Microscale Gas Chemistry

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Abstract

This article starts with a historical overview of the chemistry of gases from the first mention of air by Empedocles down through Lavoisier's Oxygen Theory. Gas generating equipment is reviewed along the way. The traditional macroscale apparatuses of the 19th and 20th centuries are reviewed. We next discuss the tenets of microscale chemistry and how these apply to gas chemistry. Before introducing the Alyea-Mattson method for generating gases in 60 mL syringes, a variety of microscale gas methods have been developed and these are reviewed. Detailed instructions for generating gases in large syringes are given. We finish with an overview of the eleven gases that can be generated by this method and list the experiments and classroom that can be performed with each. Our free website, dedicated to microscale gas chemistry is described.

A Brief History of the Study of Gases

The story of the early days of gas chemistry is interesting and important. It spans the entire 18th century and serves as an example of how an erroneous theory can shape and misguide understanding and investigation. It is a story in which the chemical behavior of the gases eventually allowed the genius of one man, Antoine Lavoisier, to first postulate the precepts of modern chemistry as we know them even to this day. But before we can fully appreciate the significance of the 18th century and the development of modern chemistry through the study of gases, we need to look back to the earliest ideas about gases.

The philospher Empedocles of Acagras in Sicily (492-432 BCE) provided the world with the four-element description of substances: all matter was composed of some combination of *earth*, *air*, *fire*, and *water*. This first attempt to develop a comprehensive philosophy that explained all aspects of the material world was broadened a century later by Aristotle so that earth represented the solid state, air represented the gaseous state and water represented the liquid state. In addition, every substance consisted of primary matter, *impressed with form*, which was the hidden cause of the properties of the substance. The four forms were *hot*, *dry*, *moist* and *cold*. Unfortunately for science, Aristotle rejected a much more accurate concept of the material world proposed by two earlier Greek philosophers, Leucippus (5th century BCE) and Democritos (455- 370 BCE) who believed that substances were built from small, indivisible particles called *atoms*. Aristotle's stature among scholars was so great that for nearly twenty centuries after his death he was still widely regarded as the ultimate authority on matters of philosophy, from which science eventually emerged.

The Renaissance brought great advances in chemistry and the development of experimental methods and scientific thought. Some of these advances involved gases. In the 17th century Robert Boyle conducted his now famous experiments on physical properties of gases and combustion. He was outspokenly critical of Aristotle's four-element theory and proposed his own. Although Boyle's theories regarding the nature of substances were vague and not very accurate (for example, he believed that fire was a particle), he was one of the most prominent experimentalists to attack Aristotle's theory of the elements. Around 1670, Boyle collected hydrogen, which he called *factitious air* and knew it to be highly flammable. It is significant and noteworthy that he was the first scientist to collect a gas in a vessel and to give it a name.

The ability to study gases advanced significantly with the invention of an apparatus to collect gas by water displacement by Stephen Hales in about 1700. Hales's "pneumatic trough", shown in Figure 1, consisted of a vessel constructed from a bent gun barrel with one end sealed off and a large glass vessel filled with water and suspended inverted in a tub of water.

Hales placed substances in the iron vessel and heated them to drive off *airs*. He was interested in studying the amounts of gas given off from various substances and missed the opportunity to study the properties of the *airs* he produced. He did perform some chemical reactions with the device and including the reaction of acids on iron filings to produce a gas (hydrogen) that he learned was flammable. He believed that all the gases were principally ordinary air and that some had more *particles of inflammability*.

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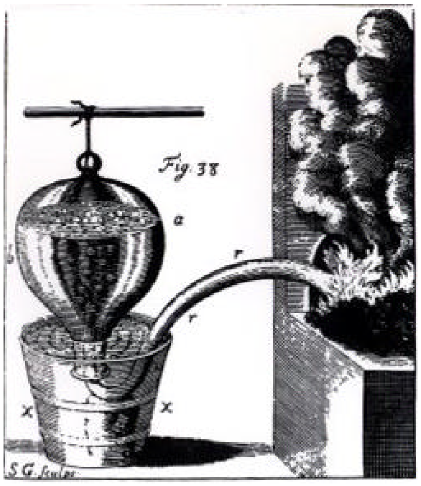


Figure 1. Collecting a gas by water displacement; originally from S. Hales, *Vegetable Staticks*; from *The Historical Background of Chemistry*, Henry M. Leicester, Dover Publications, used with permission. [Leicester, 1971]

The early 18th century brought with it the *phlogiston theory*, which rapidly grew to become the most important new theory since Aristotle's in that it dominated and framed much of scientific thought for chemists throughout the century. Johann Becher initially proposed in his 1669 text that matter consisted of air, water and three earths. His ideas were popularized by Georg Stahl in 1703 who coined the word *phlogiston* to describe a subtle material possessed by substances and could only could be detected when it left a substance. For example, when wood was burned, the phlogiston could be noted in the form of fire, heat and light. By 1720, most of the significant European chemists embraced the phlogiston theory and explained their experimental observations in terms consistent with the theory.

By the mid-1700s the age of *pneumatic chemists* in England and elsewhere was well underway. Joseph Black, an 18th century physician and lecturer in chemistry at the Universities of Glasgow and Edinburgh was among the earliest. He definitively established that gases can have chemical identities and are not simply *airs*. His work, published in a 1756 book, focused on alkaline substances and the gas they contained which he called *fixed air* (carbon dioxide). Henry Cavendish, a contemporary of Joseph Black is credited for the discovery of *inflammable air* (hydrogen) in 1766. Cavendish was an extremely wealthy and eccentric recluse as well as a masterful experimentalist. Like most scientists, Cavendish was a phlogistonist and at one point believed that *inflammable air* and phlogiston were the same.

It was Joseph Priestley who emerged as the most prolific and famous of the pneumatic chemists of the 18th century. He began his studies on *airs* at age 38 when he moved to Leeds and lived next to a brewery from which he had access to a nearly unlimited supply of *fixed air*. It was here that he discovered *soda water,* which eventually led to the invention of carbonated beverages. Using some of the equipment shown in this famous drawing from about 1770 (Figure 2), Priestley performed hundreds of experiments on gases and is credited with the discovery of eight different gases, a standing world-record. Priestley knew that the gases he produced were unique substances with their own physical and chemical properties. Despite these substantial laboratory accomplishments, Priestley understood his gases in the old phlogistonic vocabulary of his day and the actual chemical identities of these gases remained complete mysteries until the very end of the century.

Pristley's most famous discovery was that of *dephlogisticated air* (oxygen) on 1 August, 1774. Two months after his discovery, Priestley visited Antoine Lavoisier in Paris and described his experimental observations on *dephlogisticated air*. Lavoisier was more intrigued than perplexed by Priestley's results and was soon repeating this work as well as new experiments with the curious new air. Lavoisier had already questioned the value of the phlogiston theory and these new results only reinforced his suspicions.

