

# The remarkable chemistry of potassium dioxide(1-) (potassium superoxide). A series of microscale classroom demonstrations.

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Potassium dioxide(1-),  $\text{KO}_2$ , is a remarkably important compound that is only briefly mentioned by authors in general chemistry texts. Most literature references and general chemistry texts call  $\text{KO}_2$  by its traditional name, potassium superoxide. An on-line search of this journal yields only one article about inorganic superoxides using “superoxide” as the search word (1). The article appeared in 1963 and provides a nice overview of the inorganic superoxides. The first author is A. W. Petrocelli who worked for General Dynamics/Electric Boat, and studied the higher oxides “for air revitalization purposes” (in submarines, or electric boats).

What makes potassium superoxide so important? Consider these facts:

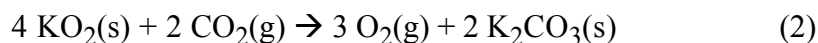
1. Most of the potassium metal produced in the US is used to make potassium superoxide (2).

This is accomplished by burning molten potassium in pure oxygen:



The same reaction occurs for rubidium and cesium. Unlike these three heavier alkali metals, lithium and sodium do not form superoxides when burned in air. Lithium forms the simple oxide,  $\text{Li}_2\text{O}(\text{s})$  and sodium predominantly forms the peroxide,  $\text{Na}_2\text{O}_2(\text{s})$ , also called sodium dioxide(2-). The accepted explanation is that larger cations favor larger anions due to lattice energies (3).

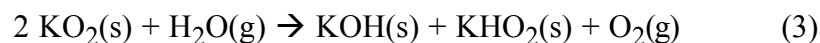
2. Potassium superoxide reacts with carbon dioxide to produce oxygen and potassium carbonate:



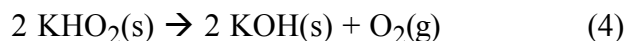
This reaction is very fast and nearly quantitative. For this reason, potassium superoxide is used in submarines, space vehicles, space suits, and by firefighters and miners.

These practical applications aside, potassium superoxide is nonetheless an interesting substance. Potassium superoxide consists of the potassium cation,  $K^+$  and the superoxide anion,  $O_2^-$ . The latter is an odd-electron species for which molecular orbital theory eloquently explains the bonding. The valence molecular orbital electron configuration is  $(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^3$  giving one unpaired electron per ion. It is common for paramagnetic materials to exhibit colors, and in the case of potassium superoxide, the salt is light yellow.

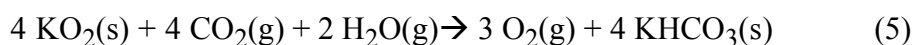
In addition to reacting with carbon dioxide, potassium superoxide reacts instantaneously with liquid water producing potassium hydroxide, potassium hydrogen peroxide, and oxygen (4):



The potassium hydrogen peroxide produced slowly decomposes to potassium hydroxide and oxygen:

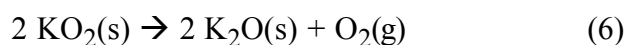


Potassium superoxide is sensitive to moisture in the air. When both carbon dioxide and water vapor are present, such as in respiration, the reaction produces potassium hydrogen carbonate:



These four reactions (2 – 5) account for potassium superoxide's sensitivity to air where both carbon dioxide and water vapor are present. Nevertheless, it is relatively easy to handle potassium superoxide in open air without special equipment such as glove bags. One must limit the length of exposure to air to a few minutes and store the reagent bottle of  $KO_2$  with the cover tightly sealed and preferably under an inert atmosphere.

Potassium superoxide does not melt, but rather decomposes by disproportionation at about 350 °C:



With this article, we provide instructions for performing two classroom demonstrations: (a) demonstration of potassium superoxide's ability to react with carbon dioxide as per Equation 2, and (b) paramagnetism of potassium superoxide.

### **Materials (5)**

For the demonstration of the reaction between potassium superoxide and carbon dioxide:

- glass Pasteur pipets, triangle file to cut the glass (or lengths of 8 mm O.D. glass tubing)
- ring stand and two clamps
- 60 mL plastic syringe, with a LuerLok fitting, two (minimum)
- syringe cap fitting, Latex LuerLok, two (minimum)
- Latex tubing, 1/8-inch (3.175 mm) ID, two 5-cm lengths and two 10-cm lengths
- pinch clamp or hemostat
- small test tubes, five
- wooden splint
- glass wool

For the demonstration of the paramagnetism of potassium superoxide:

- glass Pasteur pipets, one for each  $\text{KO}_2$  tube, (typically 3 – 4 needed per demo)
- 20 cm length of sewing thread
- 25 cm length of heavy (e.g. 12 gauge) copper wire
- 3 cm electricians' tape
- Neodymium magnet<sup>1</sup>
- a wooden base, approximately 10 cm square with a drilled hole in the center to support the copper wire

