THE CHEMISTRY OF FIXED AIR

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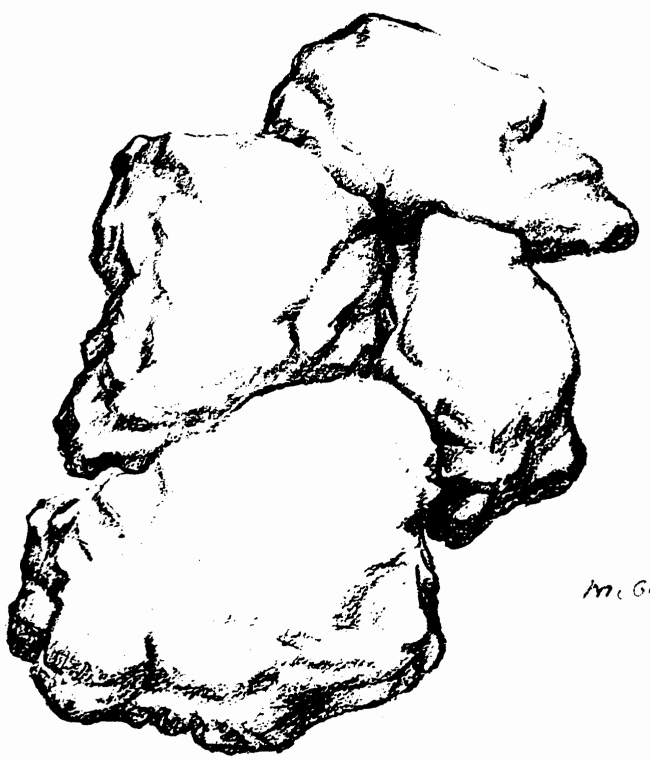

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INTRODUCTION

In this HISTORY OF SCIENCE CASE we will make a critical study of a part of the development of a major scientific idea. Although we want to learn something about this idea, our chief interest in this case will be to find out as much as we can about

- the methods used by scientists
- the means by which science advances and the conditions under which it flourishes
- the personalities and human qualities of scientists
- the interplay of social, economic, technological, and psychological factors with the progress of science
- the importance to science of accurate and accessible records, constantly improved instruments, and free communication between scientists

To study this case effectively, you will need to do more than simply read the story that appears on the left-hand pages of the first section of this booklet. In the margins to the left of the narrative you will find numerous comments and questions. These marginal notes are intended to guide your thinking and to motivate class discussions about the points illustrated by the case. On the right-hand pages, marginal questions have been repeated in expanded form and spaces in which you may write your answers have been provided. (If, however, you are instructed to write your responses on a separate sheet of paper rather than in the case booklet, be sure to number them the same as the questions to which they correspond.) These questions are different from those found in many texts. Often you will not find simple answers to the questions in this booklet. Many of them are designed to challenge you to think for yourself, to seek ideas or information from other books, and to express your own opinions and defend them.

Also included on the right-hand pages are a number of experiments which are a very important part of the study of this case. You should complete as many of them as possible to help you understand and appreciate the situations faced by the scientists as they developed their ideas. Additional activities and exercises follow the narrative, and your teacher may suggest others that you can do in connection with this case. On the last page of this booklet you will find a listing of some additional books and articles relating to the story of this particular case.

Some students may think that this case is out of date because the story is set in the scientific past. Nothing could be further from the truth. The points about science and scientists that are featured in this case are as valid today as they were in the past. The methods of scientific investigations are much the same as they have been for several hundred years; the nonscientific factors now involved in the progress of science are similar to those that were involved in it in earlier times; the characteristics and personalities of scientists have always been important factors in the story of science; and, as in the past, the progress of science today continues to be dependent upon adequate recording of information, free communication of facts and ideas, and improved instrumentation. These aspects of science were the same yesterday as they are today, and they will remain the same tomorrow.

L. E. K.

Picture reproduced by courtesy of the University of Edinburgh.

As a young medical student at the University of Edinburgh, Joseph Black carried out a series of experiments that led him to investigate the chemistry of fixed air. Black was born on 16 April 1728 at Bordeaux. At the age of twelve he was sent to school in Belfast, and in 1744 he entered the University of Glasgow. After completing his medical studies Black became professor of chemistry at the University of Glasgow in 1756. Ten years later he became professor of chemistry at the University of Edinburgh, where he remained until his death on 6 December 1799.

Joseph Black and his pioneering study of fixed air are the main focus of this case. In addition to Black, the other principal scientists you will meet are:

STEPHEN HALES, English clergyman and chemist
Born Bekesbourne, England, 1677; died Teddington, England, 1761

HENRY CAVENDISH, English chemist
Born Nice, Italy (now in France), 1731; died London, England, 1810

JOSEPH PRIESTLEY, English clergyman and chemist
Born Fieldhead, England, 1733; died Northumberland, Pa., USA, 1804

KARL WILHELM SCHEELE, Swedish pharmacist
Born Stralsund, Sweden (now in Germany), 1742; died Köping, Sweden, 1786

ANTOINE LAURENT LAVOISIER, French chemist and public servant
Born Paris, France, 1743; died Paris, France, 1794

THE CHEMISTRY OF FIXED AIR

What is "fixed air"? It is a dense, colorless, odorless gas that today is called carbon dioxide. For several good reasons it was given the name "fixed air" by Joseph Black, a Scottish medical doctor and professor of chemistry who was the first person to study this material carefully. Black's studies of "fixed air" were carried out about the middle of the eighteenth century and opened up a new and fruitful line of investigation that was to lead to some of the fresh concepts of modern chemistry.

The chemical terms that Professor Black used and taught to his students during most of his career may seem strange and unfamiliar to you. This is because in this case booklet we are dealing with an era before the introduction and general acceptance of the chemical terminology that we use today. Black does not use such familiar terms as "oxygen," "carbon dioxide," "calcium carbonate," or "sulfuric acid." He does not use chemical formulas, and he does not write equations; he says nothing about atoms or molecules. Many of these present-day names and ideas had not been invented when Black began his researches. Yet, we must remember that Black studied and lived in essentially the same physical world that we live in today. The materials he worked with and the behavior of these materials have remained the same from Black's time to ours; only the man-made labels attached to the materials and the chemist's concepts that describe their behavior have changed. We shall see, as we study this case, what Black and his contemporaries learned about the properties and chemical behavior of "fixed air." We shall see, too, some of the widespread effects of their new knowledge.

