Microscale Gas Chemistry

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The generation and study of gases has captured the imagination of scientists for centuries. Often invisible, seemingly weightless, elusive, fleeting, and dissipative, gases remained more or less misunderstood until the very end of the 18th Century. Two centuries of capturing, studying, preparing and experimenting with gases slowly revealed their mysterious nature. Johann van Helmont (coined the word *gas*), Robert Boyle, and John Mayow in the 17th Century and Stephen Hales, Joseph Black, Henry Cavendish, Joseph Priestley, Antoine Lavoisier and Carl Scheele in the 18th Century, each contributed a part to unraveling the mysteries and secrets of gases. Along the way, gases provided plenty of false leads, with the greatest one resulting in the *phlogiston theory*. Phlogiston formed the basis of chemistry understanding for most of the 18th Century — about as long as we have relied on quantum mechanics for our understanding of the atom. It was based on the four-element model of the ancient Greeks, and along with a number of interesting modifications, it explained chemical reactions in terms of gain or loss of phlogiston. The phlogiston theory was riddled with inconsistencies, especially as it pertained to mass loss or gain. Most scientist-philosophers of the era did not use balances and, of course, the law of conservation of mass was not yet known, so whether or not mass was lost, gained, or conserved was not especially important to most investigators of the time. The phlogiston theory actually became stronger towards the end of its lifetime with the alleged discoveries of phlogiston itself (hydrogen/Cavendish) and *dephlogisticated air* (oxygen/Priestley.) It was Antoine Lavoisier in 1779, and a gas, specifically oxygen, that signaled the beginning of the end of the phlogiston theory. In 1783, Lavoisier published a critical essay titled *Reflections on Phlogiston* and in 1789, his famous *Elements of Chemistry* appeared (and is still being reprinted.) Old theories die hard and converts were few and far between at first, but by 1790, the new *oxygen theory* had gained numerous followers and eventually paved the way to the era of modern chemistry. For some individuals, including Joseph Priestley, phlogiston remained the correct explanation for his understanding of chemistry.

The various pieces of equipment to study gases have ranged from simple to complex. By the late nineteenth century, chemistry textbooks described methods for students to use to make and study gases. These student laboratory methods still appear in high school and general chemistry texts today. They were often elaborate, and time-consuming, and almost all were based on pneumatic methods of the 18th Century. Within the past fifty years, laboratory equipment and methods have greatly improved, especially with the advent of microscale chemistry.

In 1992 Hubert Alyea proposed an ingenious method for the safe generation of gases, including noxious gases, for classroom use *(1).* The method, quite unlike any before it, utilized disposable plastic syringes in which two reagents were separately contained until it was time to generate the gas. The enclosed nature of the syringe potentially eliminated the risk of exposure of the gas to the experimenter. At the time that Alyea's article appeared, I was teaching a descriptive inorganic laboratory course in which we generated a number of gases using the 18th Century pneumatic trough methods. With a few adventurous students, we tried the syringe method and with some tinkering, it worked! Within weeks, the troughs were on the shelves, never to see use again!

Despite the brilliance of Alyea's idea, there were a few significant details that were not addressed in his half-page article. Alyea did not describe how one might place the cap containing the solid reagent into the syringe barrel without spilling it.[1] If even a grain spilled, it was impossible to draw the liquid reagent into the syringe. After a variety of comedic attempts, we worked out a reliable method whereby we lowered the cap of dry reagent by flotation. The second shortcoming of Alyea's method involved keeping the syringe sealed during the reaction. He described pushing the syringe opening against a rubber stopper in order to form a seal. Because it was necessary to shake the syringes in order to mix the reagents, these seals seldom held when one was performing the reaction. Accidental discharges were common and each time the reagents sprayed out, so my students continued to work in fume hoods. It was not until 1995 that I "discovered" LuerLok syringe caps, thanks to Mark Meszaros, who introduced me to this miracle product! With syringe caps (cost: 20 cents), I could generate gases in class or bring syringes filled with gases to class and perform experiments without discharging gas into the room.

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[1] 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 went on to describe the generation of hydrogen sulfide as an example!

By 1994, there were about ten gases that we could generate using the in-syringe method. In the years 1992 – 1995, we had worked out a couple of dozen experiments that could be done with these gases. Because syringe caps made gas generation easy and reliable, I decided to propose an article for ***Chem13 News***. The editor, Lew Brubacher, was interested and wondered if I could deliver a 10-part series on microscale gas chemistry with a different gas featured each month! This fortuitously coincided with my sabbatical and a period of unfettered energy in my life, so I agreed. Our first article, titled "Microscale Gas Chemistry: Generating Gases in Large Syringes" appeared in the October 1996 issue of ***Chem13 News***. Over the ensuing issues, we presented the preparation of a new gas each month along with a number of experiments and activities that could be done with each gas. Parts 2 – 10 covered, in order, carbon dioxide, hydrogen, oxygen and nitrogen, nitrogen oxides, ammonia, ethyne, hydrogen sulfide, sulfur dioxide and chlorine.