### **Chemicals required for demonstration**

- powdered potassium superoxide (CAS Number 12030-88-5)<sup>2</sup>
- carbon dioxide (CAS Number 124-38-9)
- calcium hydroxide (CAS Number 1305-62-0) or limewater (CAS Number 7719-01-9)
- universal indicator (any variety, including red cabbage juice)
- sodium hydroxide (CAS Number 1310-73-2)
- hydrochloric acid (CAS Number 7647-01-0)

### **Optional projection system.**

These are small scale demonstrations. Using them in a large classroom will require some sort of projection. For the first demonstration, the apparatus without the ring stand can be placed flat on a document camera and thus easily observed by the class. Viewing the confirmatory tests and second demonstration (of  $\text{KO}_2$ 's paramagnetism) is enhanced with a camera set up to project vertical objects.

### **Demonstration of the reaction between potassium superoxide and carbon dioxide.**

The apparatus shown in Figure 1 is constructed from a ring stand and two 3-prong clamps, two 60 mL plastic syringes and a glass tube constructed from a Pasteur pipet with the reduced diameter portion cut off and discarded. The glass tube is filled<sup>3</sup> with approximately 0.6 g potassium superoxide, which is held in place with two small plugs of glass wool, one at each end. Wear gloves while filling the  $\text{KO}_2$  tube:  $\text{KO}_2$  reacts exothermically with water, including the moisture on one's skin. The " $\text{KO}_2$ -tube" is connected to the syringes by two 5 cm lengths of Latex tubing.<sup>4</sup>  $\text{KO}_2$ -tubes can be prepared a day or more before they are needed but must be stored under inert atmosphere or with the two Latex tubes clamped closed.

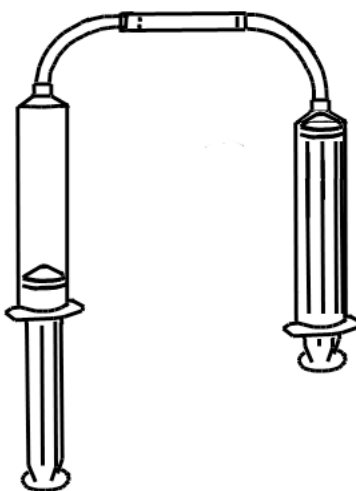
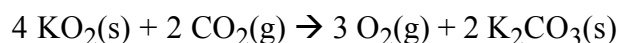


Figure 1. The potassium superoxide reaction device for gases. Ring stand(s) and clamps not shown.

Assemble the apparatus as shown in Figure 1. Fill the reagent syringe with carbon dioxide. Check that the potassium superoxide is canary yellow in color, especially if the  $\text{KO}_2$  tube was prepared well before the demonstration. The demonstration is now ready. Slowly pass the carbon dioxide through the  $\text{KO}_2$  tube.<sup>5</sup> The reaction is:



The product gas, oxygen, should have 50% more volume than the carbon dioxide used. The plunger of the receiver syringe may need some assistance in moving, especially at first.

As a teaching strategy, one may consider passing only half of the carbon dioxide through the  $\text{KO}_2$  tube so that the first two confirmatory tests, described below, can be performed on both reactant and product gases. Confirmatory tests 3 and 4 each require an additional syringe filled with carbon dioxide and product gas; these can be generated as needed or ahead of time.<sup>6</sup>

One of the most important visual observations to be noted is the color change of potassium superoxide and where the color change has taken place. The reaction between  $\text{KO}_2$  and  $\text{CO}_2$  is instantaneous so that the yellow  $\text{KO}_2$  changes to white  $\text{K}_2\text{CO}_3$  starting from the end of the  $\text{KO}_2$  tube closest to the  $\text{CO}_2$  syringe. In this way, one can estimate how much of the  $\text{KO}_2$  has reacted. This is

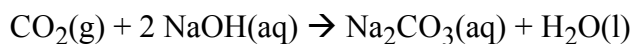
useful in determining if enough  $\text{KO}_2$  remains to pass another syringe of  $\text{CO}_2$  through the  $\text{KO}_2$  tube. The reaction is exothermic and the  $\text{KO}_2$  tube becomes hot.

