

## Synthesis, Separation and Purification of KBr and KBrO<sub>3</sub>

### Background

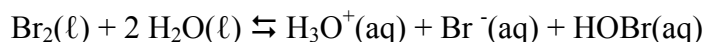
Many substances of interest to chemists and of practical use in the world at large do not occur in significant deposits in Nature or are difficult to extract economically from native sources. Because of this the routine business of chemistry is often concerned with preparing these substances (synthesis), separating them from unwanted by-products, and then purifying them adequately for their intended use.

It is unlikely that any single laboratory exercise could include even a representative sample of the many ways in which new substances are produced and isolated. This particular experiment is therefore focused on a few fairly common techniques for separation and purification which will be useful throughout the course: separating by differential solubility and fractional crystallization, suction filtration, recrystallization, etc. It also provides an opportunity to examine some of the chemistry of aqueous bromine.

The halogens are all soluble in water to some extent with that tendency decreasing as the molecules become larger (i.e., going down the column in the periodic table). Even iodine dissolves to a noticeable extent at room temperature as evidenced by the color it imparts to water.

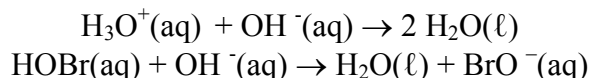
Bromine is more soluble than iodine. A saturated aqueous solution of bromine at room temperature has a concentration of about 0.2 M in Br<sub>2</sub>. This accounts for the characteristic color of aqueous bromine solutions which ranges from pale yellow at very low concentrations to dark reddish-orange when saturated. However, other colorless species also exist in the solution and these are the species of interest in this experiment.

Like chlorine and iodine, bromine reacts with water. The element *disproportionates* into two additional bromine-containing species:

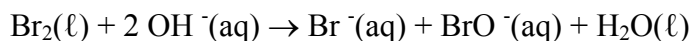


The bromine in elemental form is in oxidation state 0. *Disproportionation* is a redox process in which an element is both oxidized and reduced. In the hydrobromic acid (HBr--a strong acid which ionizes completely), the bromine is in oxidation state -1. The hypobromous acid (HOBr) is a weak acid which exists mainly in molecular form and in which the bromine is in oxidation state +1.

At room temperature this equilibrium lies far to the left. Molecular bromine is the predominant species in solution. Heating drives the reaction forward to some extent but making the solution basic causes a large shift in the equilibrium as hydronium ions and HOBr are neutralized:



Combining the three reactions shown so far, the overall reaction of bromine in basic aqueous solution is given as:



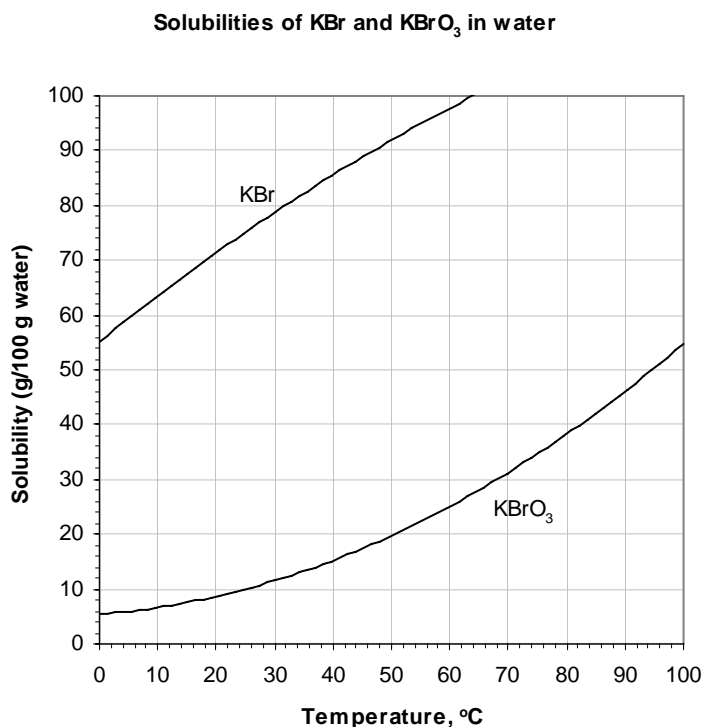
The hypobromite ion,  $\text{BrO}^-$ , is not stable in basic aqueous solution at high temperatures. Heating causes it to disproportionate as well:



The new species formed, the bromate ion,  $\text{BrO}_3^-$ , has bromine in oxidation state +5. This reaction goes rapidly and essentially to completion above  $50^\circ\text{C}$  in alkaline solution.