Is this true? (1)

In 1753 Joseph Black was a young medical student at the University of Edinburgh in Scotland. One of the requirements for obtaining a medical degree was the preparation of a doctoral thesis, for which Black was carrying out a systematic chemical investigation. We may learn of Black's particular fascination with one of his chemical experiments from a letter of 3 January 1754 that he wrote to his former teacher and friend, Professor William Cullen, at the University of Glasgow:

Do scientists write doctoral theses today? (2)

> "I fully intended to have wrote you last post, but really I happened to be intent upon something else at the proper time, and forgot it. It was, indeed, an experiment I was trying that amused me, in which I had mixed together chalk and vitriolic [sulfuric] acid at the bottom of a large cylindrical glass; the strong effervescence [bubbling up] produced an air or vapour, which flowing out at the top of the glass, extinguished a candle that stood close to it; and a piece of burning paper, immersed in it, was put out as effectually as if it had been dipped in water; yet the smell of it was not disagreeable." (By doing Experiment 1 on page 7 you can easily prepare this "air" as Black did and observe its characteristic properties.)

Are scientists "absent-minded"? (3)

Careful observations are important in scientific work.

Why were these observations so fascinating to Black, and how did he happen to be carrying out this particular experiment? To answer these questions, we must first take a brief look at the chemical ideas about the atmosphere that prevailed in the middle of the eighteenth century.

For many centuries the atmosphere that surrounds the earth had been a subject of experimentation and speculation. As new instruments and techniques were invented, observations of the atmosphere that men previously had been unable to make became possible. Numerous investigators in different countries contributed to the expanding scientific knowledge about the atmosphere. (See Activity 1 on page 30.)

What do you know about living conditions in the eighteenth century? (4)

Science is not confined to any nation or group.

(Unless instructed to use separate sheets of paper, use these right-hand pages to write your answers to the questions raised in the story of the case and to make notes on the experiments.)

1. Has the physical world really remained pretty much the same over the past two hundred years? How do we know that nature remains constant through time? Do the names and terms men use to describe the world affect our view of the world?

2. What is a doctoral thesis? Do scientists write them today?

3. Black forgot to write Dr. Cullen. Are scientists generally absentminded?

4. What do you know about living conditions in the eighteenth century? What kinds of houses did people live in? How did they heat them? What sorts of manufactured goods and materials were available? What sources of power were used?

After completing his studies at Oxford, Stephen Hales became vicar of Teddington, Middlesex, England. He remained a country clergyman for fifty-two years, refusing preferment in order to continue his scientific experiments. Hales invented many devices connected with food preservation, sea-water purification, ventilation, and other matters, and did not disdain to consider such small problems as the introduction of a cup into a pie to keep the crust from falling. By means of his new pneumatic trough, Hales collected many of the gases we now know as coal gas, oxygen, hydrogen, carbon dioxide, and nitric oxide. However, not doubting that air was an element, he made no qualitative tests and concluded that they were all "true air." *(Picture reproduced by courtesy of Historical Pictures Service, Chicago.)*

Special equipment is needed for experimentation.

About 1725 Stephen Hales perfected an apparatus for collecting gases in a water-filled jar inverted in a trough of water. Even after this new research tool became available, however, progress in the investigation of gases was slow. The beliefs of the time stifled the development of new concepts.

What is an element? (5)

Most scientists of the day believed air to be an element. This widespread belief was the starting point for discussions and explanations about the atmosphere, and it was considered necessary to fit new evidence into this framework. The atmosphere was generally regarded as a chaotic mixture of elementary particles of air and the various impurities that floated in it. Air, the element, was thought of as being permanently "elastic," or as we would say, air was believed always to exist in a gaseous state. Stephen Hales summarized in the following manner the prevailing ideas about the atmosphere in his book *Vegetable Staticks,* which was published in 1727.

Is Hales's statement a description or a concept? (6)

> "Whence it is reasonable to conclude that our atmosphere is a *Chaos,* consisting not only of elastick [gaseous], but also of unelastick . . . particles, which in plenty float in it, as well as the sulphureous saline, watery, and earthy particles, which are no ways capable of being [changed] into a permanently elastick state, like those particles which constitute true permanent air."

Can you explain why the dogs died? (7)

Since air was believed to be an element, there were some observations that puzzled the chemists. For example, in a well-known grotto near Naples, Italy, strange things were observed to happen. Dogs that wandered into the grotto soon came out gasping for breath and then died. Men who walked into the same place were not affected, and there were no unusual odors in the grotto. So many dogs died there that the site was given the name Grotto del Cane.

No need to test the air if you KNOW it's an element, is there?

Because scientists believed that air was an element that always existed in a gaseous state, they were also puzzled when acids poured on certain metals or on limestone caused an effervescence that seemed to produce air. Most chemists looked upon this phenomenon as a kind of boiling off of a modified form of the elementary air, but they did not test the air given off. Stephen Hales collected and measured the amounts of air given off when many different vegetable and mineral substances were heated, but even he did not investigate the properties of the air he obtained.

EXPERIMENT 1. Preparation of Black's "Air"

Place a few grams of powdered white chalk (or powdered limestone) in the bottom of a glass tumbler. Slowly add dilute vitriolic (sulfuric) acid. What happens?

Light a candle and place it on the table next to the tumbler. Protect your setup from drafts. What properties of the "air" are demonstrated?

Hold a piece of burning paper in the "air" in the tumbler. Why is the flame extinguished?

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5. What was the meaning of the word "element" to chemists of the eighteenth century? How is it that air was considered an element?

6. Is Hales's statement about the atmosphere a description or a concept? Before attempting to answer this question, you should explain what is meant by "concept." Is it ever possible to give a description that doesn't involve some concept? Try it.

7. Can you explain why the dogs died in the Grotto del Cane? Why didn't men die too?

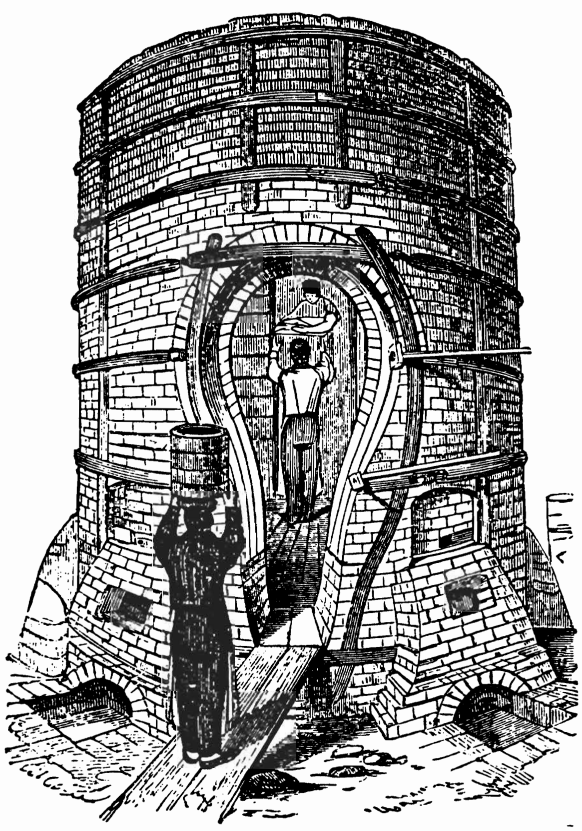
Does luck play an important role in scientific discovery? (8)

An example of technology. How is science different from technology? (9)

Woe to limestone mountains if limestone were soluble in water!

