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<u>Alum Production Pathway</u>

<u>Abstract</u>   A chemical pathway employing the amphoteric nature of aluminum and reacting the metal to produce commercially useful aluminum potassium sulfate is experimentally tested and analyzed on a small scale. The results of the reactions are mass balanced and analyzed for percent yield based on observed crystallized mass of the intended product.
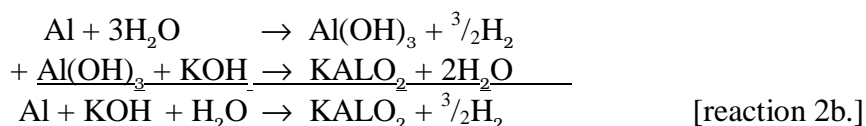
<u>Introduction</u>

A consumed soda can is the source of reagent aluminum in a set of three chemical reactions that produce potash alum as a final product. Pre-experimental analysis gives a viable pathway to be tested with small amounts of reactants. One-tenth of a mole of metallic aluminum is taken from a soda can and quickly placed in excess water, giving the following reaction:

$$Al + 3H_2O \rightarrow Al(OH)_3 + {}^3/_2H_{2\,(g)} \qquad \text{[reaction 1.]}$$
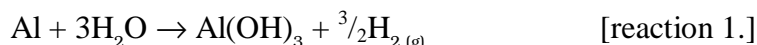
Thus, aluminum is oxidized to a +3 charge. In the water is also present potassium hydroxide, reacting with the thin but otherwise impenetrable and insoluble aluminum hydroxide surface film still forming on the metallic aluminum:

$$Al(OH)_{3\,(s)} + KOH_{\,(aq)} \rightarrow KAlO_{2\,(s)} + 2H_2O_{\,(l)} \qquad \text{[reaction 2.]}$$
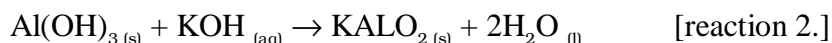
Aluminum is amphoteric, dissolving in strong alkalines or acids; in the above dehydration synthesis, all hydroxide ions are thus reduced and incorporated into water, replaced with the remaining more electronegative oxygen. This new ion then binds with the potassium forming another insoluble product that does nonetheless scatter and allow both reactions to reach completion if some excess water and potassium remain. The net reaction is given as:
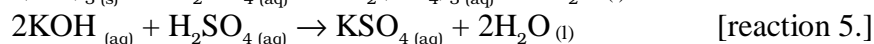
$$Al + 3H_2O \qquad \rightarrow \ Al(OH)_3 + {}^3/_2H_2$$
$$+ \ \underline{Al(OH)_3 + KOH\ \rightarrow\ KAlO_2 + 2H_2O\qquad}$$
$$Al + KOH\ + H_2O\ \rightarrow\ KAlO_2 + {}^3/_2H_2 \qquad \text{[reaction 2b.]}$$

Sulfuric acid is then added to neutralize excess hydroxide ions and to give the intended product, alum:

$$KAlO_{2\,(s)} + 2H_2SO_{4\,(aq)} \rightarrow KAl(SO_4)_{2\,(aq)} + 2H_2O_{(l)} \qquad \text{[reaction 3.]}$$
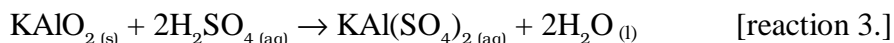
Both this reaction and reaction 2 are endothermic in that energy is required to reduce hydroxide ions and protons in solution, so that the experiment calls for these reactions to be accelerated with continuous use of a hot plate until the reactions complete.

The solution is cooled and the intended final product reaches and may exceed a saturated solution before growing alum crystals over the course of several days. It is the mass of these crystals that is formally used to calculate percent yield of the sum of reactions 2b and 3 as they occur under the conditions of this low volume manual process implemented in this experiment.

Note the possible residual acid-base reactions with sulfuric acid if reactions 1 and 2 do not consume all reactants:

$$2Al(OH)_{3\,(s)} + 3H_2SO_{4\,(aq)} \rightarrow Al_2(SO_4)_{3\,(aq)} + 6H_2O_{(l)} \qquad \text{[reaction 4.]}$$
$$2KOH_{\,(aq)} + H_2SO_{4\,(aq)} \rightarrow KSO_{4\,(aq)} + 2H_2O_{(l)} \qquad \text{[reaction 5.]}$$

One or both of these are implied if the solution maintains a basic pH until reaction 3 takes place.

Method

An aluminum can is cut into shards and added to mass a total of 0.1 mole (see equation 1 in results). To this is added an excess of water and potassium hydroxide relative to the aluminum as in the proportions given by reaction 2b, or about 100mL water and 0.1 mole potassium hydroxide (equation 3). This is done quickly to avoid oxidation of the aluminum in air that increases mass as measured and has other properties with respect to the known reactants throughout the chemical pathway.

When the metal is completely reacted to form the aluminum potassium precipitate, unreacted portions (such as the polymer film coating the can) are filtered and massed to give actual aluminum metal consumed in the reaction. In turn, the weight of a control wet filter is considered to give only unreacted polymer and metal mass (equation 2). 4.5M sulfuric acid is added in excess to produce a strongly acidic solution that does react with the mostly insoluble potassium aluminate (equation 4). Heat must be added to the beaker on a hot plate to bring this reaction to completion, when only a clear solution remains.

