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Gas Chemistry: A Microscale Kipp Apparatus

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Abstract: A new version of microscale Kipp apparatus is proposed. The gas generating process is taking place in a Beral pipets. The liquid reactant has to be inserted with a syringe into the pipet bulb. Depending on the required gas volume that should be produced, two modifications are presented. This setup provides conditions for generation of every gas that can be produced without heating in reaction between two liquids or solid and liquid substances, or even between two gases. It is especially suitable for generation of nitric oxide, chlorine, hydrogen, carbon dioxide, oxygen etc. The application of this apparatus is illustrated with several experiments. The idea provides simple, safe and low cost experiments suitable for hands-on work.

Introduction

In the history of chemistry during XVII to XVIII century with the work of many distinguished scientists the gas chemistry was born and developed into inevitable, important part of chemistry education for all ages.

Johann Baptista van Helmont (1579–1644) introduced the word “gas”. Joseph Black (1728–1799) recognized the existence of various airs (gases). Henry Cavendish (1731–1810) is a pioneer in the manipulation of gases and the one who established the accurate composition of the air. Joseph Priestley (1733–1804) discovered eight gases. Carl Wilhelm Scheele (1742–1786) discovered oxygen, chlorine and several other gases. Antoine Lavoisier (1743–1794) changed the course of chemistry with his oxygen theory. In the 19th century, the Dutch pharmacist Petrus Johannes Kipp (1808–1864) gave a special contribution to the gas chemistry with his invention, the well-known Kipp apparatus. It was first commercially produced in 1862, and since than till today this apparatus has been frequently used in chemistry demonstrations for generating hydrogen, acetylene, hydrogen sulfide, and most often for generating carbon dioxide. Its use is limited to gases that are generated by reaction between solid and liquid reactant. The reactions between two liquids that are exploited for gas generating are usually performed in apparatus consisted of a Würtz flask (or test tube) and a separatory funnel or a syringe [1].

Another eminent chemist has deserved a credit for his contribution to the gas chemistry especially in the field of microscale gas chemistry. Professor Hubert Alyea introduced gas generation with syringes in 1992 [2]. Since then, many educators have presented their own way of making gases. The prominent Professor Viktor Obendrauf from Pedagogical Academy, Graz, Austria, has proposed numerous methods [3–7] for gas generation in a test tube using 2 mL syringe for introducing liquid reactant and 20 mL syringe for collecting the produced gas. Other prominent educator of our time, Professor Bruce Mattson from Creighton University; Omaha, Nebraska, also has given his contribution in numerous gas generation methods inspired by Hubert Alyea article [2]. In this area he has given a significant contribution with a great number of articles in the journal “Chem 13 News” and his Internet page [8]. He describes several methods with 50 to 60 mL syringes. One of them is the “In-Syringe” method with general strategy of reaction of two substances in 60 mL syringe where the limiting reagent is always used in a solid form, placed in a small vial cap into the syringe barrel. Other chemistry educators have given their contribution to the development of apparatuses and methods in the field of Microscale gas chemistry as well [9–12].

This article gives a contribution to the microscale gas generation. In contrast of Obendrauf`s method that provides about 20 mL of gas and Mattson`s methods that provide about 60 mL. The proposed method provides several mL of gas.

Experimental

Techniques of a gas generation with a microscale Kipp apparatus. The design of the microscale Kipp apparatus is shown in Figure 1.II and its modification in Figure 1.III. It consists of a Beral pipet (3.5 mL) with shortened stem (a), 12 × 100 mm test tube (b), Beral pipet (3.5 mL) with cut bulb and shortened stem (c), a stand (e.g., made of gypsum or by drilling a hole in the center of a large rubber stopper) (d), 1 mL insulin syringe (e) and a rubber stopper with 2 holes (f). In addition to this, a syringe (2–10 mL) for gas manipulation is required.

Depending on the available rubber stoppers and the size of the Beral pipets test tubes with different diameters can be used for assembling the microscale Kipp apparatus. The functionality of the parts is denoted by the same marks on the drawing of the original Kipp apparatus and the microscale versions. The reaction for gas generation takes place in the pipet bulb (Figure 1.IIa).