**Confirmatory Test 1. Limewater test.** Limewater is saturated calcium hydroxide (stir 2 g  $\text{Ca}(\text{OH})_2(\text{s})$  per L water) that has been allowed to settle producing clear saturated  $\text{Ca}(\text{OH})_2(\text{aq})$ . Transfer about 2 – 3 mL of limewater to each of two small test tubes. Connect a 10 cm length of Latex tubing to each syringe. Discharge about 10 mL of carbon dioxide just above the surface of the limewater. Shake gently if necessary. A cloud of milky calcium carbonate should appear. Repeat with the product gas where no reaction is expected.<sup>7</sup>

**Confirmatory Test 2. Universal indicator test.** Prepare a solution of universal indicator (or equivalent such as red cabbage juice) in distilled water. Transfer about 2 – 3 mL of this solution to each of two small test tubes. Connect a 10 cm length of Latex tubing to each syringe. Discharge about 10 mL of carbon dioxide just above the surface of the indicator. Shake gently if necessary. The solution should turn the color associated with acidic conditions. Repeat with the product gas where no color change is expected.<sup>7</sup>

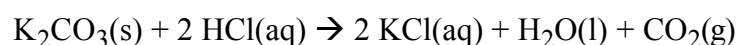
**Confirmatory Test 3. Traditional Glowing Splint Test for Oxygen.** This test works best with a full syringe of product gas,  $\text{O}_2$ . A second syringe filled with reactant gas,  $\text{CO}_2$ , may be used for comparison purposes. Conduct the experiment starting with a fresh  $\text{KO}_2$  tube if necessary. Pass enough  $\text{CO}_2$  through the  $\text{KO}_2$  tube in order to collect 50 mL or more of  $\text{O}_2(\text{g})$ . Remove and cap the receiver syringe, which should contain at least 50 mL gas. Remove the plunger and immediately thrust a glowing splint into the syringe. It should reignite and as soon as it does so, remove it from the syringe in order to prevent damage to the plastic syringe.

**Confirmatory Test 4. Carbon dioxide and aqueous sodium hydroxide react.** The reaction that takes place between  $\text{CO}_2(\text{g})$  and  $\text{NaOH}(\text{aq})$  is:



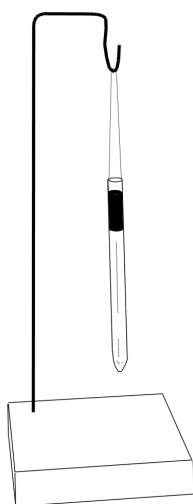
If the aqueous NaOH is 6 M, the reaction is nearly quantitative.<sup>8</sup> To perform the reaction, remove the syringe cap from a syringe filled with  $\geq 50$  mL  $\text{CO}_2(\text{g})$ , draw 10 mL 6 M NaOH into the syringe and immediately replace the cap. The plunger will be slowly drawn into the syringe as the  $\text{CO}_2$  reacts. Shaking the syringe greatly increases the rate. Repeat the reaction with the product gas syringe; no reaction is expected.

**Confirmatory Test 5. Carbonate test.** Carefully remove some of the white solid, presumably  $\text{K}_2\text{CO}_3(\text{s})$ , from the  $\text{KO}_2$  tube. Do not remove any yellow  $\text{KO}_2$ . Place the sample in a small test tube. Add a little water to dissolve the solid. No bubbles should be noticed.<sup>9</sup> Next add a few drops of 1 M HCl and look for bubbles of carbon dioxide:



#### **Demonstration of the paramagnetism of potassium superoxide.**

We have published a microscale classroom demonstration for liquid oxygen (6). The device used is shown in Figure 2 and is easily constructed from a heavy copper wire (because copper is non-magnetic), a length of sewing thread, a sealed-off glass pipet as the sample compartment<sup>10</sup> and a wooden base. The same device can be used to demonstrate the paramagnetism of potassium superoxide.



*Figure 2. Paramagnetism of potassium superoxide device*

Fill the glass tube with potassium superoxide. Suspend the pipet from the wire hook of the apparatus. Quell any random movement that the pipet may be making by touching a finger to the pipet. The demonstration is now ready! Hold the neodymium magnet near the pipet. Once the magnet is within a few mm of the pipet, it will swing towards the magnet and possibly hit it with a small, but audible ping.

### **Disposal of potassium superoxide.**

Unwanted samples of potassium superoxide can be destroyed by slow addition to water. Fizzing occurs and the solution turns basic as Reaction 3 takes place. The solution can then be pH neutralized with dilute HCl(aq) and disposed of down the drain if local statutes allow.

### **Safety Concerns and Hazards.**

Always wear safety glasses!

Potassium superoxide. MSDS entry: Strong oxidizer. Contact with other material may cause a fire. May cause severe eye and skin irritation with possible burns. May cause severe respiratory and digestive tract irritation with possible burns.

Sodium hydroxide and hydrochloric acid must be handled with great care by a trained chemical professional.

