

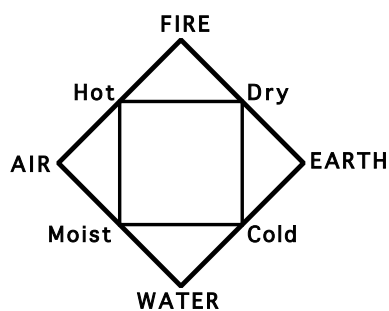
A Brief History of the Study of Gas Chemistry.

If we were to greatly simplify the history of chemistry so that each century were defined by a single major field of discovery, the twentieth century would be remembered as the Century of Nuclear Chemistry during which our considerable understanding of the subject was developed from earlier theories. Then moving backwards in time, the nineteenth century would be remembered as the Century of Organic Chemistry during which period most of the concepts and principles of organic chemistry were discovered. The eighteenth century would be the Century of Gas Chemistry, marked by the discovery of most of the common gases. Ingenious techniques with which to generate, collect and study gases were invented at that time. Entire laboratories were dedicated to the study of the new discipline of '*pneumatics*'. Their discoverers gave the gases names such as '*fixed air*', '*dephlogisticated air*', and '*inflammable air*'. Despite these substantial laboratory accomplishments, the actual chemical identities of these gases remained complete mysteries until the very end of the century. The story of the early days of gas chemistry is interesting and important. It spans the entire 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.

In order to understand the thinking of the pneumatic chemists of the 1700s, it is necessary to consider for a moment what was known and believed about chemistry and gases three centuries ago. First of all, quite a lot of chemical knowledge had been experienced by scientists and others. Numerous applied aspects of chemistry had been practiced and perfected from the earliest beginnings of recorded history. Copper and lead have been in use in Egypt from about 4000 BC. Bronze (a mixture of copper and tin) was first produced around 3000 BC. The chemical art of making durable ceramic materials had improved through 'research and development' dating back 5000 years. The pottery kilns used to fire ceramics (causing the reaction to take place) date back to 3000 BC. Other examples of applied chemistry that were highly developed by 1700 include the production of glass, paints, pigments, dyes, beers, wines and medicines. All of these

are examples of solid or liquid materials. They were all important products and for that reason the processes by which they were made were improved over the centuries. Unlike solids or liquids, gases remained poorly understood.

The philosophers of classical Greece were the first to seek knowledge for its own sake. They attempted to develop a comprehensive philosophy that explained all aspects of the material world. Around 350 BC, Aristotle was emerging as one of the most brilliant scholars of the time. He was interested in a wide variety of thoughts and ideas and his influence on subsequent thought was widespread. Unfortunately for the development of chemistry as a theoretical discipline, Aristotle rejected the earlier ideas of Democritus that substances were built from small, indivisible particles called atoms, and built on the ideas of Empedocles, who felt that all matter was composed of some combination of earth, air, fire, and water. Aristotle broadened Empedocles' four elements so that earth represented the solid state, air represented the gaseous state and water represented the liquid state. 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 and the relationship between the forms and elements is shown here:



Thus, water (representing all liquids) was cold and moist, air was hot and moist, fire was hot and dry, and earth (representing all solids) was cold and dry. Every substance on earth was some combination of the four elements. During transformations, the primary matter was unaltered but the form was changed. Aristotle's stature among scholars was such that for twenty-one centuries after his death he was still widely regarded as the ultimate authority on matters of science. Even though his theory did little to explain much of the physical world, there was no better theory and few felt they could question the ideas of Aristotle.

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 in a device similar to that shown in Figure 1. He noted that hydrogen, which he called 'factitious air' was highly flammable. It is significant and noteworthy that he was the first scientist to collect a gas in a vessel.