It was Joseph Black's good fortune that the "air" in which he became interested had properties that were strikingly different from those of atmospheric air. As we have already seen, Black's "air" was produced by effervescence when acid was poured on limestone. Limestone also gives off this "air" when it is strongly heated to produce quicklime. Even in Black's time, the roasting of limestone in limekilns was a centuries-old commercial process for making quicklime (an ingredient in mortar). It was known that during this process the limestone lost as much as 40 percent of its weight, but the reasons for this weight loss were not experimentally investigated. It was also known that, although limestone is not soluble in and does not react with water, quicklime reacts with it vigorously. As Professor Black described to his students:

> "Thus, when we pour water upon the [quick]lime, a quantity of it is quickly sucked up into the pores of the stone; and, after a short time, the masses of quicklime which we have moistened begin to grow warm and to smoke. They swell, split, and crumble down into pieces; and these are affected in the same manner, until the whole, in a few minutes is converted into a subtile white powder, greatly more bulky, and which, if too much water has not been used, is perfectly dry and dusty. While this is going on it becomes so hot, that a part of the water is evaporated in boiling hot steams . . . As soon as the lime has been reduced to a subtile powder, by a sufficient quantity of water, no more heat is produced. It cools and does not produce heat again if mixed with water. It is called *slaked lime*." (For a rather spectacular demonstration of what Black described, see Experiment 2 on page 9.)



Lime kilns such as the one shown in this picture had been used in England for centuries before fixed air was discovered. The fixed air produced by the heating of limestone escaped from the tops of the kilns. It was never collected and was of no interest to the technicians who operated the kilns. *(Picture reproduced by courtesy of the Bettmann Archive.)*

8. Does luck play an important role in scientific discovery? Do you know of any examples where it did? Does this happen often?

9. What is the difference between science and technology? The commercial roasting of limestone is an example of technology, but what is science?

EXPERIMENT 2. Slaking of Quicklime

First prepare some quicklime by strongly heating powdered white chalk or limestone. To do this, place the chalk in an iron crucible over a Bunsen burner and keep the crucible at red heat for about thirty minutes. What is the "air" that is given off? How can you test it to find out?

After heating, the chalk is reduced to about two-thirds of its original bulk. This is quicklime. Allow the quicklime to cool. Then half fill a 250-ml beaker with quicklime. (If you haven't prepared enough quicklime to do this, obtain some fresh quicklime from your instructor.) With a pipette slowly add 25 ml of cold water, a drop at a time. What is given off? Does the quicklime remain dry?

Continue adding water until the "thirst" of the quicklime is slaked. What is now in the beaker?

To the material now in the beaker, add about 100 ml of water. Stir thoroughly. Test with litmus paper. What happens? What have you prepared now?

This sketch of Black lecturing was drawn by one of his students. Unmatched as a lecturer, Black attracted ever larger audiences. One of his biographers said, "His lectures provided such a treat to his scholars that the enthusiasm spread to others, and in Black's hand, chemistry became a cultural instrument." His manipulative skill was attested by Henry Brougham, one of his students: "I have seen him pour boiling water or boiling acid from one vessel to another, from a vessel that had no spout into a tube, holding it at such a distance as made the stream's diameter small, and so vertical that not a drop was spilt." Black had many interests outside the realm of science. He was sensitive to both music and art and he was an accomplished flutist. His great charm and easygoing manner made him a favorite with women, though he remained a bachelor throughout his life. *(Picture reproduced by courtesy of Historical Pictures Service, Chicago.)*

What does this fact regarding litmus mean to a chemist? (10)

Continuing his lecture, Professor Black would explain that slaked lime is slightly soluble in water, yielding a colorless, transparent solution called "limewater." Limewater has a bitter taste, turns litmus dye blue, and may be preserved in closed bottles. Black would then add:

> "But if it be left in an open vessel, we may see, in a few minutes, a thin film produced upon its upper surface, where it is in contact with the air. This film continues to increase in thickness, until, after a number of hours, or perhaps a few days, it will form a thin stony crust. In proportion as this crust is formed on the top, the water below loses its taste and the other qualities of lime-water, and at last becomes a mere insipid water. The crusty matter itself, on examination, proves a mild calcareous earth, like the [limestone] in its natural state." (See Experiment 3 on page 11.)

Are scientists concerned with people's health? (11)

During the 1740s, the decade when Joseph Black was studying at the University of Glasgow, another remarkable property was assigned to limewater. Many physicians in England and Scotland believed that limewater was an effective remedy for kidney stones and gallstones because it could dissolve these concretions out of the human urinary tract. This remedy met with some success, but the reasons were poorly understood. Thus, when Black departed from Glasgow in 1752 to seek his medical degree at the University of Edinburgh, he had in mind to devote his thesis to the medicinal value of limewater and to an explanation of the broader problem of the chemical behavior of limewater, slaked lime, quicklime, and limestone.

Indeed, Black did begin his investigation of this subject, as we saw in the letter to Professor Cullen quoted at the beginning of this case, but on 18 March 1754 he wrote to his father:

Was Black's action really "proper"? (12)

> "I found it proper to lay aside lime-water which I had chosen for the subject of my Thesis. It was difficult and would have appeared presumptuous in me to have attempted settling some points about which two of the Professors themselves are disputing."

EXPERIMENT 3. Limewater

Pour approximately 50 ml of limewater into a 100-ml beaker. Test with litmus paper. Let the beaker of limewater stand undisturbed. Observe after a few hours; observe again the next day, and then again after two days have passed. The crust formed on the surface is limestone, but what is the liquid underneath? Test with litmus.

How do you interpret these observations on limewater? (We shall come to Black's interpretations in a few pages.)

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10. What does the fact that limewater turns litmus dye blue mean to a chemist? What is the value of ANY indicator?

11. Are scientists concerned with people's health today? In what ways?

12. Was Black's action really "proper"? Was he behaving like a coward? (What would you have done in these circumstances?)

Why was Black's thesis written in Latin? (13)

Scientific societies promote the progress of science.

Are quantitative investigations better than qualitative ones? (14)

Do scientists frequently reflect, or are they usually too busy doing experiments? (15)

Does progress in science depend on innovations? (16)

To Black, the new species of air was bound into or "fixed" in the alkaline substances.

Thus the young medical student prudently abandoned a topic about which his professors, who would have to approve and pass upon his thesis, were in disagreement. Instead he selected a noncontroversial subject. Black's thesis was devoted to the acidity of the stomach and a little-known antacid material called magnesia alba, the chemical properties of which he investigated. The thesis, titled *Dissertatio medica inauguralis, de humore acido a cibis orto, et magnesia alba,* was accepted, and Black received his medical degree on 11 June 1754. He then returned to his earlier investigations and, although he also practiced medicine at the same time, developed a thorough explanation of the chemistry of limestone and its derived materials within a year. Black described his research in a paper read to the Philosophical Society of Edinburgh on 5 June 1755. This paper, "Experiments upon Magnesia Alba, Quicklime, and Some other Alkaline Substances," has become famous as the first model of a careful quantitative investigation in the field of chemistry. (See Activity 2 on page 30.)