Between 1781-1783, Priestley and Cavendish performed a series of experiments that led to the discovery that water was composed of *inflammable air* (H_2) and *dephlogisticated air* (O_2). Cavendish accu-

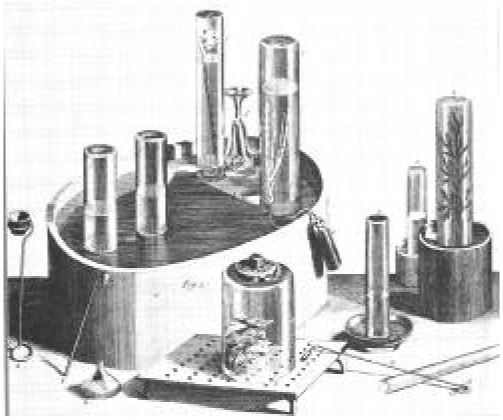


Figure 2. Priestley's apparatus for pneumatic experiments. The tub was for washing linen. The inverted in the foreground is a beer mug and contains a mouse [Priestley, 1775].

rately determined that the ratio of gases was 2.02:1. After repeating the water experiments (1783), Lavoisier asserted that water was a compound of *inflammable air* and oxygen. In the same year Lavoisier presented his new *Oxygen Theory* and simultaneously attacked the phlogiston theory in a paper titled *Reflections on Phlogiston.* His famous book *Elements of Chemistry* (1789) explained chemistry in terms of chemical elements and compounds (along with nomenclature) and within a decade, most European chemists had converted their beliefs to the oxygen theory. History will remember Priestley as an extraordinary experimentalist and Lavoisier as a theorist and the *father of modern chemistry.* Priestley's experiments played a significant role in undermining and eventually debunking phlogiston theory even though he never abandoned his faith in it.

In retrospect, phlogiston theory was not as far off the mark as it seems at first blush. Most observations explained with phlogiston can be modernized by replacing phlogiston with oxygen on the opposite side of the equation. That is, phlogiston was "-oxygen." Consider the two familiar examples that were inconsistent in that the first one suggested that phlogiston had mass while the second one suggested that it had negative mass:

charcoal → phlogiston

tin (+Heat) → calx of tin + phlogiston

In modern vernacular, these reactions become:

$C + O_2 \rightarrow CO_2$

$Sn + O_2 \rightarrow SnO_2$

No discussion of oxygen would be complete without giving proper credit due the Swedish chemist Carl Scheele. Scheele independently discovered oxygen which he called *fire air* in 1773, one year before Priestley. His work was not published until 1777, however, and by then history had already credited Priestley with the discovery. A drawing of Scheele's retort and gas bag is shown in Figure 3.

Understanding the physical and chemical properties of gases played a crucial role in the early history of chemistry. The phlogiston theory, which captured the minds of scientists for nearly a century, was created largely due to a misunderstanding of gases. The relationship between gases and phlogiston varied throughout the century as the need to explain certain observations changed. In the end, it was the experimental results based on gases that brought down the phlogiston theory.

The study of pneumatic chemistry in the laboratory has developed considerably over the last three centuries. We shall conclude our historical overview with a review of some of the equipment used down through the years. Hales's and Priestley's pneumatic troughs look odd, but the basic idea is still widely use today although it has been modified and simplified considerably. The modern pneumatic trough has changed little in the past 200 years. Figure 4 is from a 1845 textbook, but could easily have been from a modern text or laboratory manual.

A variety of methods of gas generation evolved throughout the 19th century. The Wolff's flask was a common device employed to generate gases (Figure 5.) The Kipp generator (Figure 6), was produced in a variety of sizes and is still produced and widely used in some parts of the world today. Its most useful feature is that it stores gas for immediate use and regenerates gas as it is used, thus providing chemists with an ever-ready source of gases such as H_2S. The

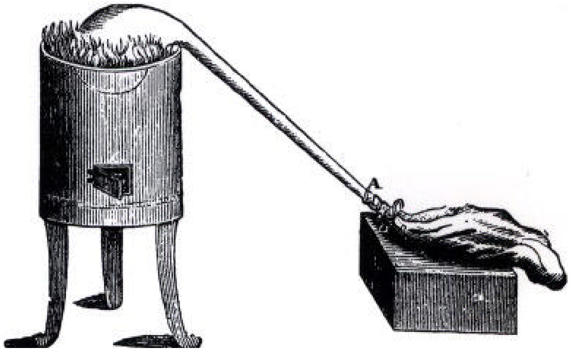


Figure 3. Sheele's retort and airbag [Partington, 1937].

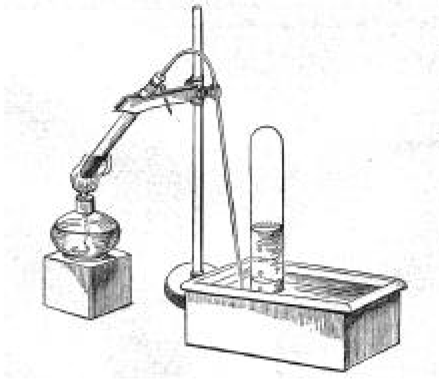


Figure 4. Use of a pneumatic trough used to collect oxygen, from an 1845 textbook of chemistry [Fownes, 1845].

Figure 5. The Wolff's flask was used to prepare a number of gases, including hydrogen [Remsen, 1886].

top reservoir of the Kipp generator contains an aqueous reagent, in this case dilute sulfuric acid which is transported to the bottommost chamber. The acid in this chamber rises and comes in contact with the solid reagent (zinc in the figure) and there the two react to produce hydrogen. When the stopcock is closed, the gas pressure pushes the acid downward until the acid and metal are no longer in contact, thus stopping the reaction. As hydrogen is released, the pressure drops and the acid rises in the middle chamber and more hydrogen is generated.

Perhaps the most familiar of the old macroscale gas generation methods is the pneumatic flask as shown in Figure 7. In this case the gas being collected is heavier than air (for example, chlorine), however other gases could be prepared with this device in conjunction with a pneumatic trough.

In 1992 Hubert Alyea proposed an ingenious method for the safe generation of gases, including noxious gases, for classroom use. The method utilizes disposable plastic syringes (Figure 8). Unlike any method before, this approach places the two reagents in the same sealed vessel and allows them to react to produce gases in a self-contained vessel.

