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Experiment 3

Solid Solutions with the Alum Structure

William R. Robinson and Brian J. Johnson

Notes for Instructors

Purpose

To grow crystals belonging to a solid solution series, with the variable composition $KAl_xCr_{1-x}(SO_4)_2 \cdot 12H_2O$.

Method

One technique that chemists commonly use to grow single crystals is that of slow solvent diffusion. In this process, the compound of interest is dissolved in a solvent to make a solution. A second liquid (one that is less dense than the first solution, which is miscible with the first solution, and in which the solute compound is insoluble) is carefully layered on top of the solution. As the two liquids mix, the concentration of the second liquid in the solution increases. This increased concentration decreases the solubility of the solute compound, and eventually a solid begins to form. Because the liquids diffuse together slowly, crystallization usually begins at a limited number of sites and crystal growth continues at these sites. Generally speaking, the slower the crystal growth process, the larger and more defect-free the crystals. *See* Chapters 6 and 10.

In this experiment, large crystals of alum–chrome alum solid solutions are produced.

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Materials

Alum, $KAl(SO_4)_2 \cdot 12H_2O$

Chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$

95% ethanol

Beakers

Stirring rods

Filter paper and funnels

13-mm × 150-mm test tubes

Ring stands and test-tube clamps

Disposable pipettes

For optional preparation of alum from an aluminum beverage can,

Aluminum can

1.4 M KOH

6 M H_2SO_4

Open-ended experiments can employ other shapes of containers (to vary the rate of diffusion), other metal salts (such as copper sulfate), potassium sulfate, other chromium salts (such as chromium nitrate or chromium chloride), or other alcohols (such as methanol, propanol, or 2-propanol).

Other Information

If students have difficulty forming two layers without generating a great deal of precipitate, have them try chilling the alcohol or the alum solution, diluting the alum solution slightly, or adding a small layer of water to the test tube (to act as a buffer region) before adding the alcohol.

Generally, the formation of a small amount of precipitate during the layering procedure is unavoidable and will not greatly affect results. The precipitate formed will often sink into the water layer and redissolve.

Likely Results of Open-Ended Experiments

The numbers refer to suggested ideas in the student directions.

1. Generally, the larger the interface between the diffusing solvents, the faster they will mix. Faster mixing will cause the formation of smaller crystals.

2. Unless the ion has the same charge and about the same size as Al^{3+}, a solid solution will not form. Instead, cocrystallization will result and

there will be a mixture of two different types of crystals present. For example, this will happen when copper sulfate is added to alum.

3. A powder will result because of cocrystallization of alum and K_2SO_4.
4. In our hands, addition of $Cr(NO_3)_3$ and $Cr_2(SO_4)_3$ to alum solutions formed crystals that looked like those of Cr-doped alum. On the other hand, addition of $CrCl_3$ formed something that was obviously different.
5. This procedure can work, though care is required.
6. This “seeding” tends to produce larger crystals than if the solution is layered, as there are fewer but better sites for crystal growth to begin.
7. Any alcohol other than ethanol seems to make it very difficult to form two layers without generating a fine precipitate of alum.
8. A dirty beaker may produce smaller crystals, as there will be many sites for crystal growth to begin. The results when tap water is used will depend on the ions present in it.
9. Small crystals will result because of seeding if any solid alum is present.
10. This approach will probably produce large, well-formed crystals that may well be of better quality than those obtained from layering.

Solid Solutions with the Alum Structure

Purpose

To grow crystals belonging to a solid solution series, with the variable composition $KAl_xCr_{1-x}(SO_4)_2 \cdot 12H_2O$.

Introduction

Chemists today use a variety of instrumental techniques to study solids. X-ray diffraction, for example, yields information about the position of atoms and the bond angles in a molecule and is perhaps the most powerful tool for determining the structure of a compound. X-ray studies, electrical conductivity measurements, and many other types of analysis are often done with single crystal samples. In this case, not only must the sample be uncontaminated, but the crystal cannot be a collection of small crystals or crystalline regions (polycrystalline) and it cannot be split or cracked.

Most chemical reactions that result in solid products give powders or polycrystalline materials, rather than single crystals of sufficiently large size. Powders and polycrystalline substances can be converted to single crystals by a variety of techniques. All of these are based on forming or providing a very small number of sites where crystallization begins (nucleation sites), followed by controlled growth at these sites.

