

## Experiment 7

### PREPARATION OF ALUM

#### Objective

The purpose of this experiment is to use recycled aluminum cans to synthesize alum (aluminum potassium sulfate dodecahydrate), including purification through recrystallization, and to prepare chromium-aluminum alum by replacement.

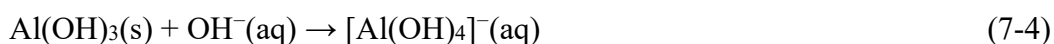
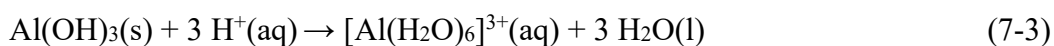
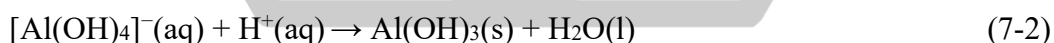
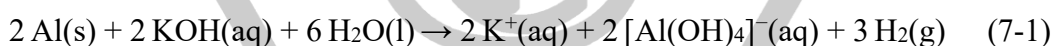
#### Lab techniques

- Operating of suction filtration, gravity filtration, and crystallization
- Weighing chemicals

#### Introduction

##### I. Synthesizing alum

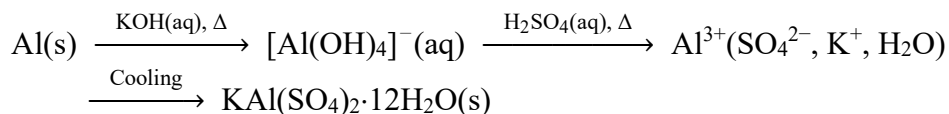
Although aluminum is an active metal, it reacts slowly with dilute acids because a thin layer of aluminum oxide protects its surface. However, alkaline solutions may dissolve the oxide layer and then react quickly with the metal. Aluminum is oxidized by excess alkali to tetrahydroxoaluminate anion,  $[\text{Al}(\text{OH})_4]^-$  (7-1), which is soluble in aqueous solution. When acid is added slowly to the solution containing this complex ion, one of the  $\text{OH}^-$  is removed, then the flocculent white  $\text{Al}(\text{OH})_3$  appears (7-2). While continuous addition of acid, the hydrated aluminum cation,  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ , is formed and the white gelatinous precipitate  $\text{Al}(\text{OH})_3$  is dissolved (7-3). Aluminum hydroxide which may react with acid and base (7-4) simultaneously is said to be amphoteric.



The general formula of alum is  $\text{M}_\text{I}^+\text{M}_\text{II}^{3+}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . It is an ionic compound that can be synthesized from sulfate ions, trivalent cations (such as  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ), and monovalent cations (such as  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ). It crystallizes out of a supersaturated solution and can grow into quite large crystals under appropriate conditions. The crystalline layer contains 12 water molecules, 6 of which are tightly bound to the trivalent cation, and the remaining 6 are weakly bound to the sulfate ion and the monovalent cation.

In the experiment, recycled aluminum cans are used to react with potassium

hydroxide and sulfuric acid in sequence to prepare alum and observe the amphoteric properties of aluminum. The flow chart is shown as follows:

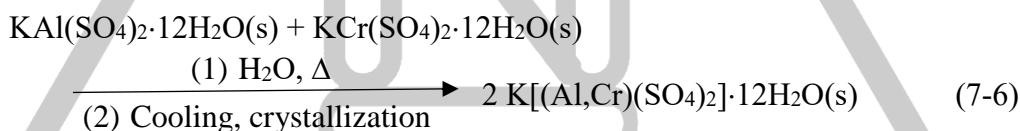


The balanced equation for the crystallization of alum is shown as equation 7-5:



## II. Crystallization of chromium-aluminum alum

In nature, it is almost impossible to find a 100% pure substance. Most substances contain varying degrees of impurities. For instance, in alum, the cations  $\text{K}^+$  or  $\text{Al}^{3+}$  can be replaced by other cations. Chromium(III) ion is one of the cations that can replace  $\text{Al}^{3+}$  easily since  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  have the same electric charge and a similar size. Accordingly, we can use this property to obtain chromium-aluminum alum (7-6).