The reactions shown illustrate a synthetic pathway for obtaining potassium bromide and bromate from an aqueous solution of bromine. If the solution is made appropriately basic with potassium hydroxide and heated, the only species present in appreciable amounts should be potassium, bromide, and bromate ions (and, of course, water). If the water is simply removed by evaporation a mixture of the two solids will result. A method of separation is needed to recover each compound separately.

Fortunately the two compounds differ in solubility at just about any reasonable temperature for an aqueous solution as the graph below shows.



At temperatures near the freezing point of water almost all of the potassium bromate should crystallize from solution with only a small amount of contamination. This application of differential solubility is common in the separation of many substances from mixtures. It is known as *fractional crystallization*. Once the potassium bromate is crystallized and removed from the mixture, the more soluble (and less heat-sensitive) potassium bromide can be recovered by evaporating the water.

Fractional crystallization rarely results in a complete separation--at least on the first try. Purification is almost always necessary and the methods used vary according to the properties of the substances and the degree of purity required. In this experiment the isolated "crude" potassium bromate can be purified by *recrystallizing* the solid from a slightly supersaturated solution of the crude solid. This is another common method for purification. It also results in inevitable loss of product and so it is better to do it right the first time than to repeat it several times. Presumably the contamination is potassium bromide.

The crude potassium bromide is contaminated with potassium bromate that did not completely crystallize out at low temperature. Because the bromate compound is sensitive to heat while the bromide compound is not, heating the crude bromide is a way to purify it (it is too soluble to be recrystallized effectively from plain water). Heating potassium bromate causes it to decompose:



It is possible to estimate the "lost"  $\text{KBrO}_3$  from the mass change of the crude KBr when it is heated.

Synthesis pathways are often evaluated for efficiency by their *yields*. The amount of product that may be expected from a process can be expressed in a number of ways. The theoretical yield is a value based solely on stoichiometric principles, assuming that the reaction goes to completion. The actual yield (often expressed as a percent) gives some indication of the practical amounts that can be recovered under good working conditions.

## The Experiment

There are three parts to this experiment:

- synthesize potassium bromate and potassium bromide
- separate the compounds
- purify the compounds

The following non-locker materials will be provided:

- glass tubing and tubing cutter
- cork to fit your 125 mL Erlenmeyer flask
- ice bucket
- clay triangle
- crucible w/cover
- solid KOH
- bromine [fume hood]
- 3 M  $\text{HNO}_3$
- 0.1 M  $\text{AgNO}_3$
- 3 M  $\text{H}_2\text{SO}_4$
- Bromthymol blue indicator

## The Chemicals

*Bromine* is a dark reddish-brown fuming liquid at room temperature, consisting of diatomic molecules. In dilute water and hexane solutions its color varies from golden to dark orange. In basic solutions at room temperature it slowly reacts to form bromide and hypobromous ions. It is a member of the halogen family and has a chemistry similar to chlorine. It attacks all metals and organic tissues and vaporizes readily at room temperature. Fumes are highly irritating to eyes and lungs.

Bromine is used for bleaching silk, disinfecting spas, and manufacturing anti-knock compounds. Pure liquid bromine on the skin can cause painful, serious burns which heal only slowly.

ADDED SAFETY NOTES: Bromine is not a substance for inexperienced handling. The instructor will dispense bromine in the fume hood directly into the prepared solutions of potassium hydroxide. Only when the mixtures have attained homogeneity will they be transported (stoppered) to the second fume hood for heating. They will remain there until excess bromine has dissipated and the samples have cooled (the following day). At that point there should be no *special* hazard associated with the mixtures.

*Potassium bromide* is a white solid which is very soluble in water (1 gram dissolves in 1.5 mL of water). It is used in the manufacture of photographic papers and in some engraving processes.