When the gas is generated by reaction between two liquids, the plastic pipet is previously filled with liquid as it is shown in Figure 2. The other liquid reagent is introduced in the pipet’s bulb with a syringe. The produced gas is displacing the liquid which goes through the stem in the test tube (Figure 1.IIb) and if there is enough liquid than it goes in the reservoir (Figure 1.IIc). The used Beral pipets have volume of 3.5 mL. When larger volume of gas is needed it might be better to perform these experiments with pipets with large capacity (5.8 mL; 15 mL or 24 mL).

The modification shown in Figure 1.III is simpler apparatus that is preferably used in case when the required gas volume is equal or less then the pipet volume (3.5 mL). The proposed microscale Kipp apparatus (Figure 1.II) has no significant capacity for the liquid, but is more educational in the teaching of construction and use of genuine

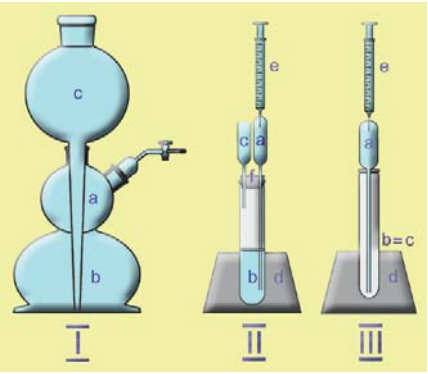

Figure 1. Kipp apparatuses: I) Original, II) Microscale with reservoir, III) Microscale simple modification.

Figure 2. Filling the plastic pipet with a solution.

Kipp apparatus and allows collecting part of the gas into the test tube, which in the other apparatus (Figure 1.III) will be spread into the air. This may allow avoiding use of fume hood when the gas is toxic or with unpleasant odor. Regarding this, one can always use the simpler modification when there is no need of explanation to genuine Kipp apparatus.

When gas generation that involves water insoluble solid substance as reactant is required, then the pipet bulb should be horizontally cut with scalpel (see Figure 3), enough to provide introducing (with forceps) small lumps (grains) of reactant (see Figure 4). The cut should be closed with an isolation tape or even better with isolation tape. In some cases, when the gas is not soluble in water, the pipet is filled with water or inert liquid to provide gas collecting in absence of air. The water dilutes the liquid reactant that is introduced with a syringe and for this reason the needle should be inserted closer to the solid substance.

In both kind of experiments (with liquids or liquid-solid) the gas is collected in an isolated space that provides relatively high purity of the gases (besides water vapor). The technique is similar to collecting gas under water. This is the way to avoid generating gas mixture with air which is common when the gas is generated in a presence of air, takes time and chemicals to collect a pure gas. This is especially important when the generated gas is toxic or with bad odor.

In some experiments, when there is no need for generation of a pure gas (with moisture), the syringe of 1 mL can be substituted with 5 or 10 mL syringe and the same syringe can be used for introducing the liquid reactant and for collecting the produced gas by drawing it and adding new portion of the liquid reactant again, if needed. This technique with inserting reactant in and drawing out the gas product that is toxic or with bad odor should be performed with the apparatus shown in Figure 1.II. After repeating the cycle: adding liquid reactant drawing the gas, the reaction of gas generation continues in the test tube, in the liquid. This means that part of the gas is evolved into the test tube and if there is no rubber stopper it spreads in the surrounding air. Instead of spreading out, if one uses the mentioned apparatus, the gas is collected in the test tube increasing the pressure and displacing the liquid into reservoir (Figure 1.IIc). Another way of avoiding this problem with the gas spreading in the surrounding air (due to the low reaction rate) is to add another liquid (solution), into the test tube that reacts with the solution that comes from the pipet and terminates the reaction of the gas production.

A) Generation of gas in reaction between liquids

Generation of NO. Fill a Beral pipet (in a position as it is shown in Figure 2) with aqueous solution of $FeSO_4$ prepared by dissolving 1.5 g of $FeSO_4 \cdot 7H_2O$ in 30 mL 15–20 % HCl. There should be no air bubbles in the pipet. If there is some, invert the pipet upside down with a bended stem, with the end in the same solution and by squeezing, the air is pushed out and by releasing the pipet bulb is filled with the solution.

