Synthesis and Crystallization of Alum, $KAl(SO_4)_2 \cdot 12H_2O$

INTRODUCTION

Alums are a class of “double” sulfates (salts containing the SO_4^{2-} anion) in which one cation is monovalent and the second cation is trivalent. Th e general chemical formula of an alum is **M(I)T(III)**$(SO_4)_2$**·x**H_2O where **M(I)** represents the **M**onovalent cation (most often potassium (K^+), sodium (Na^+□),ammonium (NH_4^+), etc.) and **T(III)** the **T**rivalent one (most often aluminum (Al^{3+}), but also Iron (Fe^{3+}), Chromium (Cr^{3+}), etc.) and x, the number of moles of water of crystallization is usually equal to 12. Th e most common form of alum is potassium aluminum sulfate, called potassium aluminum alum or just plain alum, $KAl(SO_4)_2.12\ H_2O$. Th e full chemical name of this substance is **potassium aluminum sulfate dodecahydrate**.
Th is material occurs naturally as the mineral called alum.
Aluminum is the third most abundant element in the earth’s crust. The metal and its salts are used extensively in everyday chemical processes. Alum has been used by humans for centuries. It is used in industry as a clarifier (in water purification), in the manufacture and application of dyes, in the tanning of leather, in marble and porcelain cements, and medicinally as an astringent (a substance that draws together or constricts tissues) and styptic (to control bleeding).
Alum has found extensive application in the paper industry as a sizing agent (a material that fills the spaces between the paper fibers to control its porosity and to bind other additives). Unfortunately, the acidity of the aqueous Al^{3+} ion makes the paper mildly acidic and, therefore, contributes to its disintegration over the long term. Chemical processes that neutralize this acidity are currently in use in major libraries.
Alum has also played a major role in economic history. The mixed alum of K^+, Al^{3+}, and Fe^{3+} was isolated from its natural deposits during the Roman Empire. Alum itself was prepared commercially in chemically pure form in Turkey in the 13th century and continuously, since 1450, near Rome from a related mineral, alunite (or alumstone). The process was similar to that described in this exercise.

Aluminum is an active metal that dissolves in strong acids and in strong bases. It doesn’t seem like an active metal in everyday use because it forms a tightly bound oxide coat on its surface which protects it from further oxidation. In today’s lab, you will dissolve aluminum in a potassium hydroxide solution:

$$2\ Al\ (s)\ +\ 2\ KOH\ (aq)\ +\ 6\ H_2O\ (l)\ \rightarrow\ 2\ KAl(OH)_4\ (aq)\ +\ 3\ H_2\ (g)$$

The substance $KAl(OH)_4$ consists of a K^+ ion and the aluminate ion, $Al(OH)_4^-$. The four hydroxides in the aluminate ion are arranged around the Al with tetrahedral geometry, pointed towards the corners of a four-sided pyramid.

You will react the potassium aluminate with sulfuric acid:

$$KAl(OH)_4\ (aq) + 2\ H_2SO_4\ (aq) \rightarrow KAl(SO_4)_2\ (aq) + 4\ H_2O\ (l)$$

The acidic hydrogens in the sulfuric acid form water as they strip off and react with the OH^- ions bound to the aluminum in the aluminate ion. The Al^{3+} ion, now free of the OH^- ions, becomes surrounded by 6 water molecules, arranged around the aluminum ion lwith octahedral geometry ike an xyz set of graph axis. Potassium ions are also surrounded by 6 water molecules.

As the potassium aluminum sulfate solution cools, crystals of $KAl(SO_4)_2 \cdot 12H_2O$ form. The "$\cdot 12H_2O$" in the formula indicates that these 12 water molecules are intimately bonded in the crystal. The raised dot before the water formula is used to show that this is a hydrate, that is, a crystal that has water molecules as an integral part of the crystal. When calculating molecular masses, the mass of water in a hydrate must be included.

$KAl(SO_4)_2 \cdot 12H_2O$ is one of many compounds classified as alums. A mono-positive ion and a tri-positive ion bound to 2 sulfate ions, with 12 water molecules of hydration, identify the alums. The mono-positive ion is usually in group 1 of the periodic table, and the tri-positive ion is usually aluminum, gallium, indium, vanadium, chromium, iron or cobalt. The aluminum family alums are colorless, while the transition metal alums are colored.

You will use an aluminum can as the source of aluminum. This is not recycling, since the major cost in producing aluminum is the cost of the electricity needed to get aluminum from its ionic state into its metallic state. Rather, you will use the can, which usually hold a nice cool drink, to make really cool crystals of alum.

Name ___________________________________ **Date** _______ **Grade** ____

PRE-LAB QUESTIONS

MUST be completed before an experiment is started. The COPY pages will be collected as you enter the lab.

Please answer the following questions and show all work and units. Express all answers to the correct number of significant digits.

Q1. Based on the general formula of an alum, give formulas for three alums.

Q2. Aluminum hydroxide, $Al(OH)_3$, is amphoteric. What steps in the synthesis confirm this property?