One technique that chemists commonly use to grow single crystals is that of slow solvent diffusion. In this process, the compound of interest is dissolved in a solvent to make a solution. A second liquid (a miscible liquid that is less dense than the first solution and in which the solute compound is insoluble) is carefully layered on top of the solution. As the two liquids mix, the concentration of the second liquid in the solution increases. This increased concentration decreases the solubility of the solute compound, and eventually a solid begins to form. Because the liquids diffuse together slowly, crystallization usually begins at a limited number of sites and crystal growth continues at these sites. Generally speaking, the slower the crystal growth process, the larger and more defect-free the crystals.

In this laboratory, you will perform crystallization experiments, as described, and then have a chance to design your own. All of them will be based on growing crystals of alum, $KAl(SO_4)_2 \cdot 12H_2O$. This solid contains potassium ions (K^+), aluminum ions (Al^{3+}), and sulfate ions (SO_4^{2-}). The water molecules are arranged so that six of them are located around each of the cations. Crystals of this compound have long been admired for their beautiful octahedral shape.

NOTE: This experiment was written by William R. Robinson, Department of Chemistry, Purdue University, West Lafayette, IN 47907; and Brian J. Johnson, Department of Chemistry, The College of St. Benedict and St. John's University, St. Joseph, MN 56374.

A related compound is chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$. It has the same formula as alum, except that Al^{3+} has been replaced by Cr^{3+}. Furthermore, the cations, anions, and water molecules are arranged in the same way in crystals of chrome alum as they are in alum. This feature is primarily due to the like charge and similarity in size of the aluminum and chromium ions.

When solutions of alum and chrome alum are mixed, the resulting crystals contain chromium and aluminum ions randomly distributed in the M^{3+} ion positions throughout the alum structure. This means that there is a continuous variation in composition possible for such crystals. By varying the amounts of alum and chrome alum present, the composition can be controlled or continuously tuned and for values of x ranging between 0 and 1, is denoted $KAl_xCr_{1-x}(SO_4)_2 \cdot 12H_2O$. Such a family of related solids is called a *solid solution*. Unlike a physical mixture of alum and chrome alum crystals (in which microscopic examination of the solid would reveal only chunks of pure alum and of pure chrome alum), all solid solution crystals with a given composition (for example, $KAl_{0.3}Cr_{0.7}(SO_4)_2 \cdot 12H_2O$) are identical.

An analogy to the solid solution would be a liquid solution of water and alcohol (ethanol). These liquids can be mixed in any proportion to generate homogeneous solutions. No part of a water–ethanol solution appears to be any different than another part, and properties such as density would be continuously variable from that of pure ethanol to that of pure water, depending on the mole ratio of the two compounds. On the other hand, oil and water do not mix, so a homogeneous solution of the two is not possible.

Procedure

Preparation of Crystals of Alum, $KAl(SO_4)_2 \cdot 12H_2O$

Dissolve 3 g of $KAl(SO_4)_2 \cdot 12H_2O$ in 30 mL of deionized or distilled water in a clean beaker. Stir well and make sure that all of the solid has dissolved. If some material remains undissolved, filter the solution. Transfer enough of the solution to a 13-mm × 150-mm test tube so that it is about one-third full. Clamp the test tube to a ring stand so that it will remain steady. Then tilt the test tube at about a 10–15° angle from the vertical. Using a disposable pipette, carefully add ethanol to the test tube by slowly allowing the alcohol to run down the inside of the tube. If this is done with care, the alcohol will not mix with the alum solution but will form a layer on top of it. Continue to add ethanol to the test tube until it is within an inch or so of being full. Stopper the test tube to prevent the ethanol from evaporating, remove it from the clamp, and set it carefully in a location where it can remain undisturbed for several weeks.