Assemble the microscale Kipp apparatus with 1 mL of 10 % NaOH in the test tube and fill insulin syringe with 0.1 mL of saturated aqueous solution of $NaNO_2$. Prepare one 5 mL syringe with needle and a beaker with water and acid-base indicator. Insert the needle of the insulin syringe in the pipet bulb and carefully add small amount of solution of $NaNO_2$. Sodium nitrite reacts with Fe^{2+} and colorless gas (NO) is obtained and the solution changes the color to black according to equation 1:

$$Fe^{2+}(aq) + 2H3O^{+}(aq) + NO_2^{-}(aq) \longrightarrow NO(g) + Fe^{3+}(aq) + 3H_2O(l) \quad (1)$$

After the pipet bulb has approximately 2–3 mL of a colorless gas, insert the needle of the 5 mL syringe and withdraw the gas (no more than 2 mL) into the syringe and then close the syringe with a syringe stopper [19]. Note the color of the gas and then draw air or better 1 mL oxygen, into the syringe. A reaction of NO and O_2 takes place:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad (2)$$

Note the color change. The product of the reaction is brown gas due to the equilibrium between NO_2 (brown) and N_2O_4 (colorless). Next, in the same syringe, draw some water with acid-base indicator that changes color in acid media.

$$2NO_2(g) + H_2O(l) \longrightarrow HNO_3(aq) + HNO_2(aq) \quad (3)$$

Note the changes. NO_2 reacts with water producing a mixture of acids, which decreases the gas pressure in the syringe and as a result air is getting into the syringe and bubbles can be noticed.

One can collect more than 5 mL NO using cycle technique with adding liquid reactant and drawing the gas in the syringe. In this case NaOH(aq) should be avoided in the test tube. With 10 mL syringe filled with 0.5 mL $NaNO_2$(aq) one can collect 10 mL NO.

Warning: NO is toxic. Avoid breathing this gas. This experiment should be performed under a fume hood. Due to the corrosive nature of acids and alkaline solutions a special care should be taken (wear rubber gloves and safety goggles).

Generation of Oxygen. Fill a Beral pipet with 6 % hydrogen peroxide solution and assemble the microscale Kipp apparatus. Fill 1 mL syringe with 0.5 mL of 2–3 % solution of potassium permanganate in 2 mol/dm^3 H_2SO_4. Attach a needle with a wide diameter of the hole on the syringe's Luer-Lok connector and insert it into the pipet bulb. After that, slowly add the potassium permanganate solution into the pipet bulb. Oxygen generation is described with the equation 4:

$$5H_2O_2(aq) + 2KMnO_4(aq) + 3H_2SO_4(aq) \longrightarrow 5O_2(g) + 2MnSO_4(aq) + K_2SO_4(aq) + 8H_2O(l) \quad (4)$$

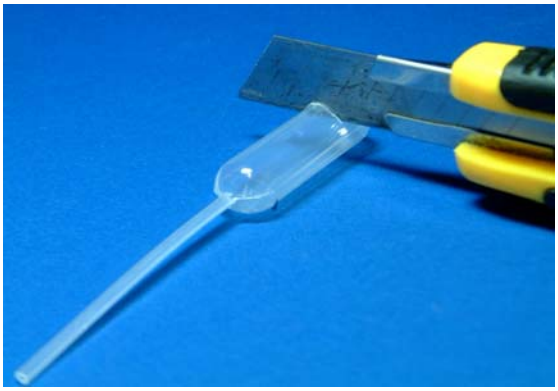

Figure 3. Cutting the plastic pipet.

Figure 4. Inserting Zn granules into the plastic pipet.

The obtained oxygen can be used for reaction with NO or H_2 etc.

Warning: Hydrogen peroxide solution may cause irritation. Avoid contact with eyes, skin, and clothes. Wash thoroughly after handling. Keep container closed.

Generation of SO_2. Fill a plastic pipet with saturated solution of Na_2SO_3 or $Na_2S_2O_5$. Place 1 mL of 10 % NaOH aqueous solution into the test tube and assemble a microscale Kipp apparatus. Draw 0.2 mL concentrated sulfuric acid into insulin syringe. Attach a needle (with a wide diameter of the hole) on the syringe's Luer-Lok connector and insert it into the pipet bulb. Add slowly sulfuric acid in small portions. The acid reacts with sulfite ions and sulfur dioxide is obtained as shown in the equation 5:

$$Na_2SO_3(aq) + H_2SO_4(l) \longrightarrow SO_2(g) + Na_2SO_4(aq) + H_2O(l) \quad (5)$$

Draw 2 mL very diluted solution of methylene blue in one 5 mL syringe. Attach a needle on the syringe's Luer-Lok connector and insert it into the pipet bulb and withdraw some amount (~ 3 mL) of SO_2. Close the syringe with a syringe stopper [19] and shake it. The solution of methylene blue will be decolorized due to the reduction properties of SO_2.