*Potassium bromate* is a bread and flour improving agent ("bromated flour" is often sold as "bread flour"). Ingestion may cause vomiting, diarrhea, and renal injury.

*Potassium hydroxide* consists of white or slightly yellow pellets or flakes which absorb water and CO<sub>2</sub> rapidly from the air. It is soluble in about 0.9 parts water and dissolves with the liberation of considerable heat. The compound and its solutions are very caustic to tissue. It is used in the manufacture of liquid soaps, in the treatment of cotton for fabrics, in paint and varnish removers and in photoengraving. Ingestion may produce violent pain in throat and eventual collapse. Untreated ingestion may be fatal.

*Sulfuric acid* is a clear, colorless, oily liquid in concentrated form (98%). It is highly corrosive and has a high affinity for water, abstracting it from wood, paper, sugar, etc., leaving a carbon residue behind. Dilution of concentrated sulfuric acid generates a tremendous amount of heat. Here in the lab your instructor prepares the dilute sulfuric acid you use by pouring the concentrated acid slowly over ICE while stirring! Even so, the resulting solution is very warm. As with all acid dilutions, acid is added to water, not the reverse, since the heat generated can boil the water at the point of contact and cause spattering.

Sulfuric acid is used to make fertilizers, explosives, dyes, parchment paper, and glue. It is used, in concentrated form, in automobile batteries as the electrolyte. It is corrosive to all body tissues and contact with eyes may result in total blindness. Ingestion may cause death. Frequent skin contact with dilute solutions may cause dermatitis.

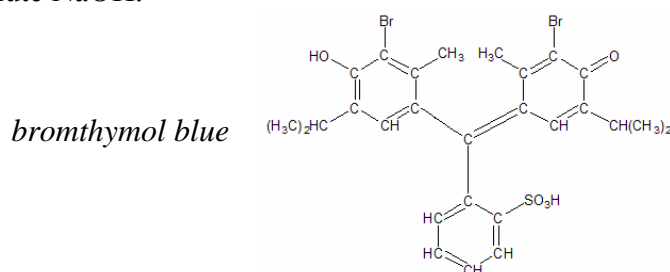
*Nitric acid* has been called "aqua fortis" (strong water). It is generally produced by the oxidation of ammonia followed by reaction of the gaseous products with water. When pure it is a colorless liquid that fumes in air with a characteristic choking odor. "Concentrated" nitric acid is a water solution containing 70% HNO<sub>3</sub>. Even dilute solutions will stain woolen fabrics and animal tissue yellow. It is a very strong oxidizing agent, reacting violently with most organic matter.

Nitric acid is used in the manufacture of fertilizers, dye intermediates and explosives.

*Silver nitrate* forms colorless, transparent crystals. It is stable and not darkened by light in pure air but darkens in the presence of organic matter and  $\text{H}_2\text{S}$ . It decomposes at low red heat into metallic silver. It is used in photography and the manufacture of mirrors, silver plating, indelible inks, hair dyes, etching ivory and as an important reagent in analytical chemistry.

It has been used as a topical antiseptic in a 0.1 to 10% solution. However, it is caustic and irritating to skin. Silver nitrate stains skin and clothing. These stains will wear off skin in a few days to a week but clothing is generally ruined. Swallowing silver nitrate can cause severe gastroenteritis that may end fatally.

*Bromthymol blue* (3,3'-dibromothymolsulfonphthalein) is used as an indicator, pH 6.0 being yellow and pH 7.6 being blue. The indicator solution is generally prepared by dissolving the solid material in dilute NaOH.



## Technique Discussion

Of primary concern in every synthesis is yield. Although the amounts used in this experiment are not critical they need to be tracked through the various operations.

5 g of KOH dissolved in about 30 mL of distilled water (125 mL Erlenmeyer flask) is sufficient material to work with. Measuring out solid KOH (or NaOH) can be problematic as the solids are very deliquescent and become visibly wet in the time it takes to determine a mass on the rough balance. Bottles of these solids should *never* be left open for the "next person". The next person is able to unscrew a cap. Spills should be cleaned up completely right away because of the corrosive nature of the concentrated alkali. Spilled material can go into the sink to slowly dissolve. If the solid is inadvertently handled thorough washing is in order until no slimy residue can be felt.