Q3. If 25 students perform this experiment in a laboratory, and each student begins with 3.00 g of aluminum,

a. How many moles of H_2 gas are produced by each student?

b. What volume of H_2 gas is produced by each student at STP?

c. What total volume of H_2 gas is produced in the laboratory?

d. If the laboratory dimensions are 12 m x 10 m x 4 m, what is the volume of the laboratory in liters? (1 m3 = 1,000 L)

e. A concentration of more than 10 volume percent of H_2 gas in air is explosive when ignited. Is it safe for all 25 students to carry out the dissolution of aluminum at the same time? Would it be safe if each student used 1.00 kg?

Q4. If the starting weight of aluminum in grams is the sum of the last three numbers in your student ID divided by 10,

a. what is the theoretical yield of alum in grams from this starting weight?

Starting weight __________

Theoretical yield __________

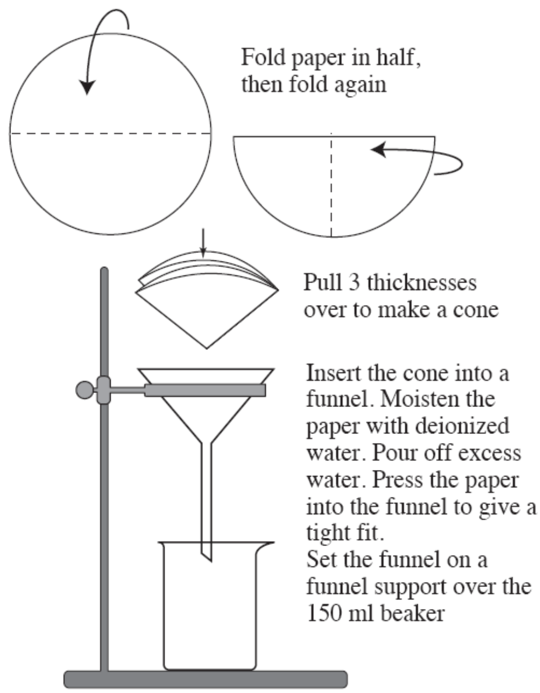
b. what is the minimum volume of 1.5 M KOH that will be required to dissolve this weight of aluminum?

Q5. Potassium salts are much more expensive than ammonium salts. Ammonium aluminum alum can often be used interchangeably with potassium aluminum alum. What is the maximum weight of ammonium aluminum alum that can be made from 2.20 g of aluminum?

Q6. Aluminum foil includes a small amount of iron. Suppose we choose to dissolve the aluminum in acid instead of base as the first step of synthesis. Describe the steps of this synthesis. Can you suggest any advantages or disadvantages to this synthetic pathway?

EXPERIMENTAL PROCEDURE

CAUTION: Be careful with the use of 1.4 M KOH. and 9 M H_2SO_4 solutions.
1) Prepare the aluminum sample: Set the aluminum on a piece of scrap paper, and clean off the painted surface by vigorously rubbing with sand paper. The inside of the aluminum can is painted with a clear varnish, so scour it as well. Cut any still-painted edges off, as it is hard to clean around the edges. Rinse and dry the cleaned aluminum. Make many parallel cuts along one edge (like making a hula skirt from construction paper), and then cut it into tiny confetti-sized pieces (2 mm square) onto some dry paper towel. Zero out a sheet of weighing paper on a balance, and weigh between 0.4 and 0.6 grams of the aluminum. Record the weight.
2) Set up a gravity filtering apparatus as shown below. Make sure you are using the large piece of filter paper.



3) Mark your initials in the white square on a 150-ml beaker and transfer the aluminum into it. In the hood, add 25 ml of 1.4 M KOH and place the beaker on the hot plate at low setting. Stir occasionally. Make sure you know which beaker is yours, and be careful of other student's beakers when you stir yours. No more than 3 or 4 beakers should be on any one hotplate. The aluminum will fizz as hydrogen gas is given off. The solution will turn dark from bits of paint and alloying elements in the aluminum can. All of the aluminum should dissolve in 10 to 20 minutes.
4) Use a beaker tongs to bring the beaker onto a fiberglass pad in the hood. SLOWLY and CAREFULLY add 10 ml of 9 M H_2SO_4 to the contents of the beaker. Heat is given off to cause the solution to boil up as you add the acid. Be prepared for this; take time and care in pouring small portions of acid in the beaker. Stir the mix, grasp the beaker with the beaker tongs, and carefully navigate back to your lab work area. Moisten the filter paper on the funnel with the solution. Pour the hot solution into the filter paper in the funnel. The volume is such that it should comfortably fit, but make sure that you don't overfill the funnel. The filtrate exiting the funnel should be clear and colorless. Transfer the

filtrate into a clean and dry 50-mL beaker.

5) While the filtration is finishing, fill one third of a 400-ml beaker with ice. Add water to just under the ice level. Set the beaker with the filtrate into the ice-bath. Stir the filtrate occasionally. Be careful that you don’t get water from the ice bath into the beaker with the filtrate. You should see the solution turn cloudy in a few minutes. Stir a few times a minute. When the filtrate is milky white and ice cold, you are ready for a second pressure-assisted filtration using a Büchner funnel.