At this point, any remaining aluminum and potassium hydroxides are also neutralized to give the respective sulfate salts of each (reactions 4, 5). If pH remains basic in the presence of excess potassium hydroxide dictated by these methods, then at least this potassium sulfate salts should be formed at this stage, but in a fairly insignificant mass in comparison to the desired end product, alum. Reaction 5 should occur considerably less because its rate is known to be negligible as given in the experiment description. The purity of resulting alum crystal structure(s) should be affected by varying amounts of these other aqueous salts.

Finally, after the solution is allowed to cool to a point of saturation and crystals form, these are rinsed with a nonpolar volatile fluid, dried, examined, and massed to give the basis for calculating percent yield, and their shape gives a sense as to impurities contributing to error in the assumed mass of pure alum crystals.

Results

Equation 1:   26.98g/mole x 0.1000 mole = 2.698g Al to be reacted

Equation 2:   (filtrate & wet filter mass) – (wet filter mass) = filtrate mass
                8.7250g – 7.0140 = 1.711g filtrate (unreacted)

Equation 3: $(39.10 + 16.00 + 1.02)$ g/mole KOH x 0.1000 mole = 5.610g KOH

Equation 4:   1 L H_2SO_4 / 4.5 moles x 0.2000 moles x 1000.0 mL / 1 L = 44 mL H_2SO_4

Equation 5:   Actual mass aluminum can – Equation 2 = actual mass aluminum reacted
                2.6926g – 1.711g = 0.9816g Al reacted = 3.638×10^{-2} mole Al

Equation 6:   Mass of 4.5M sulfuric acid used = molar mass x 4.5 moles / 1000 mL x volume used (mL)
                $(2.02 + 32.07 + 64.00)$ g /mole x 4.5 moles / 1000 mL x 84.4 mL = 37.25g

Equation 7:   Mass of reactants = 0.9816g Al + 22.411g KOH + 37.25g H_2SO_4 = 60.64g

     By equation five, 0.9816g aluminum was reacted with excess water (100mL) and an actual mass of 22.411g KOH (or approximately equation three results times 0.4 mole, to give excess hydroxide ions in solution). The aluminum oxidation was brought to completion in a 250 mL beaker again by 7-10 minutes of sustained heat – until the solution began to boil. The entire contents were moved to a 600 mL beaker.

     Sulfuric acid was added more than once (see table 1). Note the total volume of the solution increase less than the sum original volume plus the added sulfuric acid (~30 mL water is consumed).

Table 1:   Observed Conditions during Alum Chemical Pathway Completion

Added Acid volume (mL)	Total Solution Volume (mL)	Measured pH	Other Observations / Actions
0.00	~248	> 12.5	Room temperature; very cloudy.
44.4		12.5	Cold to touch, murky.
20.0		3.0	Cold, less murky.
10.0	~320	2.5	Heated 10 min, still murky white.
10.0	300-305	2.0	Heated 5 min, less murky; after 5
84.4 total			additional min, cloudiness disperses.

After a final application of heat for 5-7 minutes, the solution was very clear.

     Five days later, the solution was checked and one large crystal (volume of ~ 20 mL) was massed at 35.74g. Some very small crystal dendrites remained in the beaker above the current level of solution. Volume of the solution without the crystal, 250 mL shows a further decrease in volume of 50-55 mL, presumably not due to evaporation because the beaker was covered.

     By stoichiometric analysis, 1:1 mole ratio is given for aluminum reacted to alum salt produced, thus by equation five, 3.638×10^{-2} mole of alum salt may be produced at maximum. Before calculating percent yield, the mass of anhydrous alum salt still in solution can be calculated by Equation 8, accurate only if the solution is primarily one of alum). Percent yield is given by equation 9. If consideration is given to dissolved alum in 8, there is even a more impossible yield greater than 100% calculated.

Equation 8: Equation 7 (60.64g) total reactants – 35.74g crystal mass = 24.90g in solution (anhydrous) = (39.10 + 26.98 + 2(32.07) + 2(64.00))) g/mole = 24.90g / 258.2g/mole = 0.9339 mole anhydrous alum in solution
Hydrous: 258.2 + 12(18.02)) or 216.2 g/mole = 474.4 g/mole

Equation 9: Theoretical yield = [3.638 x 10^{-2} mole $KAl(SO_4)_2$ x molar mass $KAl(SO_4)_2$ · $12H_2O$ = 3.638 x 10^{-2} x 474.4 g / mole = 17.26g (!)

Percent Yield: Actual mass yield / Theoretical = 35.74 / 17.26 = 2.071 or 207% (!)
Considering
Equation 9b: 35.74g crystal + 24.90g solution + 12 H_2O (in g)

Conclusions

Error seems to be present in calculations because it is impossible to experimentally achieve more than 100 percent yield. The most interesting observation is that volume of solution does indeed go down as alum salt fuses with water to become hydrous in its crystalline form. It is possible that confusion between anhydrous and hydrous weights in equations 8 and 9 produce the error. Crystal dendrites could be measured, as well as unexpected total mass of the remaining solution, however, these would not decrease percent yield, but rather skew it higher. Nonetheless, it would seem that the chemical pathway used is indeed efficient and converting aluminum metal (almost) completely to alum salt, as given by disappearance of cloudy precipitates given by reaction 2b.