Because the addition of liquid bromine to a warm or hot solution can be hazardous and the dissolution of KOH is exothermic, the solution should be cooled under running tap water until it is near room temperature.

The instructor will add 2.5 mL of liquid bromine to the sample in the fume hood and stopper it. Careful swirling will bring the bromine into solution at which point the mixture should be warmed on a hot plate (also in the fume hood) until it boils gently. Boiling should continue until the color of the mixture is similar to white wine (pale yellow). Upon cooling overnight the mixture should precipitate potassium bromate. Additional crystals can be coaxed from the mixture by cooling in an ice bath.

The solution should be checked for pH prior to filtering with a few drops of bromthymol blue. This information can help confirm limiting reagent and yield calculations/assumptions later. The indicator is susceptible to oxidation by residual bromate ion in the solution, however, so the observation must be done carefully and immediately upon contact of the indicator with the solution. The solid potassium bromate can be separated from the solution in a number of ways. Gravity filtration is simple but can be slow. Suction filtration, which utilizes a special funnel and a special receiving flask attached to the vacuum line, is much faster and is commonly used in synthesis work. Techniques related to the use of this equipment can be found in the **Introduction to the Laboratory**. Ice-cold distilled water should be used sparingly for washes during filtering to minimize the amount of potassium bromate that dissolves.

There are several approaches to transferring material for filtering from its container into a funnel. If there is a lot of fine precipitate it can quickly clog the pores of the filter paper and make even suction filtration a slow business. Such mixtures are best dealt with by decanting as much liquid as possible and then attempting to transfer the solid near the end of the process. With mixtures containing coarse crystals it is generally more efficient to break up the crystal mass mechanically and then suspend as much material as possible before pouring. This will minimize the amount of solid left in the original container. Care must be exercised to avoid spilling or splashing the filtrate if it contains some desired material (as in this experiment) and pouring too quickly onto the filter bed of a Büchner funnel *can* dislodge the paper resulting in solid escaping along with the filtrate. Pressing the paper down with the end of a stirring rod or rubber policeman while pouring sometimes works to prevent this mishap. Most students have only two hands and a little bit of careful thought before pouring goes a long way in simplifying this part of the experiment.

Because of the solubility of potassium bromate in water it is best to recycle the filtrate if solid has remained behind after the initial filtration rather than rinse it out with water (pouring lots of distilled water onto the crystals collected on the filter bed will also result in loss of potassium bromate....). At some point in the transfer process more is lost than gained. This is a judgment call. It is impossible to recover every last molecule.

The recovered potassium bromate crystals on the filter bed should be washed with two small (2 mL) portions of ice-cold distilled water. "Washing" in this context generally means turning off the suction and releasing the vacuum. Then the washing liquid is added carefully (so as not to float the filter paper) and finally withdrawn by suction. The idea is to wash off any adhering potassium bromide solution while dissolving as little potassium bromate as possible. Depending on timing the crystals can either be left to air dry or they can be tapped out onto a large filter paper circle and sandwiched under a second piece. Pressing gently with the bottom of a beaker should dry them out quickly. A crude mass is required for the yield calculations *and* the recrystallization procedure.

The crude potassium bromide in the filter flask is rinsed into a pre-massed 250 mL beaker. Potassium bromide has a tendency to "creep" out of containers from an evaporating aqueous solution so it is best not to use too much water for the transfer. The beaker (*which should have your locker number on it*) goes into the oven at this point to evaporate to dryness overnight.

The crude potassium bromate is probably contaminated with KBr. A simple test for this involves taking a small amount of the solid, dissolving it in about 2 mL distilled water and adding a few drops of 3 M  $\text{HNO}_3$ . When a drop of 0.1 M  $\text{AgNO}_3$  is added a white/cream precipitate or cloudiness of AgBr indicates contamination. If the material is shown to be impure it must be recrystallized.

