound than there is in the potassium compound.

Energetics. As should be clear from the discussion of the Navy's chlorate candles, practical applications almost always have to consider energy changes associated with reactions. Most chemical and physical processes are accompanied by changes in energy – some release energy as they proceed, and some require an input of energy in order to sustain the process. We will examine some elementary concepts of energy changes associated with the reactions observed over the course of the semester.

Safety Data Sheets and International Chemical Safety Cards. Any institution where chemicals are used is required to have copies of the Safety Data Sheets, SDS, (formerly material safety data sheets, MSDS) available for inspection by anyone using those materials. 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 SDS for potassium chlorate will be used to help guide the experimental study of its decomposition reactions.
(See https://beta-static.fishersci.com/content/dam/fishersci/en_US/documents/programs/education/regulatory-documents/sds/chemicals/chemicals-p/S25482.pdf .)
In general, prior to any chemical procedure, the relevant SDS 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 material SDS and Safety Cards are available on-line through links found on the Chemical Safety Information page of the Plebe Chemistry website, https://www.usna.edu/ChemDept/plebeChem/safety.php.

PROCEDURE:

Part A: Determination of the Stoichiometry of the Decomposition Reaction of Potassium Chlorate

1. Add a small amount of manganese(IV) oxide (about half as large as a pea) to a clean, dry test tube and determine the mass of the tube and manganese(IV) oxide on an *analytical* balance. Record this mass, using the proper number of significant figures and units, in the Data Section.

2. Use the *top-loading balance* to pre-weigh about 1.5 g of pure potassium chlorate into a plastic weighing boat. It is <u>not</u> necessary to record this mass yet. If any clumps of potassium chloride are present, break them up with a spatula, and then add the potassium chlorate to the test tube containing the MnO_2. **Be careful not to introduce any foreign material into the bottles of potassium chlorate since explosive mixtures could be produced.**

3. Determine the mass of the test tube and its contents on the same analytical balance used initially (in step A.1) and record the mass in the Data Section.

4. Carefully tap the test tube against your hand to mix the contents to obtain a uniformly gray mixture. Do NOT insert any stirring devices to avoid removing material and changing the mass! Tapping the test tube should also knock down to the bottom any materials which may be adhering to the upper inside walls.

5. Place a *<u>loose</u>* plug of glass wool in the mouth of the test tube. This will allow oxygen to escape but prevent any solid from spilling out of the tube. Determine the total mass of the tube and its contents (including glass wool) on the same analytical balance used previously and record the mass in the Data Section.

6. Clamp the test tube to a ring stand at a <u>slight</u> angle as shown in Figure 2. Be sure that the clamp does not have plastic sleeves as these will burn during the experiment. Place the clamp near the open end of the test tube so that the clamp will not melt while the test tube is being heated. (Don't squeeze the clamp too tightly as you may crack the tube.) Be sure the open end of the test tube is not pointed toward anyone or toward the lab aisles.

7. **Carefully observe what happens as you heat the sample.** Heat the tube gently at first since oxygen is driven off quickly as the decomposition of the potassium chlorate begins. Move the flame from the burner back-and-forth to achieve uniform heating of the sample. The inner cone of the flame is the hottest part, so to increase the rate of heating, move that part of the flame closer and closer to the test tube as you continue to move the flame back-and-forth. Continue for an additional three or four minutes. (Note – keep the flame position moving! Strongly heating one spot can melt the test tube and/or decompose the MnO_2.)

8. <u>Allow the tube to cool</u> to room temperature. Holding your hand **around** the test tube is a safe way of checking its temperature without burning your fingerprints onto the side of the glass. Determine the mass of the cooled tube and its total contents, including the residue and the glass wool, on the same analytical balance used previously. Record the mass in the Data Section. *While the tube is cooling,* answer the following in-lab questions:

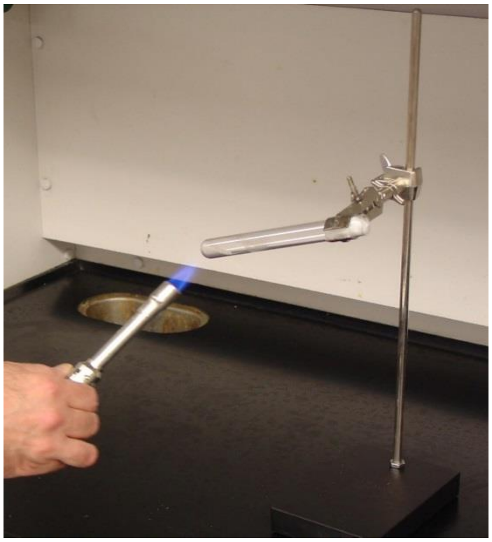

Figure 2. Experimental set-up.