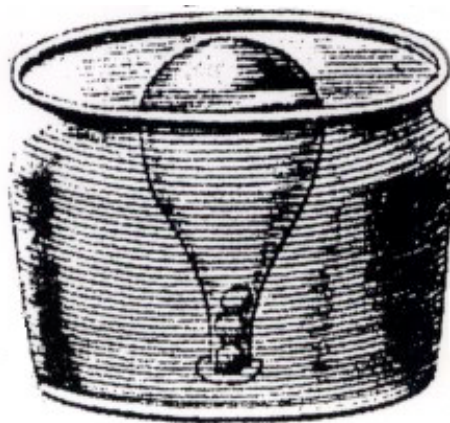


Figure 1. From A Short History of Chemistry by J. R. Partington, Harper and Brothers, 1937

The ability to study gases advanced significantly with the invention of the pneumatic trough by Stephen Hales in about 1700. Hales's pneumatic trough, shown in Figure 2, consisted of a vessel constructed from a bent gun barrel with one end sealed off and a large glass vessel which was filled with water and suspended inverted in a tub of water.

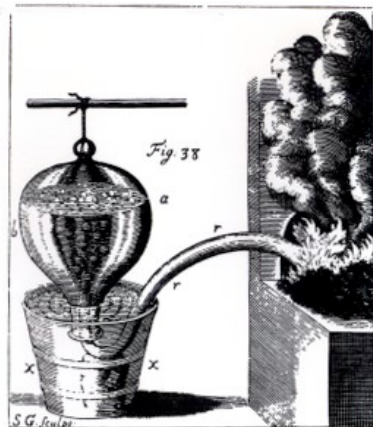


Figure 2. From S. Hales, *Vegetable Staticks and The Historical Background of Chemistry* by Henry M. Leicester, Dover Publications, Inc., New York, 1956.

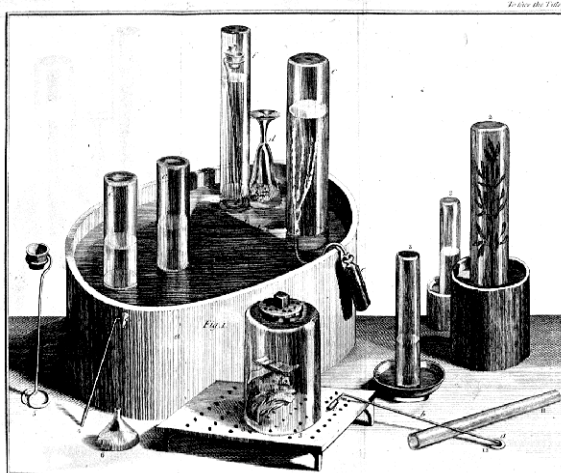
Substances were placed in the iron vessel and heated to drive off 'airs.' Hales missed the opportunity to study the properties of the 'airs' produced and was more interested in studying the amounts given off from various substances. He also performed some chemical reactions with the device that did not require heat. He produced hydrogen by the reaction of acids on iron filings and know that it was flammable. He believed that all the gases were principally ordinary air and that some had more 'particles of inflammability'.

The 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 only simmered until they were 'improved' and popularized by Georg Stahl in 1703. Stahl coined the word '*phlogiston*' which was a subtle material possessed by substances and could only 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 the time Stahls' textbook appeared in 1723, 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 made numerous

important contribution to chemistry and in particular to the chemistry of gases by establishing that gases can have chemical identities and are not simply 'airs.' His work, published in a 1756 book, focused on alkaline substances and contained much discussion on the unique properties of a gas he called *fixed air* (now know to be carbon dioxide).

Joseph Priestley was one of the most important pneumatic chemists of the 18th century. A contemporary of Joseph Black, Priestley began his studies on gases 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.' Using some of the equipment shown in this famous drawing from about 1770 (Figure 3), Priestley performed hundreds of experiments on gases and is credited with the discovery of many of the gases that will be prepared and studied in this book. He is credited with the discovery and study of nitric oxide (NO), nitrogen dioxide (NO₂), nitrogen (N₂), carbon monoxide (CO), carbon monoxide (CO₂) and oxygen (O₂). Priestley knew that the gases he produced were unique substances with their own physical and chemical properties. Although he never abandoned his faith in the phlogiston theory, his experiments played a significant role in undermining and eventually debunking it.