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### **Notes**

1. The use of a neodymium magnet is critical for the success of this demonstration. They can be purchased from a variety of vendors for less than \$10. We used a large trapezoidal shaped magnet, purchased from Educational Innovations, Part Number M-100. Educational Innovations sells worldwide ([www.teachersource.com](http://www.teachersource.com)). Another supplier is Rare Earth Magnets ([www.rare-earth-magnets.com](http://www.rare-earth-magnets.com)).

2. Powdered potassium superoxide is available from a variety of vendors including Fisher Scientific and Sigma-Aldrich. A 25 g bottle of potassium superoxide powder from Sigma-Aldrich, Part Number 27,890-4, costs \$36.40.

3. Filling the small diameter glass tube can be facilitated by using a scoopula and filling funnel fabricated from a thick-stem disposable transfer pipet: To make the funnel, cut the transfer pipet about



1 cm above the point where it constricts to form a dropper. Cut off the bottom (narrowest) 3 cm or so of the dropper, so that the funnel just fits inside the glass tube to be filled. Scoopula: Cut the bulb portion of pipet at a 45-degree angle to form an inexpensive curved scoopula. If the powder becomes stuck at any point, it can be pushed along by a wire or glass pipet, etc.

4. The tubing indicated in the list fits perfectly over the LuerLok fitting on the syringe. The same tubing makes an air-tight fit if worked *inside* the glass  $\text{KO}_2$  tube. This is accomplished by moistening the tubing with alcohol and working it inside the glass tubing while turning as if it were threaded.

5. Excellent control over the rate of gas delivery can be attained as such: Grip the plunger in the palm of the hand, and with the thumb and forefinger of the same hand, draw the syringe barrel inward. This prevents sudden discharges of gas.

6. One does not have to use all of the confirmatory tests to confirm that the reaction, as written, has taken place. Additional  $\text{KO}_2$  tubes will be necessary for additional confirmatory tests; we have found that each  $\text{KO}_2$  tube containing 0.6 g  $\text{KO}_2$  is capable of converting about 90 mL  $\text{CO}_2$  into  $\text{O}_2$ .

7. “False positive” results occur when some  $\text{CO}_2$  makes its way through the  $\text{KO}_2$  tube and is collected along with  $\text{O}_2$  in the receiver syringe. To reduce the chances of this happening, pass the  $\text{CO}_2$  slowly and replace the  $\text{KO}_2$  tube while there is still some yellow  $\text{KO}_2$  present.

8. The reaction is so close to quantitative that one can estimate the amount of  $\text{CO}_2$  originally present in a gas mixture by noting how much gas was originally present and how much remains.

9. If bubbles are observed upon adding water to the solid, it is probably  $\text{O}_2$  from unreacted  $\text{KO}_2(\text{s})$ . One may continue with the confirmatory test, however. The gas produced upon adding  $\text{HCl}(\text{aq})$  can be confirmed as  $\text{CO}_2$  by Confirmatory Test 1. To do this, draw 5 – 10 mL of the gas produced in the test tube into a syringe via a 10 cm length of tubing. Hint: Do not draw a volume into the syringe that exceeds the capacity of the test tube.

10. Other options to the sample compartment as described: 1. One can also use a small test tube as a cell compartment. 2. We have created a permanent sample tube for classroom use by placing  $\text{KO}_2$  into a sealed glass pipet as shown in Figure 2, however, we pre-filled the tube with argon and then sealed the top closed in a Bunsen burner flame. 3. The  $\text{KO}_2$ -tube, used in the first demonstration can also be used in the demonstration of paramagnetism: Use a small square (2.5 x 2.5 cm) of plastic film (grocery sack, sandwich bag, etc.) fastened to the glass tube with tiny rubber bands fabricated by cutting two short (2 mm) lengths of Latex tubing.

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### Literature Cited

1. Petrocelli, A. W.; Kraus, D. L. "The inorganic superoxides", *J. Chem. Educ.* **1963**, *40*, 146.
2. Greenwood, N. N.; Earnshaw, A., *Chemistry of the Elements*, Pergamon Press, **1984**, 85.
3. Cotton, F. A.; Wilkinson, G., Murillo, C. A.; Bochmann, M., *Advanced Inorganic Chemistry*, **6<sup>th</sup> Edition**, John Wiley & Sons, Inc., 1999, 98.
4. *Ibid.*, 461.
5. Syringes and related equipment can be ordered from a variety of vendors including Educational Innovations, Flinn Scientific (US sales only), Micromole and Fisher Scientific. Part numbers and links to their websites are provided at our microscale gas website, [http://mattson.creighton.edu/Microscale\\_Gas\\_Chemistry.html](http://mattson.creighton.edu/Microscale_Gas_Chemistry.html).
6. Mattson, B. "Demonstrating the Paramagnetism of Liquid Oxygen with a Neodymium Magnet," *J. Chem. Educ.* **2007**, *84*, 1296 – 1298.