The first part of Black's paper contains an abridged report of the experiments on magnesia alba that he had included in his *Dissertatio*. These experiments turned out to be helpful:

> "When I reflected on the experiments already described, they appeared to me to lead to an explication of the nature of lime, which easily accounted for the most remarkable properties which we find in it, and for many phenomena relating to it and to other alkaline substances.
>
> "By these experiments, it was made evident that magnesia [alba] and the vegetable alkali, in their ordinary states, contain a large quantity of air, in an elastic, solid, or fixed state, which makes up a considerable part of their bulk and weight; and that their effervescence with acids is a discharge or separation of this air from the alkaline part of these substances . . ."

Following this reasoning, Black introduced his bold innovation that marks the downfall of the belief that the air of the atmosphere was an element:

> "I was necessarily led to perceive a distinction between atmospherical air, or the greater part of it, and that sort of air with which the alkaline substances are disposed to unite . . . To this particular species I gave the name of *fixed air,* [to denote that it] is condensed and fixed in different bodies, and is a part of their constituent principles."

Black now had the clue he needed. His new idea was that fixed air was something different from the ordinary air of the atmosphere. Moreover, this fixed air had the property of combining with various materials and becoming a part of them. Thus he was able to give a theoretical explanation for the chemical behavior of limestone, quicklime, slaked lime, and limewater.

(Before you turn the page to find out about Black's explanation of limestone and its derivatives, it is only fair to warn you that you will not find the same explanation that is given in today's chemistry textbooks when the same substances are discussed. If this is so, isn't Black wrong? No, Black is not wrong at all. As you will see, he gives a perfectly consistent explanation of the observations he made in his experiments. Black imagines three substances—lime, fixed air, and water—to which he assigns properties. Then he uses these substances and their properties to account for his observations. This is the same procedure that scientists use today in giving a theoretical explanation, and it is as correct now as it was in Black's time. Since one purpose we have in studying this case is to see how scientists go about explaining observed phenomena, a close look at Black's "theory of lime" can be most instructive.)

13. The title of Black's thesis may be translated as "Inaugural Dissertation in Medicine on the Acid Humor Arising from Food, and Magnesia Alba." The entire thesis, as well as the title, was written in Latin. Why? Theses and scientific papers are seldom written in Latin today. What has been lost by abandoning this practice? What has been gained?

14. Distinguish between "quantitative" and "qualitative." Are quantitative investigations better than qualitative ones? Is a choice always possible?

15. Do scientists frequently reflect, or are they usually too busy doing experiments?

16. Does progress in science depend on innovations? (The answer to this question appears below, but directly thereafter is another, more interesting question for you to answer.)

An innovation represents a new idea. One of the principal aims of science is to discover new and more meaningful interpretations of observations and experimental data. This means that new ideas are important. Yes, progress in science depends on innovations to a large degree.

If new ideas are so important, what kind of person is most needed in science? Or are many kinds of persons needed in science? Back up your answer with evidence.

The following account of his "theory of lime" was given by Black to students during his lectures as a chemistry professor at the University of Edinburgh. It was his explanation of the observed chemical changes in limestone and its derivatives.

Do you need help in following Black's "theory of lime"? (17)

"With respect to the calcareous earth [limestone] . . . I imagined that, when it is exposed to the action of a strong fire, and thereby converted into quicklime, the change it suffers depends on the loss of the large quantity of fixed air which is combined with this acrid earth in its natural state; that this air is expelled by the heat [Reaction 1]; and that the solubility in water, and the remarkable acrimony [bitterness] which we perceive in quicklime . . . are essential properties of this earth, depending on an attraction for water, . . . but that this attractive power or activity remains imperceptible, so long as the lime is in its natural state as calcareous earth, in which it is saturated and neutralized by the [fixed] air combined with it."

Black explains the formation of slaked lime from quicklime by relating this reaction to the formation of crystals by chemical salts. He then points out another parallel in the behavior of salts and these "lime" chemicals:

Today we give the name "water of crystallization" to the water joined to salts in this way.

"The calcareous earth, in its quicklime state, . . . as it has an attraction for water, will be found to resemble the salts in several particulars in the mode of this attraction. The salts . . . are disposed to combine with water in two different ways. With a certain quantity of water they unite closely, and with considerable force, to constitute the crystals of salt,—in which the water is joined with the particles of salt in such a manner as to become solid along with them. There are some of the salts which become very hot in uniting with this portion of water . . . After this, if more water be added, the salt unites with it in a different manner, so as to . . . form a solution of liquid, in which the salt is dissolved in the water . . .

"In the same manner, if water be added to quicklime, a certain quantity of it is attracted by the quicklime, and deprived of its fluidity with violence and heat; and it adheres to the lime with considerable force, constituting with it a dry powder, which is called *slaked lime* [Reaction 2]. But if this slaked lime be mixed with a much larger quantity of water, a part of it dissolves, and composes with the water a *lime-water* [Reaction 3].

And so the cycle is completed.

"When this fluid is exposed to the open air, the particles of lime which are at the surface gradually attract fixed air, which is mixed with the atmosphere; but while the lime is thus saturated with [fixed] air, it is thereby restored to its original state of mildness and insolubility. And, as the whole of this change must happen at the surface of the lime-water, the whole of the lime is successively collected there, in its original form of an insipid calcareous earth [which is limestone] [Reaction 4]."

From the above account, we can see that Black's "theory of lime" provides a rather good explanation of the observed phenomena. At the same time, Black's explanation is quite different from the explanation for the same events that we would give using modern chemical terminology. (See Activity 3 on page 31.) But remember that the observations being explained remain the same; the difference has been in the interpretations that scientists make of their observations. Such a changing of explanatory systems is one of the important characteristics of science.

Black did not set out to discover fixed air. Scientific discoveries can seldom be foreseen.

Black realized full well the significance of his discovery of fixed air. It meant the downfall of the belief that atmospheric air was an element. As he later told his students:

17. In following Black's explanation, it will be helpful to introduce three symbols to stand for the main actors in his "theory of lime." (These symbols, which were not used by Black but are supplied by the editor of this case, were chosen arbitrarily. Many other sets of symbols might be used to represent the idea in Black's "theory of lime." Remember that chemical symbols are chiefly a tool to help express chemical ideas concisely and consistently.) The symbols we shall use and the properties of each substance are as follows:

Symbol:	□	○	▱
Stands for:	**LIME**	**FIXED AIR**	**WATER**
Properties:	**(1) an acrid earth** **(2) soluble in water**	**(1) combines with lime** **(2)**	**(1) dissolves lime** **(2)**

After reading Black's account on the opposite page, fill in the blank spaces above with the pertinent properties of fixed air and water that have been omitted. Then, using the three symbols given above, write in the spaces below the "formula" for each material and "equation" for each of the reactions in Black's account. (The first item and part of the second have been worked out for you.)