*Figure 3. Priestley's apparatus for pneumatic experiments. The tub was for washing linen. The inverted jar in the foreground is a beer mug and contains a mouse. From **Joseph Priestley** by F. W. Gibbs, Doubleday & Company, Inc., Garden City, New York; 1967.*

Another pneumatic chemist contemporary of the times was Henry Cavendish, credited for the discovery of hydrogen in 1766. Cavendish was an extremely wealthy and eccentric recluse as well as a masterful experimentalist. Some of the equipment that he used is shown in Figure 4.

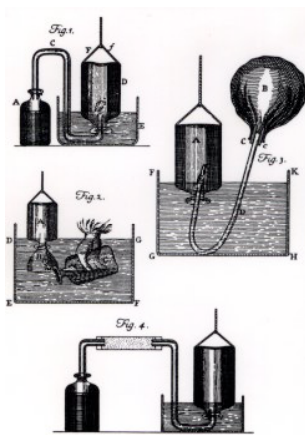
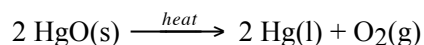


Figure 4. Apparatuses used by Cavendish for manipulating gases from *A Short History of Chemistry* by J. R. Partington, Harper and Brothers, 1937

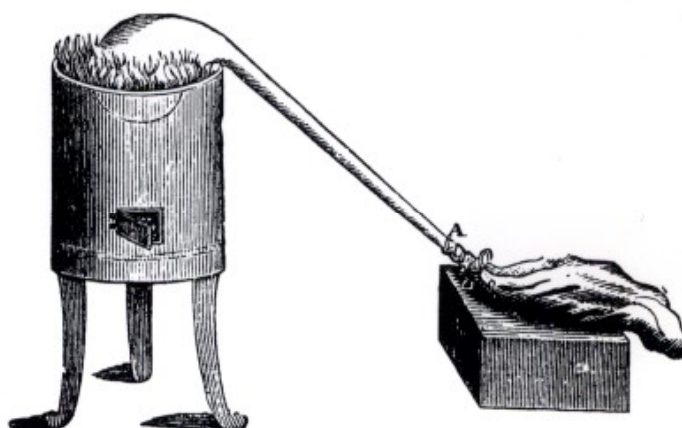
Like Priestley and most prominent English scientists of the period, Cavendish was unwaveringly dedicated to the phlogiston theory. He performed numerous studies on *inflammable air* (hydrogen) and came to believe that it was phlogiston itself.

Priestley's most famous discovery was that of oxygen in 1774. While investigating the properties of substances given to him by his friend, John Warltire, Priestley directed a 12-inch diameter lens on one of these materials, *mercurius calcinatus per se* (HgO). The lens allowed Priestley to heat the compound to a high enough temperature that it decomposed into mercury and an 'air.' In modern terms, he performed the following reaction:



This observation posed a dilemma that could not be explained by the phlogiston theory. The problem was that when mercury has heated at low temperatures, it formed *mercurius calcinatus per se* (HgO) and in doing so had given up phlogiston. When Priestley heated *mercurius calcinatus per se* to an even higher temperature, it was expected that it could yield nothing more. Further, the gas formed made a candle burn brighter and with remarkable vigor and was better than air to breathe. Priestley noted that this new substance, which he called *dephlogisticated air* made 'his breast felt peculiarly light and easy for some time afterwards'. The dilemma related to the fact that *mercurius calcinatus per se* contain this 'dephlogisticated air.'

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 the scientific community had already credited Priestley with the discovery. Scheele was one of the great scientists of the 18th century. He is credited with the discovery of chlorine in 1774. A drawing of Scheele's retort and gas bag is shown in Figure 5. (Retorts are seldom used in modern times, but their use was still widespread up through the mid-20th century.)