Warning: Due to the corrosive nature of acids and alkaline solutions a special care should be taken (wear rubber gloves and safety goggles).

Generation of Cl_2. Fill a Beral pipet with domestic bleaching solution (20 % sodium hypochlorite). Add 1 mL of 10 % NaOH aqueous solution into the test tube and assemble a microscale Kipp apparatus. Draw 0.5 mL concentrated hydrochloric acid in 2 mL syringe and attach a needle (with a wide diameter of the hole) to the syringe's Luer-Lok connector and insert it into the pipet bulb. Slowly add the acid into the bulb. The acid reacts with ClO^- ions and generates chlorine according to equation 6:

$$ClO^-(aq) + 2HCl(aq) \longrightarrow Cl_2(g) + Cl^-(aq) + H_2O(l) \quad (6)$$

Approximately 2 mL can be obtained. The solution that goes into the test tube reacts with NaOH and becomes alkaline again, which stops chlorine to be spread in the surrounding air.

Draw 2 mL diluted solution of potassium iodide (with few drops of starch "solution" (colloidal system, as an indicator) that were previously added) in 5 mL syringe. Then, attach a needle on the syringe's Luer-Lok connector and insert it into the pipet bulb and draw some Cl_2. Close the syringe with syringe stopper and shake it. Note the color change due to the reaction shown with equation 7:

$$Cl_2(g) + 2I^-(aq) \longrightarrow I_2(s) + 2Cl^-(aq) \quad (7)$$

The color change into deep blue is due to the formation of iodine starch compound.

Warning: Chlorine is toxic. Avoid breathing this gas. This experiment should be performed under a fume hood. Due to the corrosive nature of acids and alkaline solutions a special care should be taken (wear rubber gloves and safety goggles). The bleaching solution may cause irritation. Avoid contact with eyes, skin, and clothes. Wash hands after handling.

B) Generation of gases in reaction of liquid and solid

Generation of H_2. Make a small horizontal cut on the pipet bulb with a scalpel and add two granules of zinc or ~7 mm long Mg strip. Use an isolation tape to close the cut of the pipet. Fill the pipet with water and assemble a microscale Kipp apparatus. Fill one 2 mL syringe with 1 mL concentrated hydrochloric acid. Set the needle on the syringe and insert it into the pipet bulb closer to the metal. Slowly add the acid as close as possible to the zinc granules.

After the gas is collected (see Figure 5) fill one 5 mL syringe with 2 mL of hydrogen and 2 mL chlorine according to the previous experiment. In the fume hood, behind a protective door irradiate the gas mixture by a photo flash. This does not work with all kinds of photo flashes because some of them do not provide enough energy for the photocatalytic process that is followed by an explosion that generates HCl gas.

The generated hydrogen can be used for other reactions (with oxygen, reduction of heated CuO in a tube or a test tube etc.), as well.

Warning: Chlorine is toxic. Avoid breathing this gas. This experiment should be performed under a fume hood. Due to the corrosive nature of acids a special care should be taken (wear rubber gloves and safety goggles).

Generation of O_2. Make a small horizontal cut in a Beral pipet bulb with a scalpel. Add a granule made of mixture of MnO_2 and cement 1:1 [3]. Use an isolation tape to close the cut of the pipet. Fill the pipet with water and assemble a microscale Kipp apparatus. Fill one 1 mL syringe with 1:1 solution of hydrogen peroxide and water. Set a needle on the syringe and insert it into the pipet bulb. Add the peroxide solution as close as to the granule. Around 3 mL of gas can be obtained. Fill one syringe with 1 mL of oxygen. Using the previously described experiment generate NO and with the same syringe take 2 mL of NO. A reaction with color change occurs:

$$NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad (8)$$

Generation of H_2S. Insert one grain of pyrite or FeS into the pipet bulb and close the cut with isolation tape. Place 2 mL of 10 % NaOH aqueous solution into the test tube and assemble a microscale Kipp apparatus. Draw 0.5 mL hydrochloric acid (the one for domestic use) in 1 mL syringe. Attach a needle on it and insert it into the pipet bulb and add several drops of the acid on the grain surface. The following reaction occurs:

$$FeS(aq) + 2HCl(aq) \longrightarrow H_2S(g) + FeCl_2(aq) \quad (9)$$

Figure 5. Hydrogen generation.