Formula for limestone: □ ○

Equation for Reaction 1: □ ○ + **heat** → ○ +

Formula for quicklime:

Equation for Reaction 2:

Formula for slaked lime:

Equation for Reaction 3:

Formula for limewater:

Equation for Reaction 4:

“Here a new and boundless field seemed to open before me. We know not how many different airs may be thus contained in our atmosphere, nor what may be their separate properties . . .

Even today scientists often do not have enough time for research.

“I fully intended to make this [fixed] air, and some other elastic fluids which frequently occur, the subject of serious study. But my attention was then forcibly turned to other objects. A load of new official duties was then laid on me, which divided my attention among a great variety of objects.”

How did others find out about Black's work? (18)

Nevertheless, Black carried out some experiments on the properties of fixed air, although the major work fell to others. In the year 1756 Black found

“. . . that this particular kind of air, attracted by alkaline substances, is deadly to all animals that breathe it by mouth and nostrils together . . . I convinced myself, that the change produced on wholesome air by breathing it, consisted chiefly, if not solely, in the conversion of part of it into fixed air. For I found, that by blowing through a pipe into lime-water . . . the lime was precipitated . . . [Here Black describes a test for fixed air. Have you ever tried it? See Experiment 4 on page 17.] I was partly led to these experiments by some observations of Dr. Hales, in which he says, that breathing through diaphragms of cloth dipped in alkaline solution made the air last longer for the purpose of life.

Every scientist builds on the work of other scientists, past and present.

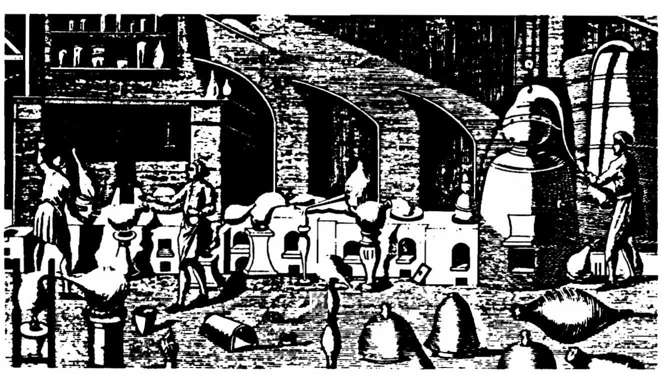
“In the same year I found that fixed air is the chief part of the elastic matter which is formed in liquids in the vinous fermentation. Van Helmont had indeed said this, and . . . [it] could not long be unknown to those occupied in brewing or making wines . . . I convinced myself of the fact by going to a brewhouse with two phials, one filled with distilled water, and the other with lime-water. I emptied the first into a vat of wort fermenting briskly, holding the mouth of the phial close to the surface of the wort. I then poured some of the lime-water into it, shut it with my finger, and shook it. The lime-water became turbid immediately . . .

What happened? (19)

Scientists work with mind and hand.

“In the evening of the same day that I discovered that it was fixed air that escaped from fermenting liquors, I made an experiment which satisfied me [that fixed air was produced when charcoal burned]. Unfixing the nozzle of a pair of chamber-bellows, I put a bit of charcoal, just red hot, into the wide end of it, and then quickly putting it into its place again, I plunged the pipe to the bottom of a phial, and forced the air very slowly through the charcoal, so as to maintain its combustion, but not produce a heat too suddenly for the phial to bear. When I judged that the air of the phial was completely vitiated, I poured lime-water into it, and had the pleasure of seeing it become milky in a moment.”

Does this experiment explain the nature of burning? (20)



Chemists of the eighteenth century often had to use equipment that was primarily designed for apothecaries. Other equipment was designed, and often built, by the scientists themselves. Although the apparatus of Joseph Black shown in this picture appears crude by modern standards, it was adequate to enable chemists to discover many properties of gases. *(Picture reproduced by courtesy of the Science Museum, London.)*

18. How did other scientists find out about Black's work? List five possible ways.

19. What happened to the limewater? Explain, using Black's "theory of lime."

20. Does Black's experiment here explain the nature of burning? What is an "explanation" in science?

EXPERIMENT 4. Test for Fixed Air

Black's test has become the standard laboratory test for fixed air. What is the white precipitate that is formed in this test? You will have a chance to find out more about this test (and about yourself) in the following variation of Black's test.

Measure out 5 ml of limewater into each of two test tubes. Through a piece of glass tubing, blow into the first test tube, and stop when you have a good milky-white color. How long does it take you to obtain this precipitate?

Now do some exercise that makes you pretty tired. Then blow through the glass tubing into the second test tube of limewater. How long does it take you to obtain the same degree of milky-white color that you have in the first tube?

What have you learned?

What was the significance of this discovery? (21)

Was this a new scientific journal? (22)

After the pioneering work of Black, the next thorough investigation of the properties of fixed air was carried on by Henry Cavendish, who also made the effective discovery of another new gas, which he called "inflammable air" (and which we call hydrogen today). Cavendish had read about Black's experiments on magnesia alba and lime and was thereby led to further study of the gases that effervesced from solids. He read two papers reporting his experiments on fixed air to the Royal Society of London—the first on 6 November 1766 and the second a week later. Both papers were later published in Volume 56 of the *Philosophical Transactions*. In a series of careful experiments, Cavendish tested the gas given off by brown sugar fermenting in water and by fermenting apple juice. He reported:

> "It appears from these experiments, that the air produced from the sugar by fermentation, and in all probability that from all the other sweet juices of vegetables, is of the same kind as that produced from marble by solution in acids . . . and may therefore justly be called fixed air." (See Experiment 5 on page 19.)

However, when he studied the gas produced in the putrefaction of a gravy broth, Cavendish found that it contained inflammable air as well as fixed air.

Specific experimental tests must be made to find out the properties of a substance.

Cavendish determined the amount of fixed air that would dissolve in water at different temperatures, finding that fixed air was more soluble in cold water than in hot. He learned that water, when boiled and exposed to the atmosphere, loses the fixed air it has dissolved. He determined the quantity of fixed air that could be absorbed by a solution of lye, by alcohol, and by oil. He measured the density of fixed air and found that at 45°F it was 1.57 times heavier than common air. (Can you match Cavendish as an experimenter? See Activity 4 on page 31.) This high density of fixed air and the fact that it is injurious to life finally provided an explanation fcr the strange happenings at the Grotto del Cane. As Joseph Black explained to his students:

The explanation is easy when a great deal is known!

> ". . . The floor of the Grotto del Cane, in Italy, is lower than the door; and this hollow is always filled with fixed air, which can rise no higher than the . . . threshold of the door, but flows out like water. If a dog go in, he is immersed in the fixed air and dies immediately: But a man goes in with safety, because his mouth is far above the surface of this deleterious air."