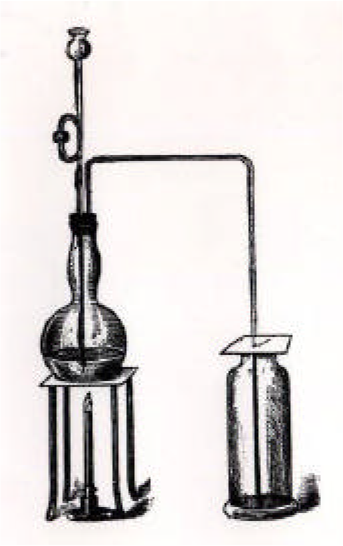


Figure 7. Preparation of Cl_2 and HCl in the 1929 text *Intermediate Inorganic Chemistry* [Bailey, 1929].

The generation and study of gases has been an important endeavor in the history of modern chemistry. It has also been an endeavor that has captured the imagination of scientists for centuries. From Aristotle to Alyea the properties of the gases have been gradually unveiled. The mysterious nature of gases — their invisibility, their oft lack of color and odor — have made them subjects of fascination for generations of chemists. Equipment to study gases has ranged from simple to complex. In the eighteenth century the experiments were done by the

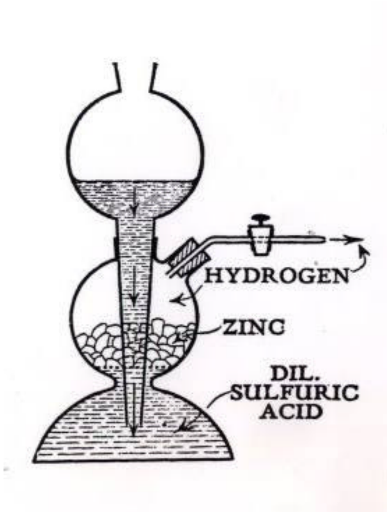


Figure 6. A Kipp generator for generating H_2, H_2S and many other gases [Brownlee, 1931].

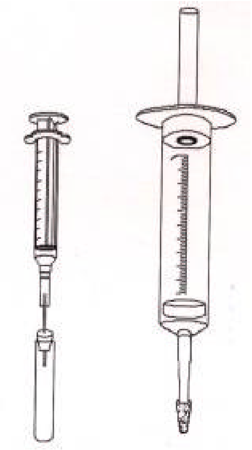


Figure 8. Hubert Alyea first described the generation of gases in syringes in 1992 [Alyea, 1992]. Used with permission from the *Journal of Chemical Education*, copyright 1992, Division of Chemical Education, Inc.

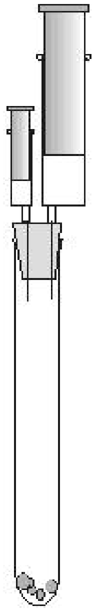


Figure 9. Viktor Obendrauf uses a small test tube containing a solid reagent with the second reagent in a small syringe; the large syringe is the gas receiving syringe [Obendrauf, 2002].

pneumatic chemists. By the late nineteenth century, chemistry textbooks described methods for student use although these were often elaborate, and time-consuming. Within the past thirty years, laboratory methods have greatly improved, especially with the advent of microscale chemistry.

Other Microscale Methods for the Study of Gases

A variety of microscale gas chemistry methods are currently in use. Our method, which we will describe later, is based on Alyea's 60-mL syringe method (Figure 8, right) in which a solid and an aqueous chemical solution are mixed inside a syringe. The reaction takes place in an enclosed syringe, virtually eliminating the possibility of exposure of the gas to the experimenter.

Viktor Obendrauf (Austria) has developed numerous methods of gas generation using 10-20 mL syringes, small test tubes, soft latex stoppers or septa and blunt needles similar to that proposed by Alyea (Figure 8, left). His refinements include the use of a reagent syringe (Figure 9). Much of his work with microscale gas chemistry (methods and numerous interesting experiments) has appeared in German-language journals such as *Chemie & Schule* (Salzburg) but a good overview of his methods can be found in his web-based article in *Chemical Education Journal* [Obendrauf, 2002]. Among many ingenious features, Obendrauf uses a syringe packed with charcoal to absorb unwanted gases as they continue to generate in the reaction test tube. Obendrauf's methods using medical apparatuses (septa, needles, etc.) for the generation of gases have led to various companies marketing the necessary equipment for European markets [Menzel, web].

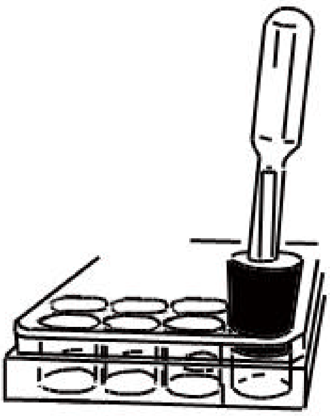


Figure 10. Slater and Rayner-Canham describe the generation of gases in a 24-well plate.

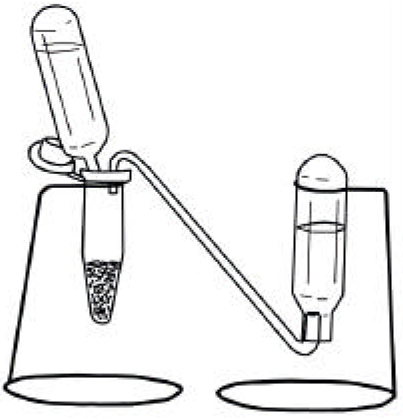


Figure 11. Kvittingen and Verley's apparatus is similar in principle to the traditional 19th Century equipment – only 100 times smaller.

Alan Slater and Geoff Rayner-Canham generate gases in one cell of a 24-well plate and collect the gas in pipet bulbs (Figure 10) [Slater, 1994].

An ingeniously small-scale, inexpensive apparatus is described by Lise Kvittingen and Richard Verley (Norway) in which the reaction vessel is a centrifuge tube and the dropping funnel is a thin-stem pipet. The gas collection vessel is a wide-stem pipet and used the method of water displacement (Figure 11) [Kvittingen, 2004].

Certain gases are readily produced by electrochemical methods and microscale methods for generating gases this way using pipet bulbs have also appeared. Per-Odd Eggen and Lise Kvittingen have described the electrolysis of water using one or two pipet bulbs as shown in Figure 12 [Eggen, 2004].

Ozone is also conveniently produced by an electrochemical method as described by Jorge Ibáñez and Bruce Mattson and shown in Figure 13. This method is well-suited for use of gases *in situ* [Ibáñez, 2005a].

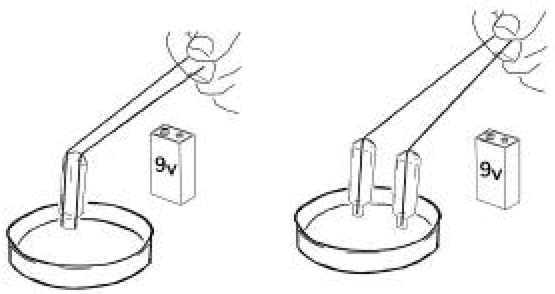


Figure 12. Electrochemical method for the generation of gases using a pipet bulb and a 9-volt battery.