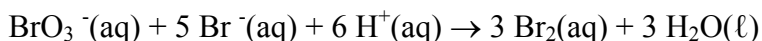
Recrystallization is something of an art. The general principal is to choose a solvent in which the solid is soluble at higher temperatures but insoluble at lower temperatures. In organic synthesis mixed solvents are common but in this case water will suffice. How much? Too much water and the crystals will dissolve, never to be seen again. Too little and the process will need to be repeated several times, each time compounding the loss of sample.

Use the solubility graph for  $\text{KBrO}_3$  to determine the minimum amount of water needed to dissolve the crude crystals at about  $80^\circ\text{C}$ . Add this amount to the solid in a small beaker. Because this volume will be small, it is best to heat the beaker on a hot plate while holding the beaker by the rim *with your hand*. **This is not typical technique**, but it is effective in this case. Constantly move the beaker around on the surface of the hot plate, swirling the solution until the crystals just dissolve. This should happen before the water boils. Boiling will cause the loss of too much water and the crystals will then become insoluble, even at the elevated temperature. Once the crystals have dissolved remove the beaker from the heat immediately and allow it to cool to room temperature, then cool in an ice bath. Plunging the beaker directly into an ice bath is a foolish error inviting mechanical failure of the glass, but it is also a tactical error as rapid formation of large crystals will tend to trap the material that is supposed to remain behind in solution, in this case the contaminating  $\text{KBr}$ .

If the solid does *not* dissolve, remove the beaker from the heat and add a small amount of water. Try again. Recover the recrystallized solid by suction filtration, washing with a small amount of ice-cold distilled water. Retest for purity. A successful test should be shown to the instructor for approval. A final mass is required.

After a mass is obtained for the crude, dry  $\text{KBr}$  the solid should be transferred to a pre-massed crucible.

Purification of the potassium bromide is a relatively hands-free operation. The crucible containing the sample is heated to redness, with lid slightly askew, for about 15 minutes. When it is safe to do so a small sample is removed and tested for purity. In an acidic solution any bromate impurity will react with bromide to yield bromine:



About 1 mL of sulfuric acid is sufficient for this test. Any elemental bromine imparts a distinct yellow color to the mixture. The absence of this color indicates acceptable purity. This test should be shown to the instructor who will initial your notebook. A final mass of the purified product should be taken.

The purified materials should be turned in for evaluation. If the  $\text{KBr}$  has fused inside the crucible do not attempt to dislodge it as the crucibles are quite fragile and will probably break. If necessary submit the sample in the crucible.

## The Report

Your initial calculations should include:

1. The overall balanced molecular reaction in this experiment and, based on the quantities of  $\text{Br}_2$  and  $\text{KOH}$  used, the limiting reagent.
2. The theoretical yields of potassium bromide and potassium bromate.
3. The % yield for the crude products.
4. The % yield for the purified products.

You should try to account for all of the material that originally went into the synthesis. For example, if your potassium bromate yield is low, why could that be? Can the loss be accounted for in the impurity of the potassium bromide (as measured by the mass change during heating)? Is mass conserved in the overall reaction? Be sure to look carefully at techniques you used and other places in the synthesis where loss is probable. Try to separate the losses into avoidable and unavoidable. Is it theoretically possible to get a significantly higher actual yield? Perhaps you can poll your classmates to compare yields and get a broader perspective.

Then there is the nature of the synthesis reaction itself. Does it go to completion? Are the limiting reagent assumptions appropriate? Think back to what the initial reaction looked like as it took place on the hotplate. You might also want to consider the data below which was gathered from a series of experiments in which the relative amounts of  $\text{KOH}$  and  $\text{Br}_2$  were varied.

	<b>Trial 1</b>	<b>Trial 2</b>	<b>Trial 3</b>
initial $\text{KOH}$ , g	6.00 (excess)	5.00	5.45
initial $\text{Br}_2$ , g	7.78	9.33 (excess)	7.78
pH of final reacted mix	10	10	10
total solid yield, g	8.21	7.40	6.82
expected solid yield, g	12.90	11.32	12.33

In each trial the “total solid yield” was determined by evaporating the water from the “finished” reaction mixture. The “expected solid yield” was calculated based on the limiting reagent as determined from the starting masses of reactants and including any excess solid that would not theoretically have reacted.