Henry Cavendish was afflicted with a speech defect throughout his life. An extremely shy and retiring person, he shunned publicity of any sort and conducted his scientific investigations solely for his own satisfaction. In 1766 Cavendish discovered the properties of inflammable air (hydrogen), which he identified as an element, and in 1781 he determined the composition of the atmosphere. In 1797 he designed and built an apparatus similar to a torsion balance with which he was able to determine the value of the universal gravitation constant for the first time. This made it possible to "weigh the earth," that is, measure its mass and, since its volume was known, its mean density. Cavendish obtained a value of 5.448 for the earth's mean density, showing only a 1 percent discrepancy from our more recent calculation of 5.527. *(Picture reproduced by courtesy of the Bettmann Archive.)*

21. What was the significance of Cavendish's discovery of "inflammable air"? Why did he choose this name?

22. Was the "Philosophical Transactions" a new scientific journal at this time? What was its purpose?

EXPERIMENT 5. Fermentation of Sugar

You can check Cavendish's statement about the nature of "the air produced from sugar by fermentation" by letting some sugar ferment and then collecting and testing the gas that it produced. One way of doing this is suggested in a book by K. Laybourne and C. H. Bailey.

Fit a 2-liter flask (or ½-gallon jug) with a one-hole rubber stopper and a delivery tube bent twice at right angles so that the end of the tube dips just below the surface of some limewater contained in a test tube. Put 50 gm of cane sugar and 500 ml of warm water into the flask, and swirl the liquid until the sugar is dissolved. Add about 30 gm of fresh brewers' yeast (or the kind of yeast used for home baking). Shake well. Allow the flask to stand in a warm place (about 25°C) for two or three days. Observe regularly. What is happening in the flask? What is happening at the end of the delivery tube in the limewater? Is Cavendish correct? Do the fermentation of sugar and the placing of marble in an acidic solution produce the same kind of "air"?

When no more gas appears to be coming from the fermenting sugar, remove the stopper from the flask and cautiously smell the mixture. Do you recognize the material formed by this fermentation? DO NOT DRINK THIS MIXTURE.

Returning to Cavendish's paper, we see that he carried out another interesting experiment with fixed air that provided a valuable new technique for handling water-soluble gases:

Can you explain why lye absorbs fixed air? (23)

> "I also filled another Florence flask with fixed air, and kept it with its mouth immersed in a vessel of quicksilver . . . for upwards of a year, without being able to perceive any air to be absorbed. On removing it into a vessel of [lye], the [fixed] air was quickly absorbed . . .
>
> "It appears from this experiment, that fixed air has no disposition to lose its elasticity, unless it meets with water or some other substance proper to absorb it, and that its nature is not altered by keeping."

We shall see later in this case that the collection of gases over quicksilver (or mercury) was to prove very useful indeed in the work of Priestley and Lavoisier.

Before we turn to this development, however, let us summarize the characteristics of fixed air that have been identified thus far. Black and Cavendish between them had discovered that fixed air—

Which of these are physical properties? Which are chemical properties? (24)

1. Exists in the gaseous state.
2. Is colorless.
3. Is odorless.
4. Is denser than air.
5. Is evolved when limestone is roasted.
6. Effervesces from limestone, chalk, or marble when acid is added.
7. Precipitates limestone when it is bubbled into limewater.
8. Dissolves in water.
9. Is absorbed by solutions of lye.
10. Makes alkaline solutions mild (or neutralizes them).
11. Is not soluble in mercury.
12. Does not burn.
13. Does not support combustion.
14. Is "deadly" to life.
15. Is produced in breathing.
16. Is produced in burning charcoal.
17. Is produced in fermentation.
18. Is produced in the putrefaction of animal tissues.

Techniques and ideas go hand in hand.

This impressive list of characteristics, most of which are quite different from the characteristics of atmospheric air, showed clearly that the investigators were dealing with a distinctive substance. Moreover, the identification of fixed air as a "distinct species" of gas suggested that other gases, each with its own distinguishing properties, might be discovered. As we shall see, it was not long before such a discovery was made.

Why has Sweden made many contributions to science? (25)

How could Bergman demonstrate this? (26)

After the publication of Cavendish's work, quite a number of chemists became interested in the study of gases. Among the investigators who were attracted to the new "pneumatic chemistry," we may mention two men who did their work in Sweden. While continuing the study of water solutions of fixed air, Torbern Olof Bergman, professor of physics at the University of Uppsala, learned that these solutions are acidic. In a paper that he read before the Royal Academy of Sciences at Uppsala, Bergman remarked that, since "the acidity of fixed air [has been,] as I think, demonstrated . . . [and since] . . . in the aerial ocean, which, under the name of atmosphere, surrounds our globe, this vapour is continually present," he had adopted the name "aerial acid" for this gas.

23. **Can you explain why lye absorbs fixed air? Try to give your explanation in two ways: (1) in terms similar to Black's "theory of lime" and (2) in modern chemical terms.**

24. **Which of the listed characteristics of fixed air would you call physical properties? Which are chemical properties?**

25. **Can you explain why Sweden, a minor political power in Europe, has made many contributions to science? What are some of the factors that will produce a sizable number of scientists in a given country?**

26. **How could Bergman find out that water solutions of fixed air are acidic?**

Between 1770 and 1773 Karl Wilhelm Scheele, a Swedish apothecary, carried out a series of brilliant experiments on the chemistry of combustion. Scheele reported his findings in a book titled *Chemische Abhandlung von der Luft und dem Feuer* (Chemical Treatise on Air and Fire), which, although sent to the printer in 1775, was not published until 1777. In the opening section of his book, Scheele states some of his ideas on air and fixed air:

Note how Scheele's statement differs from what Hales had said about the atmosphere (see page 6).

> "Air is that fluid invisible substance which we continually breathe, which surrounds the whole surface of the earth, is very elastic, and possesses weight . . . The air, however, is also mixed with another elastic substance resembling air which differs from it in numerous properties and is, with good reason, called aerial acid by Professor Bergman. It owes its presence to organized bodies, destroyed by putrefaction or combustion."

Scheele goes on to call to task those scientists who still cling to the belief that air is an element. He points out that this ancient opinion is not supported by experimental evidence and explains how the observations made on gases should be interpreted:

"Philosophers"??? (27)

> "Nothing has given philosophers more trouble for some years than this subtle acid or so-called fixed air. Indeed it is not surprising that the conclusions which one draws from the properties of this elastic acid are not favorable to all who are prejudiced by previously conceived opinions. The defenders of the Paracelsian doctrine [that air is an element] believe that the air is in itself unalterable, and with Hales, that it really unites with substances, thereby losing its elasticity; but that it regains its original nature as soon as it is driven out of these by fire or fermentation. But, since they see that the air so produced is endowed with properties quite different from common air, they conclude, without experimental proofs, that this air has united with foreign materials, and that it must be purified from these admixed foreign particles by agitation and filtration with various liquids.
>
> "I believe that . . . [one could accept] this opinion, if one could only demonstrate clearly by experiments that a given quantity of [common] air is capable of being completely converted into fixed or other kind of air by the admixture of foreign materials; but since this has not been done, I hope I do not err if I assume as many kinds of air as observation reveals to me. For, when I have collected an elastic fluid, and . . . discover in it properties and behaviour different from those of common air, then I consider myself justified in believing that this is a distinct variety of air."