*Figure 5. Scheele's retort and airbag from **A Short History of Chemistry** by J. R. Partington, Harper and Brothers, 1937.*

Priestley visited Antoine Lavoisier in October, 1774, two months after his discovery of dephlogisticated air. While Priestley related his recent investigations and how greatly he was perplexed by the results, Lavoisier was not nearly as surprised. He had already suspected that a gas was removed when a metal *calx* (oxide) was reduced to the metal. This encounter with Priestley led to Lavoisier's most famous experiment using the apparatus shown in Figure 6 to both oxidize and then reduce mercury.

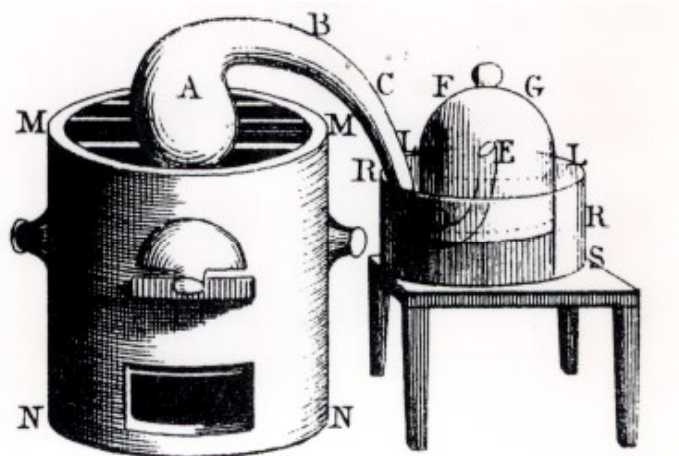
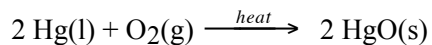


Figure 6. Lavoisier's mercury calx apparatus from *The History of Chemistry*, John Hudson, Chapman & Hall, New York, 1992.

In the first part of the experiment, Lavoisier used this apparatus to heat mercury in air. After twelve days of heating to near boiling, the mercury had developed a coating of *mercury calx* (HgO) which floated on the surface and the volume of air had decreased by about one-sixth. Chemically, he performed the following reaction with O₂(g) as the limiting reagent:



Lavoisier found that the 'air' remaining in the retort was neither fit for combustion nor respiration. He called this *mephitic air*. Next he placed the mercury calx in a smaller retort and heated it more strongly to convert the calx back into mercury as Priestley had done earlier (the exact opposite of the above reaction). Lavoisier measured the volume of the gas produced and found it to be identical to the volume of air lost when the calx was formed. He also noted the special properties of the gas produced, which he called *eminently respirable air*.

By this time Lavoisier was convinced that the phlogiston theory was wrong. In February, 1773 (19 months before Priestley's visit) Lavoisier wrote a prediction in his laboratory notebook that the whole of scientific investigations currently underway in Europe would "bring about a revolution in physics and chemistry." Lavoisier was aware that the current investigations throughout Europe were likely to cause increasing doubt in the phlogiston theory. He noted that chemists were making phlogiston suitably vague in

order for it to fit the explanations required of it. Sometimes phlogiston had weight, sometimes it was weightless. Sometimes it was free fire, sometimes it was fire combined with earth. Lavoisier's prediction prove to be accurate and Lavoisier, himself, turned out to be the architect of the revolution. In 1779, five years after its discovery, Lavoisier proposed the name '*oxygen*' and began formulating the tenets of the '*oxygen theory*'. Lavoisier did not have to wait long for the conclusive proof he needed to confirm his new theory.

In the years 1781 - 1783, Priestley and Cavendish performed a series of experiments that led to the discovery that water was composed of *inflammable air* (H₂) and *dephlogisticated air* (O₂). Cavendish accurately determined that the ratio of gases was 2.02:1. In 1783 Charles Blagden, Cavendish's assistant, visited Lavoisier in Paris and related the results of these studies. After repeating the water experiments, 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*.