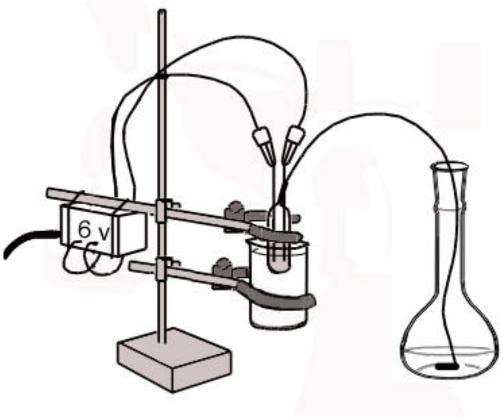


Figure 13. Electrochemical generation of ozone in a pipet bulb.

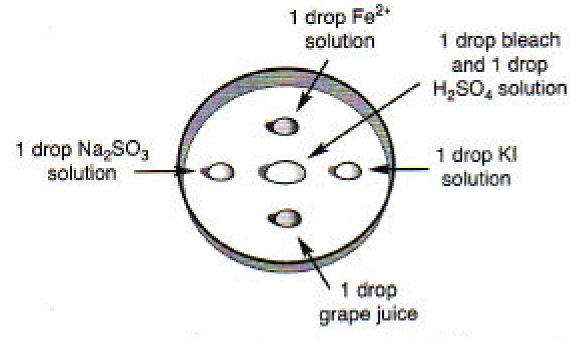


Figure 15. Gas chemistry by diffusion. [Choi, 2002] Used with permission from the Journal of Chemical Education, copyright 2002, Division of Chemical Education, Inc.

Generation of chlorine dioxide for *in situ* use has also been described by Ibáñez, Anderson and Mattson. The device which uses a Beral pipet as the generation chamber is shown in Figure 14. This method could be extended for use with a wide variety of gases. In this and the previous example, the stem of a Barel pipet has been stretched to 30 cm or more in length so that the gas can be conveniently delivered to the desired destination [Ibáñez, 2005b].

Microscale gas chemistry need not involve expensive or expensive apparatus. Martin Choi describes making chlorine in a drop of solution in a Petri dish and allowing gas diffusion to carry the chlorine to various reagents present in other drops in the dish (Figure 15) [Choi, 2002].

Using a test tube and Beral pipet with slits cut into the bulb, James Kilroy and Mary Virginia Orna describe the simple device pictured in Figure 16 in various attitudes. An especially nice feature is that one can stop gas generation at any time by lifting the reaction chamber out of the aqueous reagent [Kilroy, 1994].

The Kipp generator, described above and pictured in Figure 6 has inspired similar small-scale devices. A 20-mL gas capacity one-piece clear plastic Kipp generator, pictured in Figure 17 was invented in the former Federal Republic of Germany and popularized by Andreas Kometz and others [Kometz, 2001].

From its inception, microscale methods have developed along two lines in terms of equipment sophistication and expense. Glass manufacturers have created ingeniously small apparatuses that tend

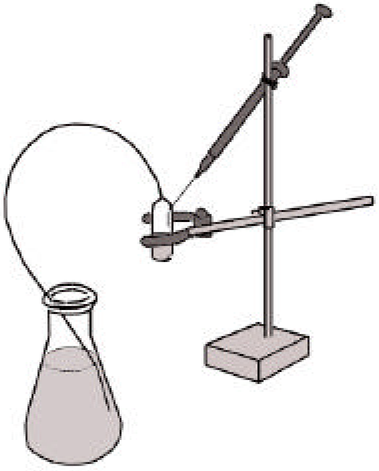


Figure 14. Use of a pipet bulb to generate gas in situ – especially useful for gas samples that cannot be stored because they are unstable.

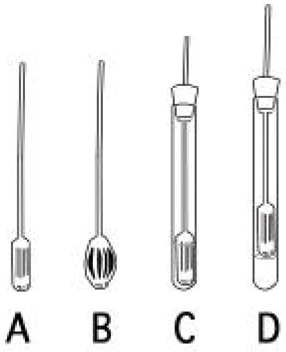


Figure 16. From left: A. Beral pipet with slits cut into the bulb; B. Opening the slits to add solid reagent; C. Pipet in contact with aqueous reagent and concomitant production of gas; D. Pipet raised out of aqueous solution to stop gas generation

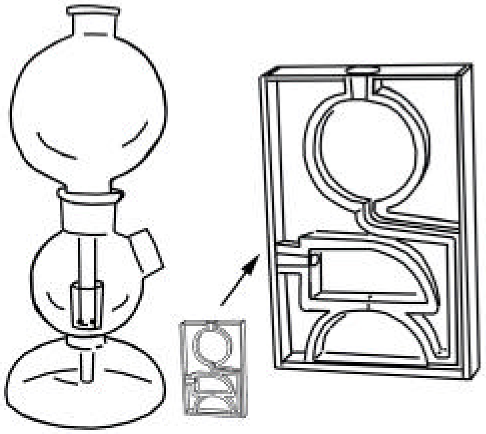


Figure 17. A 20 mL Kipp generator standing next to a traditional 2.5 L model from the 19th century.

to be expensive, while other methods tend to be inexpensive and use "consumable" plasticware. Figure 18, pictures an example of the former, a micro-Kipp generator about the size of a 250 mL beaker and described by Jinhua Wang [Wang, 2003]. The aqueous reagent is placed in the left reservoir and the solid reagent goes in the right reservoir where it rests on a sintered glass frit that separates it from the aqueous reagent.

What is Microscale Chemistry?

Among the pioneers in developing and promoting the movement towards microscale chemistry are Mono Singh, Zvi Szafran, and Ronald Pike, founders of the National Microscale Chemistry Center (NMCC). The tenets of microscale chemistry according to the NMCC's website [Singh, web] are: "to maintain a pollution-free environment, eliminating chemical waste at the source without compromising the quality and standard of chemical applications in education." The benefits of microscale chemistry, according to the NMCC website, are:

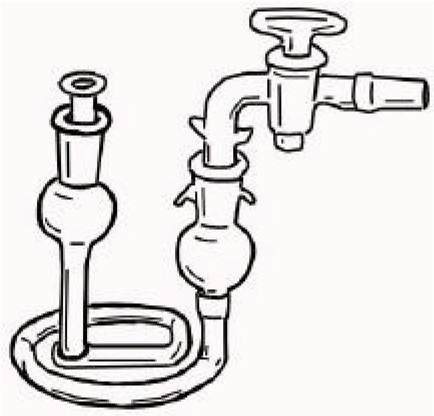


Figure 18. Another design of a microscale gas chemistry generator.

— It reduces chemical use promoting waste reduction at the source.
  It offers vastly improved laboratory safety by:
  - Better laboratory air quality.
  - Least exposure to toxic chemicals.
  - No fire and explosion hazards.
  - No spills and accidents.