Chromium is a transition metal, and the splitting energy of its 3d orbitals corresponds to the energy of visible light (refer to experiment 10). Hence chromium alum is colored. By using a small alum crystal as a seed crystal, we will obtain a single crystal out of a supersaturated solution containing chromium(III) ion and alum, and then observe the special color and octahedral structure of this crystal.

### Apparatus

Vacuum filter flask, Büchner funnel, rubber stopper, iron ring, funnel, graduated cylinder (50 mL), beaker (100 and 30 mL), glass rod, Styrofoam bowl (for ice-water bath), filter paper (110 and 55 mm), toothpick, and aluminum soft-drink can (self-prepared).

Shared: electronic balance, suction pump (water-flow type), stirrer/hot plate, scissors, sandpaper (No. 120) or nail grinder, cotton string, and Vaseline.

### Chemicals

1.4 M Potassium hydroxide, KOH






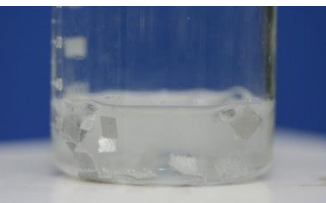
9 M Sulfuric acid,  $\text{H}_2\text{SO}_4$


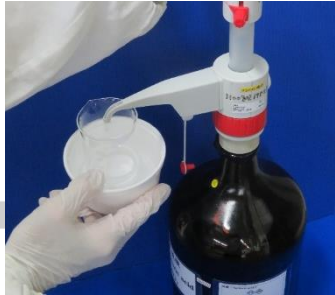

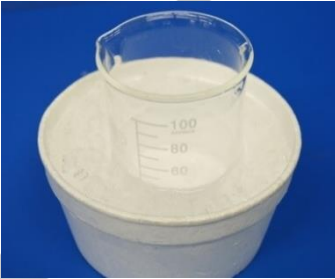

Aluminum potassium sulfate dodecahydrate, alum,  $\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O}$




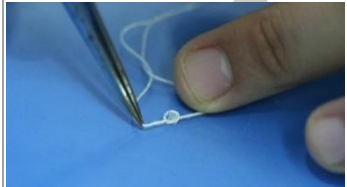

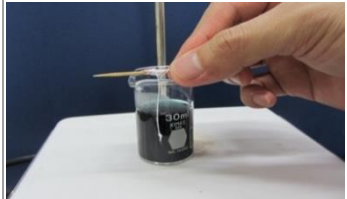
Chromium(III) potassium sulfate dodecahydrate, chrome alum,  $\text{KCr(SO}_4)_2 \cdot 12\text{H}_2\text{O}$

Ethanol/water mixture (1:1, v/v)

## Procedure

Procedure		Illustration
I. Preparation of alum		
1.	Each group brings an empty aluminum can to the laboratory.	
2.	<p>Cut out a piece of aluminum about 5 cm by 5 cm, and scrape off any paint as completely as possible with sandpaper or a nail grinder. Then cut it into smaller pieces.</p> <p><b>Caution:</b> Sharp edges may cut fingers while cutting the aluminum can. Handle these pieces with caution.</p> <p><b>Note:</b> This step can be completed before the laboratory session. It is recommended to wear cotton gloves for this step.</p>	 
3.	Weigh <i>ca.</i> 0.5 g of aluminum pieces. Record its exact weight.	
4.	<p>Place the aluminum pieces into a 100 mL beaker. Add 25 mL of 1.4 M KOH. Gently heat the mixture on a hot plate in a fume hood to speed up the reaction.</p> <p><b>Caution:</b> The reaction produces hydrogen gas, which is flammable. A pungent smell is also produced. Hence this step must be performed in the fume hood. Keep any open flames away from the hood.</p>	
5.	During the reaction, the aluminum pieces will rise and fall periodically in the solution. Suggest and write down an explanation in the lab report. The reaction is complete when the evolution of hydrogen gas ceases.	