The end of the phlogiston theory and the birth of modern chemistry occurred quite quickly and is largely credited to Lavoisier. In less than a decade, most of the chemists had converted their beliefs to Lavoisier's 'oxygen theory'. Lavoisier believed that there were numerous elements and introduced a nomenclature which is still used today. For example, *inflammable air* became the element hydrogen, named by Lavoisier from the Greek words *hydro genes* meaning water-forming. His ideas regarding the chemical elements triggered a 20-year revolution in chemical thinking that had not been seen in all of history prior to that and has not been rivaled since. Lavoisier set forth his ideas in a book titled *Elements of Chemistry* (1789) which was quickly translated into many languages. In many respects, modern chemistry books are similar to this pivotal work by Lavoisier.

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.

Lavoisier's theory set chemistry on the right course. Two other theories of the 19th century brought chemistry into sharper focus and largely established our present understanding of the subject. John Dalton's atomic theory, set forth in the early 1800s, was developed from the ideas of Democritus 2200 years earlier, and established the nature of atoms and how they combine to form compounds. Mendeleev's development of the periodic arrangement of the elements in 1869 established order and the ability to predict and expect analogies between various elements.

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' pneumatic trough (Figure 2) looks odd, but the basic idea is still widely used today although it has been considerably modified and simplified. By 1830, retorts were used to generate gases (Figure 7).

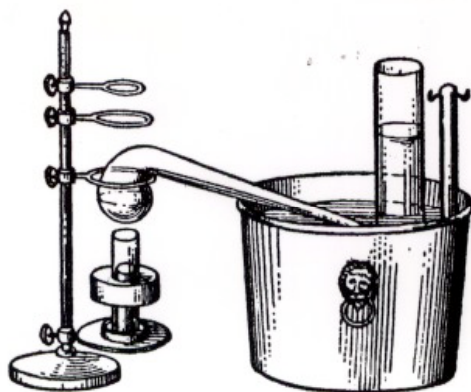
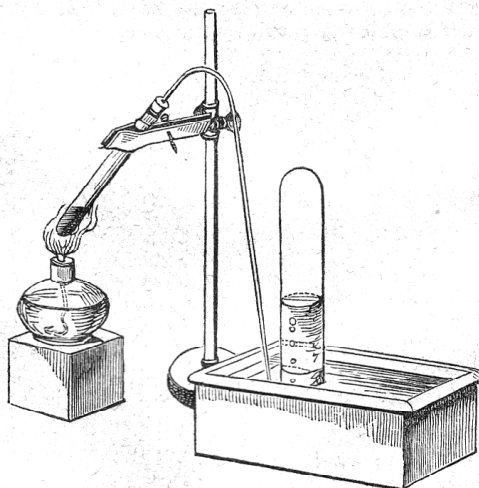


Figure 7. Use of a retort to produce and collect gases. Note the lion's head handle on the trough.

The modern pneumatic trough has changed little in the past 200 years. This diagram (Figure 8) is from a 1845 textbook.



*Figure 8. Use of a pneumatic trough to collect oxygen. From Fownes, G., **Elementary Chemistry, Theoretical and Practical**, Lea & Blanchard Publishers, Philadelphia, 1845.*

Chemists on a budget could follow the advice of Storer & Lindsay in their 1874 textbook to construct a cheap pneumatic trough from a stoneware pan and a flower-pot saucer (Figure 9).

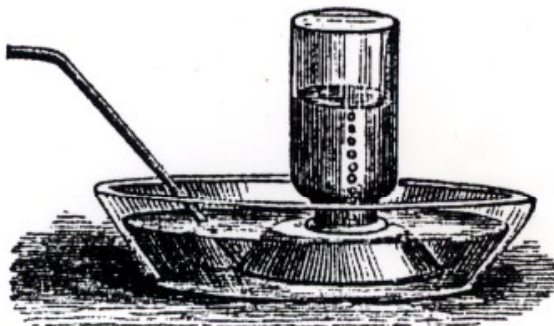


Fig. XXI.