6) Place the smaller piece of filter paper into the Büchner funnel. Moisten it with deionized water, pouring off excess water. Firmly insert the funnel into the filter flask. Turn on the water, connect the flask, and make sure that the water aspirator is drawing a vacuum. Stir the contents of the beaker thoroughly, and then quickly pour the entire contents into the Büchner funnel. You should see water running out into the filtering flask. When all of the liquid has run into the flask, the funnel should have a nice fine white residue in it. Pour 5 mL of methanol into the funnel. After it has filtered through, repeat with another 5 mL of methanol. These rinsings remove excess water and sulfuric acid from the crystals. Keep the aspirator going for 5 to 10 minutes, while you clean up your area. The air forced through the funnel will evaporate methanol from the crystals.

7) Meanwhile, turn up the setting on the hotplate to 6. After 5 to 10 minutes, unplug the filter flask from the water aspirator, turn off the water, and remove the top portion of the funnel. Weigh a clean and dry 50-ml beaker and record the weight. Slam the top portion of the funnel face down onto this beaker to release the solid from the funnel. Spread the powdery crystals in the beaker to dry for 10 minutes.

Dispose of the liquid in the filtering flask into the waste container.

8) After the 10 minute drying time, weigh and record the weight of the beaker containing alum. Show these crystals to your instructor, and have the instructor make note of the appearance on the data sheet.

9) Double the rounded weight of the solid, and add (this number plus 2 mL of deionized water to the beaker. For example, if the solid weighed 5.755 g, then 6 times 2 gives 12, plus 2 is 14, so add 14 ml of deionized water. Place the beaker on the hotplate (set to 6), and stir occasionally until the liquid is nearly boiling and all the solid has completely dissolved. Place the beaker of solution inside a larger beaker and cover the secondary beaker with a watch glass. Store the assembly in your lab drawer until next lab session. Crystallization should occur over the next day or two.

10) In the next lab session, pour the liquid (called the mother liquor) off of the crystals, pat them dry with paper towel, and weigh the crystals. Give these crystals to your instructor.

Clean-Up. Clean all glassware that was used before leaving the laboratory. Place all waste solutions/precipitates into proper waste containers.

Synthesis and Crystallization of Alum

Name ______________________________ Date ________

Partner's Name __________________________

DATA AND CALCULATIONS (show your work)

1) Mass of aluminum used ___________ g

2) Moles of aluminum used ___________ moles
"show your calculations"

3) Moles of $KAl(SO_4)_2 \cdot 12H_2O$ theoretically produced ___________ moles
"show your calculations"

4) Mass of $KAl(SO_4)_2 \cdot 12H_2O$ theoretically possible ___________ g
"show your calculations"

5) Mass of $KAl(SO_4)_2 \cdot 12H_2O$ actually produced ___________ g
(from first crystallization)

6) Instructor comment on crystals: _______________________________________

7) Mass of $KAl(SO_4)_2 \cdot 12H_2O$ actually produced ___________ g
(from second) crystallization)
"show your calculations"

8) Percent yield ___________ %
"show your calculations"

Name ____________________________ **Date** ______ **Grade**_____

Post-Lab Questions and Exercises

(All questions must be answered during the lab and submitted with your lab report at the end of the lab period).

Please answer the following questions and show all work and units. Express all answers to the correct number of significant digits.

Q1. How many moles of KOH are measured in this experiment? See the volume and molarity information given in the section of experimental procedure.

Q2. How many moles of KOH reacted with the amount of Al you used? Refer to the reaction equation in the first few lines of the experiment.

Q3. How many moles of KOH were left over?

Q4. How many moles of H_2SO_4 are measured in this experiment? Again, see the volume and molarity information.

Q5. How many moles of H_2SO_4 reacted with the amount of $KAl(SO_4)_2$ you theoretically produced in the experiment? Refer to the second reaction equation in the experiment.

Q6. Some of the H_2SO_4 reacted with the excess KOH calculated in question 3. The reaction produces potassium sulfate and water. Write the balanced equation, and calculate how many moles of H_2SO_4 are required to react with the excess KOH.

Q7. From the amounts of H2SO4 calculated in questions 4, 5, and 6, how much H_2SO_4 is in excess?

Q8. If you added sodium bicarbonate, $NaHCO_3$, to neutralize the excess H_2SO_4. The reaction produces sodium sulfate, water, and carbon dioxide. Write the balance equation, and calculate how many grams of sodium bicarbonate are required for the neutralization.

Q9. Assuming you have used exactly 50 mL of 1.5 M KOH, 20 mL of 9.0 M H_2SO_4, and your actual weight of aluminum and your final solution contains theoretical yield of alum before crystallization, what other substance(s) is/are in the final solution and at what concentration(s)?

Q10. What factors in this experiment might contribute to an actual yield of less than 100%?