Identify a new species of gas by its properties.

(a) Why do simultaneous discoveries often occur in science? (b) Can scientific secrets be kept for long? (28)

By following this guide in his research, Scheele identified several new substances. Among his discoveries was a new gas that he called "fire air" (and which we call oxygen today). Unknown to Scheele, Joseph Priestley, a clergyman who was also a scientific experimenter, had independently discovered the same gas at about the same time in England.

Priestley, who was elected to membership in the Royal Society of London in 1766, became interested in the study of gases in an amusing way. He tells us:

Priestley's independent work is quite similar to that which Black did.

> "It was in consequence of living for some time in the neighbourhood of a public brewery, a little after Midsummer in 1767, that I was induced to make experiments on fixed air, of which there is always a large body, ready formed on the surface of the fermenting liquor, . . . within which any kind of substance may be very conveniently placed . . ."

27. Why does Scheele refer to scientists as philosophers? Are scientists also philosophers?

28. (a) Two or more scientists working independently often make the same discovery at about the same time. Why do such simultaneous discoveries often occur in science?

28. (b) What does this tell you about the possibility of keeping scientific "secrets" for any length of time?

Unlike the other principal figures in this case, Karl Wilhelm Scheele did not receive a university education. At the age of fifteen he was apprenticed to an apothecary. He worked in pharmacies in several cities in Sweden. Scheele's means were invariably modest and his scarce leisure hours were spent in a small, crudely equipped laboratory. Nevertheless, Scheele made a large number of important discoveries; among them, the elements that today we call oxygen, chlorine, and manganese; inorganic compounds such as silicon fluoride, hydrofluoric acid, nitric oxide, and nitrous acid; and several organic acids. *(Picture reproduced by courtesy of Historical Pictures Service, Chicago.)*

What do you imagine the navy did with the soda water? (29)

Priestley made use of this ready source of fixed air for many experiments. In one of these he put a vessel of water into the fixed air above the fermenting liquor and, by agitating the vessel, produced an artificial mineral water. Priestley later improved on this process of making soda water and prepared a pamphlet on *Directions for Impregnating Water with Fixed Air* for the British navy in 1722. (You can make your own soda water by following the instructions in Activity 5 on page 32.)

Can you guess our present-day names for these gases? (30)

An ingenious technique. What advantages does it have? (31)

Having become adept in pneumatic chemistry as a result of his work on fixed air, Priestley prepared and studied the properties of many more gases. He collected and handled those gases that were soluble in water by placing them over mercury, as had been suggested by the work of Cavendish. Among the gases that Priestley first prepared were, as he called them, "alkaline air," "marine acid air," and "nitrous air." What was probably his most important discovery, however, was made when he placed a sample of red *"mercurius calcinatus per se"* (mercuric oxide) in a bottle of mercury that was inverted in a basin of mercury. He then heated the red powder by means of a large lens and found:

What does this show? (32)

Priestley had found Scheele's "fire air"!

> "With this apparatus . . . on the 1st of August, 1774, I endeavoured to extract air from *mercurius calcinatus per se;* and I presently found that, by means of this lens, air was expelled from it very readily. Having got three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprized me more than I can well express, was, that a candle burned in this air with a remarkably vigorous flame . . . I was utterly at a loss to account for it."

In October 1774 Priestley visited Paris and had the opportunity to discuss his discovery with the chemists there:

Scientists exchange ideas through journals, meetings, and personal contacts.

> "I frequently mentioned my surprize at the kind of air which I had got from this preparation to Mr. Lavoisier, Mr. le Roy, and several other philosophers, who honoured me with their notice in that city . . . "

Observations do not speak for themselves; they must be interpreted.

Afterward both Priestley and Lavoisier continued the investigation of the newly discovered gas. Working in his characteristically methodical way, Priestley uncovered many of the identifying physical and chemical properties of the gas, which, in accordance with his interpretation of the phenomena under study, he named "dephlogisticated air." To Priestley, dephlogisticated air was a particularly pure kind of air, since he found that it supported combustion and respiration much better than common atmospheric air. He reported his observations and interpretations on dephlogisticated air in great detail in his book *Experiments and Observations on Different Kinds of Air,* which was published in 1775. In Volume II, Section V, of this book, Priestley reflected about this new "pure" air:

What a horrible thought!

> "From the greater strength and vivacity of the flame of a candle, in this pure air, it may be conjectured, that it might be peculiarly salutary to the lungs in certain morbid cases, when the common air would not be sufficient to carry off the phlogistic putrid effluvium fast enough. But perhaps, we may also infer from these experiments, that though pure dephlogisticated air might be very useful as a *medicine,* it might not be so proper for us in the usual healthy state of the body; for, as a candle burns out much faster in dephlogisticated than in common air, so we might, as may be said, *live out too fast,* and the animal powers be too soon exhausted in this pure kind of air. A moralist, at least, may say, that the air which nature has provided for us is as good as we deserve . . .

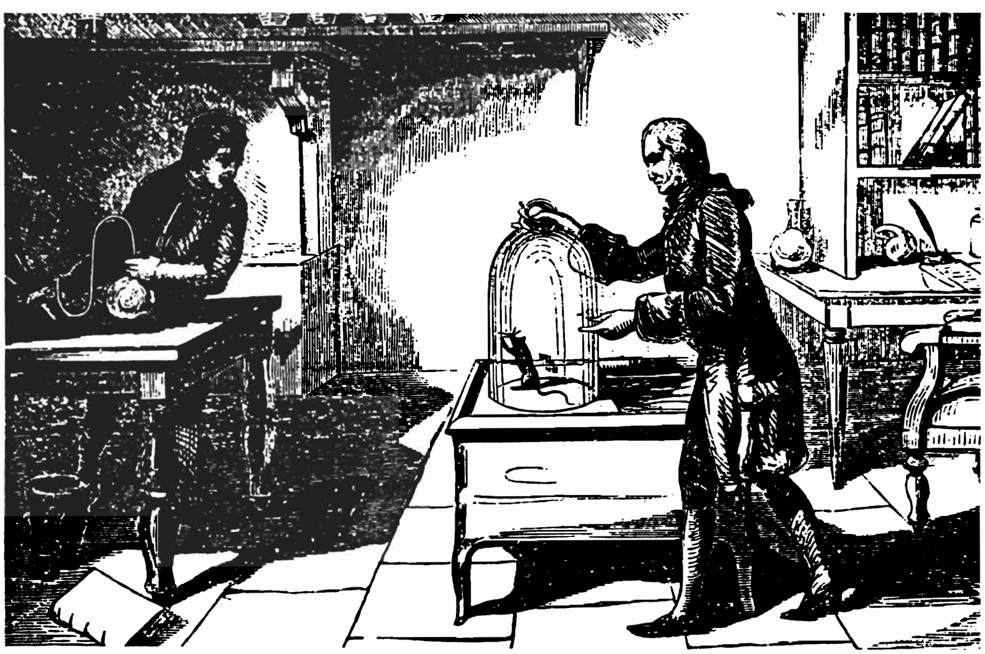
29. What do you imagine the navy did with the soda water? Would you call this an example of a technological application of a scientific discovery?