✍ **Answer Questions #1 - #3 on page E4E-5.**

9. If time permits, heat the same sample a second time and record its mass when cooled.

Part B: Determination of the Percent by Mass of Potassium Chlorate in an Unknown Mixture

1. From your instructor, obtain an unknown sample containing a mixture of potassium chlorate and an inert substance. **Record the unknown number in the space provided in the Data Section.**

2. Repeat the procedure outlined in Part A, using approximately 1.5 g of your assigned unknown in place of the pure potassium chlorate. Record all masses, using the proper number of significant figures and units, in the Data Section.

Clean Up:

1. Place all used test tubes, including their contents, in the **<u>designated solid waste container</u>** in the laboratory, NOT in the broken glass box.

Name____ Section ________________

Partner _______________________________________ Date __________________

DATA SECTION
Experiment 4E

Part A: Determination of the Stoichiometry of the Decomposition Reaction of Potassium Chlorate

Mass of tube + MnO_2 ________________

Mass of tube + MnO_2 + $KClO_3$ ________________

Mass of $KClO_3$ ________________

All recorded mass measurements made on analytical balances – record to 4 decimal places!

Mass of tube and total contents (including glass wool)

Before heating ________________

After heating ________________ ________________*

Mass of oxygen gas evolved ________________ ________________*

Part B: Determination of the Percent by Mass of Potassium Chlorate in an Unknown Mixture

Unknown number ___________

Mass of tube + MnO_2 ________________

Mass of tube + MnO_2 + unknown ________________

Mass of unknown ________________

All recorded mass measurements made on analytical balances – record to 4 decimal places!

Mass of tube and total contents (including glass wool)

Before heating ________________

After heating ________________ ________________*

Mass of oxygen gas evolved ________________ ________________*

* If time permits, heat the sample a second time.

Name ______________________________________ Section _____________

Date _______________

✍ IN-LAB QUESTIONS ✍
Experiment 4E

Complete these questions during lab.

1. a. Record your observations as the mixture is heated.

   b. How do you know when the decomposition of potassium chlorate is near completion?

2. a. What is the purpose of MnO_2 in this experiment?

   b. Why doesn't the MnO_2 affect the stoichiometry of the reaction?

3. Why do you think it would be advisable to heat the sample a second time?

DATA TREATMENT
Experiment 4E

Part A. Determination of the Stoichiometry of the Decomposition Reaction of Potassium Chlorate

In this section the balanced chemical equation for the decomposition of potassium chlorate will be determined. From the mass information recorded in the Data Section, you will calculate the number of moles of potassium chlorate present in the test tube before heating (question A.1) and the moles of oxygen gas generated (question A.2). After these two calculations, determine the stoichiometric ratio between potassium chlorate and oxygen gas (A.3) and generate the correct balanced chemical equation (A.4). This equation should also include the chemical formula for the solid material left in the test tube after heating. *Show all work*.

(A.1) From the mass of potassium chlorate used, calculate the number of moles of potassium chlorate that decomposed.

(A.2) From your mass loss data, calculate the number of moles of oxygen gas (O_2) evolved.

(A.3) Based on your answers above, calculate the numerical value of the following mole ratio (your instructor may ask you to record your ratio on the board):

$$\frac{moles\ O_2\ produced}{moles\ KClO_3\ decomposed} =$$

(A.4) Balance the three reactions below, as done in the Pre-Lab, and show the ratio moles O_2/moles $KClO_3$ for each reaction.

$$\frac{moles\ O_2\ produced}{moles\ KClO_3\ decomposed} =$$

a. ___ $KClO_3(s)$ → ___ $KClO_2(s)$ + _____ $O_2(g)$ _______

b. ___ $KClO_3(s)$ → ___ $KClO(s)$ + _____ $O_2(g)$ _______

c. ___ $KClO_3(s)$ → ___ $KCl(s)$ + _____ $O_2(g)$ _______

(A.5) Which of the three reactions best fits your experimental data? Explain your answer below.

Part B. Determination of the Percent by Mass of Potassium Chlorate in an Unknown Mixture

Having determined the balanced chemical equation for the decomposition of potassium chlorate (from page E4E-6), it is now possible to determine the percent by mass of potassium chlorate in an unknown mixture containing $KClO_3$ and an inert ingredient. As before, heating the sample will cause the decomposition to occur and oxygen gas will be produced. By calculating the number of moles of oxygen produced (B.1), the moles and mass of potassium chlorate originally present in the unknown sample (B.2) can be determined. From that the mass percent potassium chlorate in the unknown can be obtained (B.3). *Show your work*.