The "10-part series" was not the end of it, however. Within a few months, other interesting ideas came to us and ***Chem13 News*** was again our venue of choice. Parts 11 – 29 have appeared over the ten years 1998 – 2007, and Part 30 is being formulated. The best way to revisit the series is on our website or by purchasing our book (both described below.) These media are continually updated as improvements are discovered.

What is Microscale Gas Chemistry?

Among the pioneers in developing and promoting the microscale chemistry movement are Mono Singh, Zvi Szafran, and Ronald Pike, founders of the National Microscale Chemistry Center (NMCC). The Center now appears dormant (since 2003), but the website is still available and I would encourage interested readers to visit the site. The tenets of microscale chemistry according to the NMCC 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 NMCC and other microscale promulgators did not address gases. Our series in ***Chem13 News*** was the first to use the phrase "microscale gas chemistry". We asked ourselves, "Are we really microscale?" We use 60 mL syringes![2] This begs the question, what

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[2] Smaller syringes can also be used. Others have described non-syringe methods to generate and study gases in vessels as small soap bubbles or pipet bulbs. These methods are reviewed in the Supplemental Materials.

exactly constitutes "microscale gas chemistry"? The word "microscale" has never been defined in terms of specific quantities, volumes or costs. For our gas chemistry, we believe that we are microscale in terms of costs and environmental impact. This resonates perfectly with the tenets of the NMCC stated above. Our three most commonly prepared gases, carbon dioxide, hydrogen and oxygen each cost just pennies to prepare 60 mL samples. In each case, the spent reagents can be pH neutralized and safely discarded down the drain. Thirdly, generating and experimenting with gases in syringes is easy and fun for the students, in large part because they can "see" the gas and deliver milliliter volumes as desired. So the syringe method actually enhances the quality of the educational experience. Plastic syringes are easy to use, inexpensive, unbreakable and last for years.

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 plastic syringes allows for this visualization.

- ***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 *Chem13 News Series*, our website and book.

What sort of classroom demonstrations and classroom experiments can be performed with gases? Most teachers are initially interested in carbon dioxide, hydrogen and oxygen. Readers can find these experiments at our website or in our book. They originally appeared in our ***Chem13 News*** series. A summary of the contents of the website/book/series is given below for these three gases.

A. Three Easy Gases

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

Preparation of Hydrogen and Experiments

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

Preparation of Oxygen and Experiments

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

B. 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.

C. Laboratory Experiments

We describe 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 six experiments, given in approximate order of difficulty are briefly described here. "Mystery Gas" is a good example of an inquiry-based learning laboratory activity. Students design and use a strategy to determine the identities of three gas samples. The "Percent Composition" lab 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. It works especially well for gases with MM >

25 g/mol. 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.

D. More gases.

Our series, website and book also describe the preparation of eight more gases. These gases 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. The gases covered include nitrogen monoxide, nitrogen dioxide, ammonia, ethyne, sulfur dioxide, chlorine, silane, and hydrogen sulfide.

E. Catalyst Tube Reactions

In 2003, we published an article titled, “Demonstrating Heterogeneous Gas Phase Catalysis with the Gas Reaction Catalyst Tube” *(2)*. The article, reproduced at our website and in our book, describs 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 that can be demonstrated are: 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; and 11. Nitrous oxide and methane.

F. Gases via Thermal Methods

Our series/website/book include the preparation and study of 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.

G. Gases via the Microwave Oven

Our series/website/book include the preparation and study of several gases in the microwave oven, including ammonia, oxygen, carbon monoxide, sulfur dioxide, methane and hydrogen chloride. For most purposes, the In-Syringe or LeBlanc (thermal) methods give more reliable results.

H. Ozone.

Ozone is a gas that we create and use as it is made. The gas is made using a chamber made from a pipet bulb with a platinum wire and a mechanical pencil lead serving as electrodes. The rate of generation is a mere 800 nanomoles/minute (enough to smell). Our ozone experiments have been published *(3, 4)* and appear at the website. They will be included in the book with the next edition.

Supplemental Materials.

We have created a website to supplement this article (http://mattson.creighton.edu/Chem13_40th_Yr_Commemorative/index.html). Contents include the following, most as pdf downloadable files:

1. This article
2. A Brief History of Gas Chemistry
3. Details for preparing gases in syringes
4. Table of contents for our book listing all 17 gases and 144 experiments
5. The complete carbon dioxide chapter (as a sample from the book)
6. The complete molar mass of a gas chapter (as a sample from the book)
7. Other microscale gas chemistry methods

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

Reference:

1. Alyea, H. N., “Syringe Gas Generators,” ***Journal Chemical Education***, 1992, **69,** 65.

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3. Ibanez, J. G.; Alatorre-Ordaz, A.; Mayen-Mondragon, R.; Moran-Moran, M. T.; Bruce Mattson, Scot Eskestrand; ***Journal of Chemical Education*** 2005, **82**, 1546-1548.

4. Mattson, B.; Michels, J.; Gallegos, S.; Ibanez, J.; Alatorre-Ordaz, A.; Mayen-Mondragon, R.; and Moran-Moran, M. T.; ***Chem13 News*** **2007**, **344**, 6 – 11.