*Figure 9. A 'cheap pneumatic trough' from **An Elementary Manual of Chemistry** by F. H. Storer and W. B. Lindsay, American Book Company, 1894.*

Another 19th century device commonly employed to generate gases was the Wolff's flask (Figure 10). This drawing was taken from Ira Remsen's 1886 textbook in which he made extensive use of the Wolff's flask to prepare and study gases.

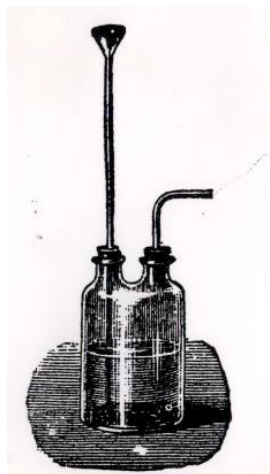


Figure 10. A Wolff's flask was used to prepare a number of gases, including hydrogen. From *An Introduction to the Study of Chemistry* by Ira Remsen; Henry Holt and Company, New York, 1886.

The 19th century Kipp's generator (Figure 11) provided chemists with an ever-ready source of gas. Gases such as H_2S were generated by this device, which allowed the chemist to start and stop the reaction by simply turning the valve. When the valve was opened, the liquid reagent flowed downward from the top reservoir into the lower reservoir. This pushed the gas out the outlet while the liquid would come in contact with the solid in the middle reservoir generating more gas. When the valve was closed, the accumulating gas forced the liquid reagent back into the reservoir and away from the solid reagent.

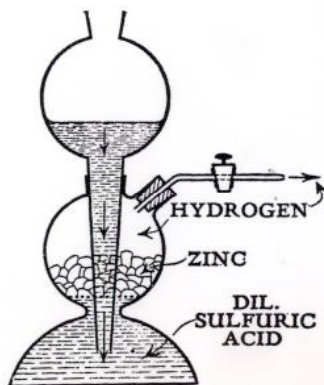


Figure 11. A Kipp's generator for generating H_2 , H_2S and many other gases. From *First Principles of Chemistry*, by Raymond Brownlee, William Hancock, Robert Fuller, Michael Sohon and Jesse Whitsit, Allyn and Bacon, 1931.

A similar but simpler alternative to the Wolff's flask was the 1 or 2-holed stoppered flask as shown in Figure 12. The left device is from 1845 and the right device is from 1886. The latter device features several refinements including the thistle funnel with an air-lock loop. This device was suggested for the preparation of Cl_2 and HCl .

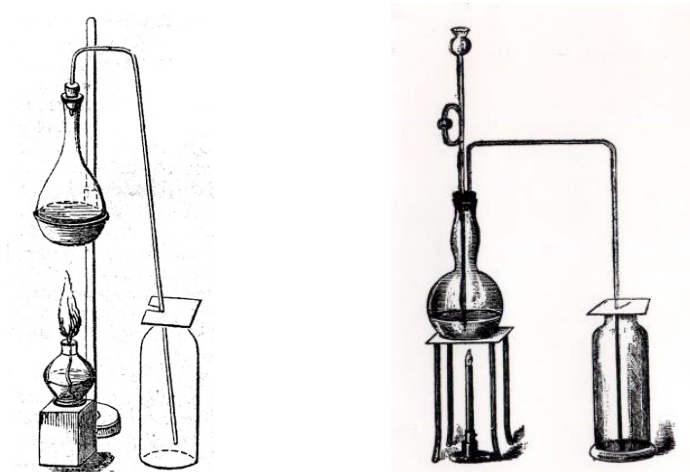


Figure 12. (a) Preparation of Cl_2 , 1845. From Fownes, G., *Elementary Chemistry, Theoretical and Practical*, Lea & Blanchard Publishers, Philadelphia, 1845; (b) Preparation of Cl_2 , 1886. From *An Introduction to the Study of Chemistry* by Ira Remsen; Henry Holt and Company, New York, 1886

In 1992 Hubert Alyea proposed an ingenious method for the safe generation of gases, including noxious gases, for classroom use. The method utilizes a large disposable plastic syringe (Figure 13). 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. Alyea's method is used in modified form throughout this book.