(B.1) From your mass loss data, calculate the number of moles of O_2 evolved when the unknown was heated.

(B.2) Using the correct stoichiometric equation, calculate the mass of potassium chlorate that must have been decomposed to provide the O_2 loss observed for the unknown. (Use the correct stoichiometry of the reaction identified in question (A.4), not you experimental mole ratio.)

(B.3) From your data, calculate the percent by mass of potassium chlorate in the unknown sample. Pay attention to significant figures.

$$mass\ \% = \frac{mass\ KClO_3}{mass\ unknown}\ x\ 100$$

Unknown number: _____________

Percent by mass of $KClO_3$ in unknown: ________________

POST-LAB QUESTIONS:

1. 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.

2. As described in the discussion, commercial chlorate candles contain other ingredients besides $NaClO_3$. Balance the following reactions pertaining to these materials.

    a. Elemental iron reacts with molecular oxygen, forming iron(III) oxide and releasing additional heat.

    b. Barium peroxide (BaO_2) reacts with toxic chlorine gas, forming barium chloride and oxygen gas.

3. If the test tube had not been fully cooled off before weighing, buoyancy effects in the balance tend to make the mass appear lighter than it actually is. In this case, what would be the effect on the calculated experimental mole ratio of oxygen : potassium chlorate? Make a logic train between "mass appears lighter" to your answer. (Too high? Too low? No change?)

4. If experimental errors cause the number of moles of oxygen determined in the data analysis to be about 3% low, what is your calculated stoichiometry of potassium chlorate to oxygen? Will this cause an incorrect chemical equation for the decomposition reaction be obtained? Why or why not?

[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.

Name ______________________________ Section ___________________________

PRE-LAB QUESTIONS
Experiment 4E

1. Select which statements(s) are true, according to the Safety Data Sheet for potassium chlorate, sections 8-11. (https://beta-static.fishersci.com/content/dam/fishersci/en_US/documents/programs/education/regulatory-documents/sds/chemicals/chemicals-p/S25482.pdf)

   a) Neither respiratory protection nor eye protection are required under normal conditions of use.
   b) $KClO_3$ is a liquid at room temperature and 1 atm.
   c) $KClO_3$ is an Oxidizer, so contact with combustible/organic material may cause fire.
   d) Oral toxicity (in terms of the LD50 Rat) is well above 500 mg/kg.

2. Since this experiment involves high temperatures, what are the melting point and decomposition temperature (both in ºC) for potassium chlorate?

   Melting Temperature: _________

   Decomposition Temperature: __________

*NOTE: Some SDSs list the decomposition temperature as the "boiling" temperature.

3. Based on the values in problem 2, what will you see happening to the potassium chlorate solid as you heat it to high temperatures?

   a) the potassium chlorate will decompose before it melts
   b) the potassium chlorate will melt before it begins to decompose
   c) the potassium chlorate will melt and decompose simultaneously

4. Following are three possible reactions that could occur when a sample of $KClO_3$ (s) is decomposed. One goal of this lab is to determine the correct one. Balance all three reactions. (Use the lowest possible integer coefficients.)

   a) ___ $KClO_3(s)$ → ___ $KClO_2(s)$ + ___ $O_2(g)$

   b) ___ $KClO_3(s)$ → ___ $KClO(s)$ + ___ $O_2(g)$

   c) ___ $KClO_3(s)$ → ___ $KCl(s)$ + ___ $O_2(g)$

Copy your results to question A.4 on p. E4E-6 as you will need them during lab.

5. Using the correct stoichiometric coefficients from the balanced equations in question 4, write the numerical (decimal) values of the ratio $\frac{\text{moles } O_2 \text{ produced}}{\text{moles } KClO_3 \text{ decomposed}}$ for each reaction:

   Reaction 4(a) ______

   Reaction 4(b)_ ______

   Reaction 4(c) ______

6. $NaClO_3$ is used on Navy submarines for what purpose? (NOTE: The chemistry of $NaClO_3$ is very similar to that of $KClO_3$. However, $NaClO_3$ has the advantage in that it is less expensive than $KClO_3$).

   a) $NaClO_3$ candles are an emergency source of light
   b) $NaClO_3$ is used as a source of oxygen for emergency situations
   c) $NaClO_3$ is added to paint to prevent corrosion
   d) $NaClO_3$ is used as a food additive.