Draw 1 mL of diluted aqueous solution that contains some of the following cations: Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Sn^{2+}, Bi^{3+}, As^{3+} or Sb^{3+} in several 5 mL syringes. Some of the solutions should be prepared with addition of acid to prevent hydrolysis. Then attach a needle on the syringe with the solution and insert it into the pipet bulb and draw out some amount (~3 mL) of the produced H_2S. Close the syringe with a syringe stopper [13] and shake it. A colored precipitate occurs and the reactions can be expressed with the following equations:

$$CuSO_4(aq) + H_2S(g) \longrightarrow H_2SO_4(aq) + CuS(s)$$
black to brown precipitate (10)

$$CdSO_4(aq) + H_2S(g) \longrightarrow H_2SO_4(aq) + CdS(s)$$
yellow precipitate (11)

$$HgCl2(aq) + H_2S(g) \longrightarrow 2HCl(aq) + HgS(s)$$
black precipitate (12)

$$Pb(NO_3)_2(aq) + H_2S(g) \longrightarrow 2HNO_3(aq) + PbS(s)$$
black precipitate (13)

$$2Bi(NO_3)_3(aq) + 3H_2S(g) \longrightarrow 6HNO_3(aq) + Bi_2S_3(s)$$
black to brown precipitate (14)

$$SnCl_2(aq) + H_2S(g) \longrightarrow 2HCl(aq) + SnS(s)$$
brown precipitate (15)

$$2AsCl_3(aq) + 3H_2S(g) \longrightarrow 6HCl(aq) + As_2S_3(s)$$
yellow precipitate (16)

$$2SbCl_3(aq) + 3H_2S(g) \longrightarrow 6HCl(aq) + Sb_2S_3(s)$$
orange precipitate (17)

Note the color change. The experiment can be performed with several syringes with different solutions and the H_2S can be drawn using just one needle by changing the syringes. The solution that goes into the test tube reacts with NaOH, becomes alkaline and stops hydrogen sulfide from spreading in the surrounding air. At the end of the experiment the excess of the $H_2S(g)$ can be eliminated by adding NaOH(aq) with syringe through the same needle used for drawing out $H_2S(g)$.

Due to the toxicity and the bad smell on rotten eggs of H_2S, the microscale Kipp apparatus is especially convenient. It allows controlled generation of small volume of the gas which is usually enough for performing some experiments.

Warning: H_2S is toxic. Avoid breathing this gas. This experiment should be performed under a fume hood. Due to the corrosive nature of acids and alkaline solutions a special care should be taken (wear rubber gloves and safety goggles). The solutions that contain Cd^{2+} may cause skin irritation. May be harmful if absorbed through the skin. The solutions that contain Hg^{2+} cause severe eye and skin irritation with possible burns. May be fatal if swallowed or if absorbed through the skin. The solutions that contain Pb^{2+} may cause eye and skin irritation. Prolonged exposure may result in skin burns and ulcerations. Wear rubber gloves and safety goggles when handling solutions of heavy metal salts.

Conclusions

Gas generation can be performed with a simple and safe procedure, cheap equipment and available chemicals in a short time at the microscale level. The proposed method could be extended to generation of several other gases such as: SiH_4, PH_3, HCN, C_2H_2, etc. The proposed novel microscale Kipp apparatus for gas generation provides conditions for hands-on experimentation. This idea makes the students active participants in the educational process.

Supporting Materials. Safety Tips and Disposal instructions are available as a PDF file (http://dx.doi.org/10.1333/s00897112396a).

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13. Syringe stoppers can be easily made of old syringe needles. Take a needle to a metal part with a forceps and with fingers to the plastic part. Heat the metal needle with flame of a micro burner and when it is heated enough just pull the metal part away. The plastic part should be heated carefully to melt and than just close the hole with the aid of tweezers or pliers.