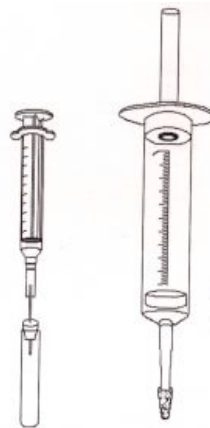
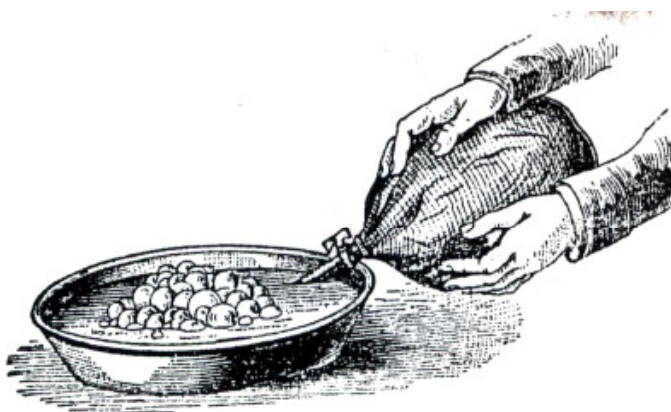


Figure 13. From Hubert N. Alyea, *J. Chem. Educ.*, **69** 65 (1992)

The generation and study of gases has been an important endeavor in the history of modern chemistry. It has also been an enjoyable endeavor that has captured the imagination of scientists for centuries. Consider the 19th century rubber gas-bag and apparatus shown in Figure 14. The figure appeared in the 1874 text by Storer & Lindsay in which they recommended filling the bag with hydrogen and oxygen. After bubbling the gas through a soap solution to prepare large bubbles, the bubbles were ignited with a tremendous bang. This very experiment is one that will be performed in this book.



*Figure 14. An airbag containing a 2:1 mixture of H_2 and O_2 .
The soap bubbles produced were then ignited. **An
Elementary Manual of Chemistry** by F. H. Storer and W. B.
Lindsay, American Book Company, 1894.*

Perhaps the most celebrated account of pneumatic chemists enjoying their endeavor is provided in the James Gillray caricature of a program at the Royal Institution around 1800 (Figure 14). The drawing captures the results of some demonstrations on the properties of nitrous oxide (laughing gas). The lecturer is Thomas Garrett. In the background with the bellows is Humphry Davy and standing at the right looking on is Count Rumford. The man shown inhaling the gas was likely a volunteer from the audience, which consisted of wealthy benefactors of the Institution.



Figure 14. Experiments with nitrous oxide at the Royal Institution from *Creations of Fire — Chemistry's: Lively History from Alchemy to the Atomic Age*; Cathy Cobb and Harold Goldwhite; Plenum Press, 1995; John F. Kennedy Library, California State University, Los Angeles.

From Aristotle to Alyea the properties of the gases have been gradually unveiled. The mysterious nature of gases — their invisibility, their 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 pneumatic chemists. By the late nineteenth century, chemistry textbooks described methods for student use. The experiments called for pneumatic troughs and elaborate equipment. Experiments were time-consuming and noxious gases were generated in quantities that were often potentially dangerous. With this book, you will learn to produce and study a variety of gases, safely contained within manageable syringes. Each gas takes no more than five minutes to generate and is immediately available for use in numerous simple experiments. From university professors to high school students, these simple methods will enhance the understanding of gases.