— It sharply reduces laboratory cost.
— It requires shorter experiment time.
— It implements excellent laboratory manipulative techniques.
— It lowers glass breakage cost.
— It saves storage space.
— It improves laboratory skills.
— It provides clean and productive environment.
— It promotes the principle of 3Rs: Reduce, Recover and Recycle.
— It creates the sense of 'Green Chemistry'.
— It changes the psychology of people using chemicals.
— It is user friendly to people with physical disabilities.

What is Microscale Gas Chemistry?

We agree with all of the tenets given by the NMCC and agree with the benefits cited. We note that the Center does not stipulate that reactions need to be performed on the smallest humanly possible scale. Nor does the NMCC define the prefix "micro" or stipulate specific mole or mass quantities. We believe that the spirit of microscale chemistry is to conduct experiments on a reasonably small scale while taking into account environmental impact and laboratory costs. We believe that one needs to consider the entire "account" when evaluating the environmental impact and chemical cost/use for each situation. With our techniques, described below, one typically uses 2 mmol of two reagents to generate 2 mmol (60 mL) of gas. This gas sample can be used for up to five separate experiments. For comparison purposes, a typical well-plate reaction, such as a precipitation, calls for 1 drop of two solutions that are typically 0.1-1.0 M, or 0.005-0.05 mmol and a typical microscale titration using a 2 mL Mohr pipet as a buret uses 0.2 mmol of each 0.1 M reagent. At first glance, one notes that our method calls for at least 10 times more chemicals. However, that is just a first glance! Two drops of solution that form a precipitate such as lead chromate result in a much larger environmental impact and laboratory cost than the generation of any of the teaching laboratory gases (CO_2, H_2 and O_2) we describe. The metal precipitate requires proper storage and eventual disposal by a commercial waste handler. Even cleaning the well-plate requires consumables such as cotton swabs and possibly disposable gloves. If the well plate is being discarded, that is an expense and environmental impact that must be considered. Compared that to the generation of 60 mL carbon dioxide via vinegar and baking soda in a 60-mL syringe, the two-drop lead chromate precipitation reaction has a much larger cost to the institution and to the environment!

The chemicals needed to generate simple gases in 60-mL syringes cost almost nothing, the resulting solution can be disposed of down the drain and the equipment can be reused over and over. All (100%) of the reagents used in producing and conducting (20+) experiments with the three gases recommended for use in the high school laboratory can be pH neutralized and disposed of down the drain. Over 95% of the reagents that our methods use in all 140+ experiments covering 17 gases can be disposed of down the drain. The 14 "other gases" and experiments lend themselves well to (a) laboratory activities by second year high school chemistry students or university students and (b) classroom demonstrations. An unintended use of our gas methods has been in research and development in private research organizations, industry and university.

Why Do Microscale Gas Chemistry?

Here are the reasons why we are "gas enthusiasts." Microscale gas chemistry:

- ***is fun and easy!*** Students find it easy to learn how to prepare gases and do the reactions. Gas samples are ready in 5 minutes.
- ***is a source of great labs and great demos!*** Students enjoy making gases and performing experiments with them. They also enjoy seeing classroom demonstrations with gases. Some of the demonstrations are nothing short of spectacular.
- ***is visual!*** The best way to ***see*** a gas is to watch it being produced. The best way to ***see*** a gas undergo a chemical reaction is to watch it being consumed. The use of large plastic syringes allows for this visualization.
- ***is microscale!*** It's microscale in terms of quantities and costs, but large enough to see (60 mL). Our techniques are in 100% compliance with each of the "benefits" described by the NMCC (listed earlier). As an added benefit, the equipment that we use is inexpensive and virtually unbreakable.
- ***is inexpensive***. In addition to inexpensive equipment, the experiments themselves are inexpensive. It costs less than $^1/_2$ cent to prepare a syringe filled with carbon dioxide. Other gases are a bit more expensive, but never more than a few cents per syringe full of gas.
- ***is green chemistry***. There is little or no chemical waste.
- ***is a valuable resource for teaching a wide variety of chemistry concepts.*** Important concepts of the high school and college chemistry curriculum can be taught with gases. Our emphasis mostly on the chemical reactions of gases, however, the list of concepts covered includes gas laws, environmental issues (acid rain, air pollution), reaction stoichiometry (limiting reagents, law of combining volume, theoretical yield), intermolecular forces, catalysis, combustion, molar mass as well as more advanced topics such as kinetics and equilibrium. Experiments involving microexplosions and rocketry are favorites among the students.

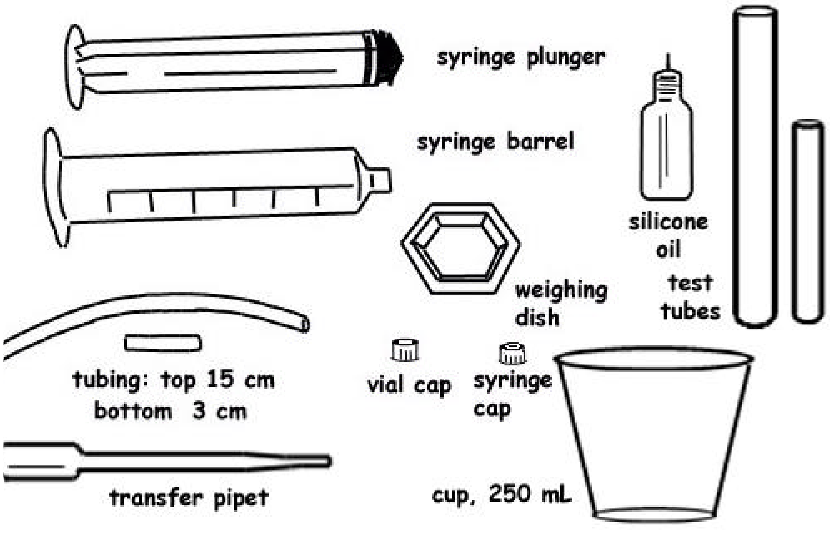
The Alyea-Mattson Method for Preparing Gas Samples

The Alyea-Mattson "in-syringe" method is used to prepare eleven different gases. Originally described by Alyea [Alyea, 1992], the method features the generation of gases by reacting two chemicals, typically one solid and one aqueous liquid, inside a plastic syringe. Getting the two reagents into the syringe before they started reacting was a definite shortcoming of the original Alyea's method. In his article, he suggested, "Into the cap put enough reagent to generate 50 mL of gas. Drop the cap into the syringe, and immediately fully insert the plunger." He also described generation of hydrogen sulfide as an example! Our contribution to the method was to develop a safe and easy way to bring the two reagents together inside the syringe, but separated so they cannot react until the plunger is in place, the syringe is sealed (closed system) and the experimenter is ready. We have spent the past decade working out 140+ experiments with 17 gases.