Preparation of Crystals of Chrome Alum, $KCr(SO_4)_2 \cdot 12H_2O$

Make a solution of $KCr(SO_4)_2 \cdot 12H_2O$ by dissolving 4 g of solid in 25 mL of deionized or distilled water in a clean beaker. Mix completely, filter if necessary, and layer a sample with ethanol. Set up a crystal-growth apparatus as described for growing alum crystals. **CAUTION: Chrome alum is an irritant. Avoid breathing dust and avoid skin contact. Dispose of this compound and its solutions in an appropriately labeled waste container.**

Preparation of a Solid Solution, $KAl_xCr_{1-x}(SO_4)_2 \cdot 12H_2O$

Using your remaining solutions, measure out a volume of alum solution (6–9 mL) and mix it with the appropriate volume of chrome alum solution so that the total volume is about 10 mL. Layer this sample as described. Repeat this procedure using 6–9 mL of chrome alum solution and a smaller amount of alum solution. Set up a crystal-growth apparatus as described for growing alum crystals.

Harvesting Crystals

When you are ready to collect your crystals, decant the liquid from the test tube into a beaker. If the solution contains chromium it should be placed in a waste container provided by your instructor. If it contains only alum it may be flushed down the sink. Rinse the crystals by pouring a small sample of ethanol into the test tube and gently dislodging the crystals from the walls of the beaker. Swirl the mixture gently and decant the ethanol. Repeat the ethanol wash two more times. The ethanol may be flushed down the sink. Allow the crystals to dry in air on a watch glass. What do the crystals look like?

Optional: Recycling Aluminum

In this procedure, alum is prepared from an aluminum beverage can. **CAUTION: Hydrogen gas is released; use a fume hood. CAUTION: KOH is a strong base. Avoid skin contact.**

With scissors, cut into small portions a 3-cm × 5-cm piece (approximately 1.0 g) of the side of an aluminum can. Place the freshly cut aluminum in a flask and add 50 mL of 1.4 M KOH.

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

Stir and heat the flask gently until all the aluminum dissolves. Filter off any scraps of paint and impurities that remain. Slowly add 30 mL of 6 M H_2SO_4 with continuous stirring. **CAUTION: H_2SO_4 is corrosive. Avoid skin contact.** A white solid should precipitate and then redissolve.

$$2\ KAl(OH)_4 + H_2SO_4 \rightarrow 2\ Al(OH)_3(s) + K_2SO_4 + 2\ H_2O$$

Heat and stir the mixture until all the white solid disappears. (If solid still remains after 10 minutes, remove the flask from the heat and filter.) Place the solution in an ice bath (ice with a little water) for about 20 minutes. Alum crystals should appear.

$$2\ Al(OH)_3(s) + 3\ H_2SO_4 + K_2SO_4 + 18\ H_2O \rightarrow 2\ KAl(SO_4)_2{\cdot}12H_2O(s)$$

Open-Ended Experiments

Design and perform experiments to answer one question of your own choosing. Be prepared to describe what you are trying to do and how you plan to do it. Sometimes there are unknown or uncontrolled variables in an experiment. (This includes but is not limited to such things as breakage or spillage by the experimenter, contamination of glassware, contamination of solutions, etc.) These effects can be minimized by performing several identical experiments and using well-designed “control” experiments that let you evaluate the effect of changing a single variable at one time. In general, you will need duplicate trials, and you will need to repeat portions of the preceding experiment as a control.

1. What happens to the size of crystals and the rate at which they grow if you use containers with diameters that are different than that of a 13-mm × 150-mm test tube?
2. What happens if you add solutions of metal ions other than chrome alum to alum?
3. Alum contains K^+ ions and SO_4^{2-} ions. What happens to crystal growth if you add a solution of potassium sulfate to the solution of alum?
4. What happens if you use chromium salts other than chrome alum to try to form solid solutions with alum?
5. Can you grow layered crystals by placing a crystal of alum in a solution of chrome alum for a while, then removing it and placing it in an alum solution, and so on?
6. What happens if you grow a crystal of alum and then place it in a fresh solution of alum?
7. Ethanol is an alcohol that has two carbons. What happens to the crystals if methanol (a one-carbon alcohol) is used? What about propanol (a three-carbon alcohol)? 2-Propanol (a three-carbon alcohol that differs in the arrangement of the atoms)?
8. What happens to crystal growth if you use a dirty beaker and tap water to prepare your solutions?
9. What happens if there is some undissolved alum powder present when you layer your solution?

10. What is the effect on crystallization if no ethanol is added and the water is allowed to evaporate slowly?

11. Is there another experiment other than those described here that you would like to try? Check with your lab instructor before attempting it.