6.	<p>Use suction filtration to filter this hot solution to remove any solid residue. Rinse the beaker with 1 mL of DI water and pour it into the Büchner funnel again.</p>	
7.	<p>Transfer the clear filtrate into a 100 mL beaker. Rinse the vacuum filter flask with <i>ca.</i> 1 mL of DI water, and combine it with the filtrate. Cool the beaker in a water bath and add 10 mL of 9 M H<sub>2</sub>SO<sub>4</sub> slowly since the neutralization reaction is exothermic.</p> <p><i>Note: As alum is water soluble; use as little water as possible for rinsing.</i></p>	
8.	<p>After sulfuric acid is added, a white gelatinous precipitate, Al(OH)<sub>3</sub>, will appear. Wipe off the water attached to the outer wall of the beaker. Heat the solution on a hot plate to boil and stir it with a glass rod to dissolve the precipitate.</p> <p><i>Note: The final volume of the solution should be less than 30 mL to ensure supersaturation.</i></p>	
9.	<p>Cool the solution (containing Al<sup>3+</sup>, K<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup>) to room temperature. If no crystals are formed, scrape the inner wall of the beaker with a glass rod to initiate crystallization. Then set the beaker into an ice-water bath to ensure complete crystallization of alum.</p> <p><i>Note: If no crystal forms from the chilled solution, the concentration of alum may be too low to reach supersaturation. Think of a way to solve this problem.</i></p>	
10.	<p>(1) Collect the alum crystals by suction filtration. Use a glass rod to flatten the products on the Büchner funnel. Rinse the remaining crystals in the beaker with <i>ca.</i> 4 mL of cold ethanol/water solution (1:1, v/v) and pour it into the funnel.</p> <p>(2) Allow the crystals to vacuum dry for about 10 min. After the crystals are dried, collect, weigh, and record the accurate weight of the products. Calculate the percent yield.</p>	

	<p>(3) Recycle the alum and aluminum pieces into designated containers.</p> <p>Note: Do not use too much ethanol/water solution to rinse the solid to avoid the dissolution of alum.</p>	
<h2>II. Synthesis of chromium-aluminum alum</h2>		
11.	<p>Refer to Table 7-1 and measure the exact amounts of alum, chrome alum, and DI water in a 100 mL beaker accordingly. Heat and stir the mixture until boiling and all solids dissolve.</p> <p>Note: Raise the heating temperature to boil the solution quickly. The final volume of solution is kept at about 20~25 mL.</p>	
12.	<p>While the solution is still hot, remove any impurities by gravity filtration and collect the filtrate in a 30 mL beaker directly. Then allow the solution to cool.</p> <p>Note: The 30 mL beaker should be washed thoroughly before use.</p>	
13.	<p>(1) Get a piece of cotton string about 10 cm long. Tie one end of the string to a toothpick in a secure knot.</p> <p>(2) Onto the other end, tie securely a moderate-sized alum crystal with a good shape as the crystal seed. Trim away excess string.</p> <p>(3) Coat the string with Vaseline to prevent crystals from growing on it.</p> <p>Note: Do not smudge the crystal seed with Vaseline which may interfere with the crystallization on it.</p>	 
14.	<p>After the Cr-Al alum solution mixture has cooled to room temperature, adjust the length of the string and suspend the crystal seed in the center of the solution (Fig. 7-1). Hand in the beaker to the lab instructor and let it stand for 2~3 weeks. You may get a nice octahedral crystal and keep it as a souvenir.</p> <p>Note: Make sure the solution has cooled sufficiently before positioning the crystal seed.</p>	



15.	Take out the crystal. Observe and record the crystal structure, color, and size.	
16.	<p>(1) Discard the remaining solution containing chromium in the waste container.</p> <p>(2) Collect, and recycle the single crystal remained on the bottom of the 30 mL beaker as crystal seed.</p> <p>(3) Wash the apparatus, clean up your benchtop, and complete the experiment.</p>	

Table 7-1 Formula for growing chromium-aluminum alum crystals

Group	Alum (g)	Chrome alum (g)	DI water (mL)
A	3.5	0	25
B	3.0	0.5	25
C	3.0	1.0	25
D	3.0	2.0	25

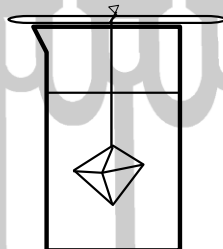


Figure 7-1 Growing a chromium-aluminum alum crystal

## References

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2. Pauling, L. *General Chemistry*; 3rd ed., W. H. Freeman and Co.: New York, 1970; pp 275, 634.
3. Wyckoff, R. W. G. *Crystal Structures*; 2nd ed., John Wiley & Sons Inc.: New York, 1965; pp 872-875.
4. *The Merck Index*; 11th ed., Budavari, S.; O'Neil, M. J.; Smith, A.; Heckelman, P. E., Eds.; Merck & Co., Inc.: New York, 1989; p 342.