Microscale Gas Chemistry Kits

Each pair of students will need certain equipment in order to prepare gases and perform experiments with the gases. We recommend organizing this equipment in stackable plastic food storage containers. Each kit should contain the following equipment as shown in Figure 19. Ordering information, including part numbers, is available at our website. Several vendors sell outside of the USA. The most expensive item in this list is the syringe. When bought in bulk (4 boxes of 30), one can obtain these for about US$ 1.10 each. Veterinarians use this size syringe and perhaps one could obtain used syringes from them. Silicone jelly from a pharmacy can be substituted for silicone oil. Other oils including mineral oil, vegetable oil, petroleum-based lubrication oil ***cannot*** be used as they are absorbed into the syringe's rubber diaphragm and thus ruining it.

- two 60 mL plastic syringes with a LuerLOK fitting
- two Latex LuerLOK syringe caps
- two plastic vial caps
- one 15 cm length of Latex tubing
- one 3 cm length of Latex tubing
- one small bottle of silicone oil
- one plastic pipet
- one clear plastic beverage cup (250 mL/9 oz)
- two small plastic weighing dishes
- one small test tube (12 x 100 mm)
- one medium test tube (18 x 150 mm)
- one birthday candle
- In addition, each pair of students will need a wide-mouth beverage bottle for draining and supporting their syringes (not shown in figure).

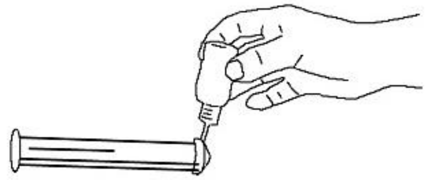


ure 19. The equipment that constitutes our microscale gas chemistry kit.

The In-Syringe Method for Preparing Gas Samples

The general strategy of the method is to react two substances in a 60 mL syringe. The limiting reagent is always used in solid form and is placed in a small vial cap. The second reagent is prepared as an aqueous solution. For example, one could generate CO_2(g) from excess aqueous acetic acid and solid $NaHCO_3$, as the limiting reagent.

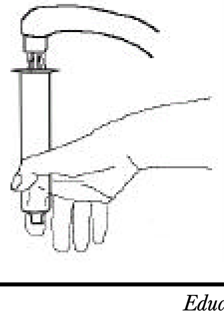
A. Getting started. Start by lubricating the seal. Lubricate the black rubber seal of the plunger with silicone oil.



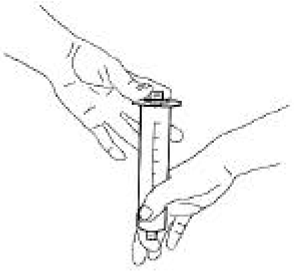
B. The solid reagent. The solid reagent is placed in the vial cap that is then lowered into the syringe barrel by water flotation. In the preparation of carbon dioxide, one would use 0.21 g baking soda, $NaHCO_3$. The following quantities of solid reagents are required for CO_2, H_2 and O_2:

To make:	**Use**:
Carbon dioxide	0.21 g sodium bicarbonate (baking soda), $NaHCO_3$(s)
Hydrogen	0.05 g magnesium, Mg(s) turnings
Oxygen	0.10 g potassium iodide, KI(s)

Fill the syringe barrel with water. Fill the barrel with water. Place your finger over the hole to form a seal. Fill completely to the top.

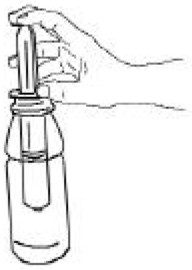


Float the vial cap. Float the vial cap containing the solid reagent on the water surface. This is easiest if the syringe barrel is filled completely to the top with water.



Lower the cap by flotation. Release the seal made by finger to lower the cap into the syringe barrel without spilling its contents. Allow the syringe to drain into a wide mouth beverage container. When successfully completed, the cap should rest upright on the bottom of a syringe with all reagent still in the cap. The syringe should always be held in a vertical position during these first steps.

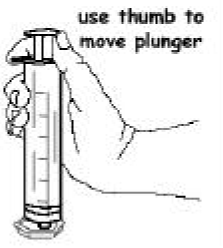
Install the plunger. Install the plunger while maintaining the syringe in a vertical position. The plunger should fit snugly against the rim of the vial cap.



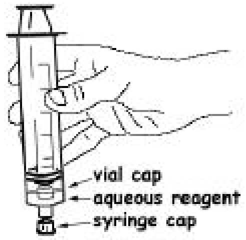
The aqueous reagent. The liquid reagent is drawn into the syringe as described below. In the preparation of carbon dioxide, one would use 5 mL vinegar, $HC_2H_3O_2$. The following quantities of aqueous reagents are required for CO_2, H_2 and O_2:

To make:	**Use:**
Carbon dioxide	5 mL acetic acid (vinegar), $HC_2H_3O_2(aq)$
Hydrogen	5 mL 2 M $HCl(aq)$
Oxygen	5 mL 6% $H_2O_2(aq)$

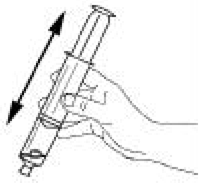
Draw aqueous reagent into syringe. The aqueous reagent, measured into a small weighing boat, is drawn into the syringe while maintaining the vertical position of the syringe. The vial cap with the solid reagent should float on the solution.



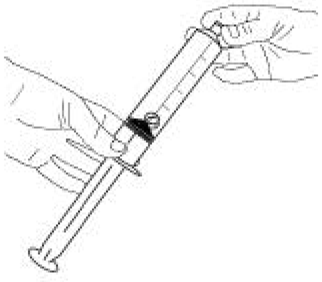
Install syringe cap. Push the syringe cap over the syringe fitting. It simply pushes on!



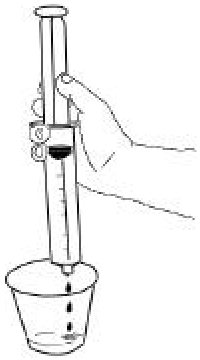
Generating the Gas. Shake the syringe in order to mix the reagents. As the liquid reagent splashes into the vial cap, gas generation will commence and the syringe plunger should move outward. It is sometimes necessary to gently help the plunger move up the barrel.



Remove cap to stop the reaction. After the plunger has reached the desired mark (usually 50 mL), tip the syringe so that it is positioned with plunger downward and syringe cap upward. Carefully remove the syringe cap assuming that the syringe may be under positive pressure.



Discharge reagents. Turn the syringe 180° and discharge the liquid reagent into the plastic cup. **Caution:** Never remove the syringe cap with the cap end of the syringe directed downward — reagents will spray out of the syringe. Immediately cap the syringe with the cap to prevent loss of gas by effusion.



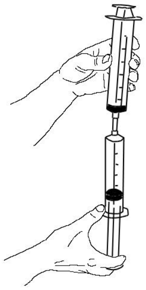
Cleaning the gas sample. The syringe filled with gas also contains droplets of excess reagents, and aqueous reaction products (sodium acetate in the case of CO_2, for example). There are two options: (1) Transfer the gas to a clean, dry syringe as described below; and (2) Wash away the drops of aqueous solutions. To do this, remove the syringe cap, draw 5 mL water into the syringe and recap. Shake the syringe to splash the water around, remove the cap and discharge the rinse water. For gases that are soluble in water, the first method must be used.

Other useful gas syringe techniques

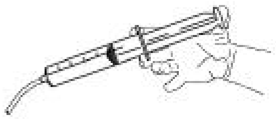
There are a four other techniques that come in handy when working with gases in syringes.

A. Syringe-to-syringe transfer procedure

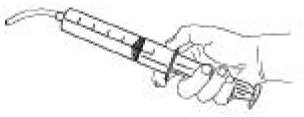
This procedure is used when two gases are to be mixed or when a gas sample cannot be washed (because the gas is water-soluble). In these instances, transfer the gas sample to a clean, dry syringe by a short connecting tube between the two syringes. The clean, dry syringe is positioned on top. Usually pushing in on the lower plunger will cause the upper plunger to move outward. Sometimes assistance is needed.



B. Controlled discharge of gas from a syringe. Plungers do not always move smoothly in their syringe barrels. As a result, gases may be discharged in large unintended portions (such as 40 mL all at once) if the method shown in the left diagram below is used. Instead, grasp the syringe by its plunger (right figure) and pull the barrel towards your hand. This simple technique will give you excellent control of gas delivery.



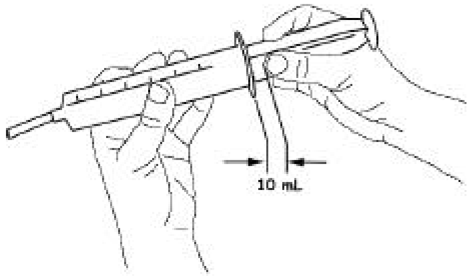
INCORRECT WAY



CORRECT WAY

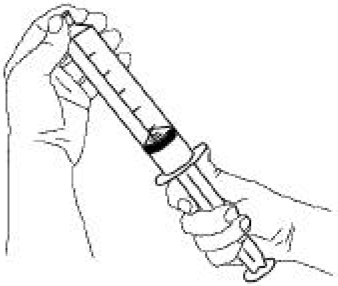
C. Discharging a specific volume of gas

Position thumb as a "stop" to discharge desired volume of gas and then push inward.

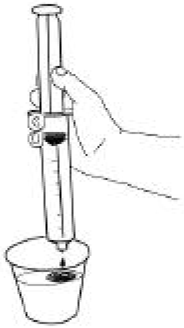


D. Preventing unwanted discharges of noxious gas

Some of the gases that can be generated by the in-syringe method are noxious and must not be discharged into breathable air. These gases are: nitric oxide, NO, nitrogen dioxide, NO_2, ammonia, NH_3. sulfur dioxide, SO_2, and hydrogen sulfide, H_2S. The use of syringes to generate such gas samples works exceptionally well and far better than any other method in preventing undesired discharges. There are two simple considerations to keep in mind whenever handling noxious gases: (1) Whenever opening the syringe (by removing the syringe cap), do so with the plunger slightly withdrawn (by 5 mL) so the contents are under a slight reduced pressure. Use your thumb to maintain the plunger in this position as shown in the drawing. This will allow a small amount of air to enter the syringe but no noxious gas will escape.



(2) After the gas sample has been generated, discharge the used reagents into a large cup of water to dilute them and prevent further reaction.



Clean-up and Storage

At the end of the experiments, clean the syringe parts, caps and tubing with soap and water. Use plenty of soap to remove oil from the rubber seal. This extends the life of the plunger. It may be necessary to use a 3 cm diameter brush to clean the inside of the barrel. Rinse all parts with distilled water. Be careful with the small parts because they can easily be lost down the drain. Store plunger out of barrel unless both are completely dry.

Experiments with Gases

Both our book [Mattson, 2003] and parallel website (described below) are organized with the teacher and student in mind. Part 1 is suited for use by a wide variety of audiences — ranging from middle school physical science students up through university-level chemistry students. Like most experiments and demonstrations, results and observations can be discussed and interpreted on a level appropriate for the students' background. Part 1 includes the preparation of carbon dioxide, hydrogen and oxygen along with over twenty experiments and demonstrations with these gases. Both book and website includes background information for each gas. The book includes questions for the students after each experiment. In most cases, there are two levels of questions depending on the students' level. (Answers are provided in the appendix.) The website includes hundreds of color photographs, a growing number of QuickTime movies and numerous links. The web version also includes electronic versions of a growing number of experiments that can be downloaded for use (with permission). The summary of Part 1 is:

Part 1. Getting Started — 3 Simple Gases

Getting Started — Generating Carbon Dioxide in a Large Syringe. (This section has been reproduced in this article.)

A. Experiments with Carbon Dioxide

1. Traditional limewater test for carbon dioxide
2. Acidity of carbon dioxide
3. Carbon dioxide extinguishes fires
4. Carbon dioxide and aqueous sodium hydroxide react
5. Carbon dioxide/carbonic acid equilibrium

B. Preparation of Hydrogen and Experiments

Preparation of hydrogen

Experiments with Hydrogen

1. Traditional test for hydrogen
2. Hydrogen forms explosive mixtures with air
3. Reversible conversion of copper metal and copper(II) oxide

4. Reduction of iron(III) oxide with hydrogen

Demonstrations and Advanced Experiments with Hydrogen

5. Effusion of hydrogen is faster than air
6. Hydrogen burns with a gentle flame
7. Disappearing/reappearing candle flame
8. Calcium and calcium hydride produce hydrogen in reactions with water
9. Deuterium isotope effect

C. Preparation of Oxygen and Experiments

Preparation of oxygen

Experiments with Oxygen

1. Traditional test for oxygen
2. Oxygen supports combustion
3. Dynamite soap
4. Hydrogen-oxygen rockets

Demonstrations and Advanced Experiments with Oxygen

5. Steel wool burns in oxygen
6. The Blue Bottle experiment
7. Oxygen makes the flame hotter
8. Mini-sponge shooter
9. Chemiluminescence

D. Gas Bags

Gases can be generated in much larger quantities using simple, ***gas bags*** made from food storage bags and this is useful when students need a supply of several gases. For example, in some experiments students need both hydrogen and oxygen for several of the experiments. The teacher may use the gas bag technique in order to prepare one or both of these gases for the students in the interest of saving time. One fascinating classroom demonstration is done with a gas bag of hydrogen: Combustion of hydrogen in oxygen demonstration. A flask as a musical instrument?

Part 2. Laboratory Experiments

Part 2 consists of six full lab period experiments that can be used with carbon dioxide, hydrogen and oxygen. These experiments are suited for use by high school chemistry students as well as university-level chemistry students.

The experiments are given in approximate order of difficulty. "Mystery Gas" is a good example of an inquiry-based learning lab. Students design and use a strategy to determine the identities of three gas samples. "Percent Composition" relates the volume of carbon dioxide produced from the acid decomposition of calcium carbonate to the composition of an antacid tablet. The "Carbonated Beverages" lab is a set of experiments that explores some of the properties of carbonated beverages and relates these observations to those made my Joseph Priestley in the 1770s. The "Molar Mass" lab works well for any gas, not just the three we have studied so far. It works especially well for heavy gases such as carbon dioxide, propane. Results are generally within a few percent of the actual value — much improved from the popular "molar mass of butane lab" that appears in many books.

The last two experiments, "Limiting Reagent" and "Barometric Pressure", along with "Percent Composition" all require the entire class to share their data that everyone will then use to complete the experiment.

Part 3. More gases

The gases described in Part 3 and the experiments that go with them should be conducted by individuals familiar and experienced with gas production using the syringe method. Five of the six gases described in this part have properties that make their proper use and handling more important than was the case for carbon dioxide, hydrogen and oxygen. As with part 1, each experiment comes with questions for the students.

A. Preparation of Nitrogen Oxides and Experiments

List of Experiments:

1. Conversion of nitric oxide to nitrogen dioxide
2. From nitrogen dioxide to nitric acid
3. LeChatelier principle and the NO_2/N_2O_4 equilibrium
4. High temperature favors the endothermic substance
5. Acid rain microchemistry
6. Acidic nature of nitrogen oxides
7. Well-plate reactions involving nitric oxide
8. Dinitrogen trioxide is a blue liquid

B. Preparation of Ammonia and Experiments

List of Experiments:

1. Ammonia is a base
2. Ammonia fountain

3. Acid-base reactions with fruit juices
4. Ammonia is more soluble at low temperature
5. Gaseous ammonia reacts with gaseous hydrogen chloride
6. Ammonia forms nitric oxide in the Ostwald process
7. Ammonia forms complex ions with transition metals

C. Preparation of Ethyne and Experiments

List of Experiments:

1. Ethyne reacts with permanganate
2. Sooty combustible of ethyne
3. Banging bubbles!
4. Ethyne/oxygen rockets
5. Ethyne reacts with aqueous bromine

D. Preparation of Sulfur Dioxide and Experiments

List of Experiments:

1. Sulfur dioxide reacts with water
2. Sulfur dioxide reacts quickly with sodium hydroxide
3. Sulfur dioxide and potassium permanganate react
4. Sulfur dioxide discolors many natural colors
5. Acid-rain microchemistry
6. Sulfur dioxide reacts with aqueous bromine

E. Preparation of Chlorine and Experiments

List of Experiments:

1. Chlorine and sodium hydroxide form bleach
2. Chlorine disproportionates in water to form acidic species
3. Chlorine discolors the natural colors of fruit juices
4. Testing colorfast fabrics
5. Chlorine reacts with aqueous sodium sulfite
6. Halogen activity series
7. Chlorine and sodium form sodium chloride
8. Hydrogen/chlorine rockets
9. Chemiluminescence and singlet oxygen.
10. Spectacular underwater fireworks!
11. Liquid and solid chlorine

F. Preparation of Nitrogen and Experiments

Part 4. Catalyst Tube Reactions

In Part 4 we describe a series of experiments that can be performed with an inexpensive, commercially available glass-encased heterogeneous palladium catalyst tube. The catalyst tube is suitable for demonstrating gas phase reactions in the classroom or teaching laboratory. In all cases, the products can be tested by simple chemical methods. The reactions include:

1. Oxidation of methane with air
2. Oxidation of ethene with air
3. Oxidation of carbon monoxide with air
4. Hydrogenation of ethene
5. Catalytic oxidation of ammonia
6. Methane and nitrogen dioxide
7. Carbon monoxide and nitrogen dioxide
8. Decomposition of nitrous oxide
9. Nitrous oxide and ammonia
10. Nitrous oxide and carbon monoxide
11. Nitrous oxide and methane

Part 5. Other Methods

In Part 5 we present five gases that cannot be generated by the In-Syringe Method because the reagents must be heated. Instead, we utilize a method that was first proposed by LeBlanc over two centuries ago and involves heating two reagents together and collecting the gas produced. We have modified the method to utilize 60 mL syringes for gas collection. The Thermal Method is used to generate hydrogen chloride, carbon monoxide, ethene, methane and nitrous oxide. For each gas, 6-11 experiments are described. Interested readers are referred to our website for more information.

In Part 5 we also introduce a third method for gas generation —using a microwave oven. We have found this method works for generating ammonia, oxygen, carbon monoxide, sulfur dioxide, methane and hydrogen chloride, however, the conditions vary wildly with the microwave oven. For most purposes, the In-Syringe or LeBlanc methods give more reliable results.

Part 6. Advanced Gases

The two gases described here are produced by the In-Syringe method. The preparation of these gases and the experiments that go with them should be conducted by individuals familiar and experienced with gas production using the In-Syringe method. These two gases are considered “advanced gases” for different reasons. Silane is an extremely pyrophoric gas and great caution must be exercised to prevent unintentional fires. For hydrogen sulfide, it is its offensive odor and high toxicity that warrant the "advanced" classification. Use of a fume hood is advised with both gases.

A. Preparation of Silane and Experiments

List of Experiments:

1. Silanes react with air
2. Silane reacts with oxygen
3. Silane reacts with chlorine
4. Thermal decomposition of silane
5. Reaction with aqueous potassium hydroxide

B. Preparation of Hydrogen Sulfide and Experiments

List of Experiments:

1. Hydrogen sulfide is slowly oxidized
2. Hydrogen sulfide is a weak acid
3. Reaction between hydrogen sulfide and aqueous sodium hydroxide
4. Hydrogen sulfide burns in oxygen with a howling blue flame
5. Reaction between hydrogen sulfide and sulfur dioxide yields elemental sulfur
6. Metal sulfide precipitation reactions
7. Oxidation of metal sulfides

Our Microscale Gas Chemistry Website

Our gas book, numerous color photographs of procedures, experiments and demonstrations, a few QuickTime movies of techniques and experiments are available on the web at our microscale gas chemistry website. Equipment ordering information and historical information are also available at the site. Use of the site is free.

http://mattson.creighton.edu/Microscale_Gas_Chemistry.html

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