30. Can you guess our present-day names for these gases? (Hint: Priestley's names are all connected with what is formed when the gases are dissolved in water.)

31. What advantages does Priestley's technique have over heating mercuric oxide in a test tube over a flame?

32. Priestley's "air" is not imbibed (or dissolved) by water. What does this show?

Joseph Priestley, like Stephen Hales, was essentially an experimentalist in science and an English clergyman. Although Priestley conducted scores of original experiments with great care and ingenuity, he did not perceive their theoretical significance. Because of his defense of the French Revolution and vigorous dissenting religious views, Priestley was condemned from many sides. On 14 July 1791 an angry mob sacked his house and laboratory. Finally, in 1794, he decided to emigrate to America where he was warmly received and spent the remaining ten years of his life. *(Picture reproduced by courtesy of Historical Pictures Service, Chicago.)*



"... My reader will not wonder, that, after having ascertained the superior goodness of dephlogisticated air by mice living in it, and the other tests above mentioned, I should have the curiosity to taste it myself. I have gratified that curiosity, by breathing it, drawing it through a glass syphon ... The feeling of it to my lungs was not sensibly different from that of common air; but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that, in time, this pure air may become a fashionable article in luxury. Hitherto only two mice and myself have had the privilege of breathing it."

What a pleasant thought!

Though both Joseph Priestley and Antoine Laurent Lavoisier displayed great moral courage in their personal lives, Lavoisier was more daring as a scientist. It is not surprising, therefore, that he derived the more far-reaching interpretations from experiments with the gas that Priestley and Scheele discovered. Lavoisier came to consider this gas, which he later named *oxygen,* as the key material in his theory of burning. His theory suggested that oxygen was one of the two principal gases in the atmosphere and that materials combined with oxygen when they burned. He supported this theory with careful quantitative experiments that he reported to the Académie des Sciences as he proceeded. In 1789 Lavoisier wrote his *Traité élémentaire de chimie* (Elements of Chemistry), in which he tells us:

Facts plus ideas.

Does this theory sound familiar to you? (33)

"Our atmosphere is composed of a mixture of every substance capable of retaining the gaseous ... state at the common temperature, and under the usual pressure which it experiences ... Our business, in this place, is to endeavour to determine, by experiments, the nature of the elastic fluids which compose the ... air which we inhabit.

"The atmospheric air is composed of two gases, ... one of which is capable, by respiration, of contributing to animal life, and in which ... combustible bodies may burn; the other, on the contrary, is endowed with directly opposite qualities; it cannot be breathed by animals, neither will it admit of the combustion of inflammable bodies ..."

How does Lavoisier's statement compare with that of Hales on page 6? (34)

Lavoisier recognized that many inflammable bodies contain a common element, to which he gave the name *carbon*. Charcoal is almost pure carbon. Thus:

What observations could lead to this idea? (35)

"Charcoal, which from all our present knowledge regarding it, must be considered as a simple combustible body, has likewise the property of [combining with] oxygen gas ... The combustion of charcoal in oxygen gas, may be effected ... in the bell-glass, placed over mercury. [See Experiment 6 on page 29.]

"By that experiment it appears that 28 parts by weight of charcoal require 72 parts of oxygen for saturation, and that the [acidic gas] produced is precisely equal in weight to the sum of the weights of the charcoal and oxygen gas employed. This [acidic gas] was called fixed air by the chemists who first discovered it; they did not then know whether it was air resembling that of the atmosphere, or some other elastic fluid, ... but since it is now ascertained to be an acid, ... it is obvious that the name of fixed air is quite ineligible."

Use of quantitative techniques of investigation.

Lavoisier gave Black's fixed air a new name—*"carbonic acid gas."* This name reflects Lavoisier's ideas about the properties of the gas that is produced by the burning of carbon in oxygen and that, in water, forms an acid. (Black, for one, did not approve of Lavoisier's terminology. See Activity 6 on page 32.)

33. Does Lavoisier's theory sound familiar to you? Is it the only possible explanation of burning?

34. Is Lavoisier's statement a description or a concept? (Do you see how interpretations are usually woven into descriptions?) Compare Lavoisier's statement about the atmosphere with that of Hales on page 6.

35. What observations could lead to the idea that many inflammable bodies contain a common element? What does Lavoisier understand by "element"?

Antoine Lavoisier is known as the father of modern chemistry. His great reputation stems from his interpretation of the work of others, rather than his own experiments. Chemistry was only a part of Lavoisier's life. His service to the French government in several capacities eventually led to his death at the hands of the Revolutionary government after the overthrow of the monarchy. Lavoisier and others were sent to the guillotine on 8 May 1794. The mathematician Lagrange remarked the next day, "Only a moment to cut off that head, and a hundred years may not give us another like it." ***(Picture reproduced by courtesy of Historical Pictures Service, Chicago.)***

What is a law in science? (36)

In a later section of his *Traité élémentaire de chimie* Lavoisier gave the first clear statement of the law of conservation of mass. Interestingly enough, Lavoisier's statement of this law occurs in his discussion of the fermentation of fruit juices. As we learned earlier in this case, Black and Cavendish had discovered that fixed air is one of the products of the process. Lavoisier says:

Law of conservation of mass.

> "This operation [of fermentation] is one of the most striking and extraordinary of all those which chemistry presents to us; and we must examine whence comes the disengaged carbonic acid gas and the inflammable spirit which is formed, and how a sweet body . . . can transform itself thus into two different substances, one combustible and the other highly incombustible . . . To arrive at a solution to these two questions, it is first necessary to know the analysis . . . of fermentable bodies and the products of fermentation; for *nothing is created in the operation of art or Nature, and it can be taken as an axiom that in all operations the quantity of matter before is equal to that found after the operation* [italics added] . . .

Lavoisier makes use of the law.

> "Upon this principle the whole art of making experiments in chemistry is founded; we must always suppose [an exact] equality between the [components] of the body examined and those of the products of its analysis. Thus, since from must of grapes we obtain carbonic acid gas and alcohol, I have an undoubted right to say that
>
> *must of grapes = carbonic acid + alcohol."*

The expression of exact equality between starting material and products that Lavoisier gives here marks one of the beginnings of the use of modern chemical equations. By coincidence, fixed air is again a participant in this forward step.

Why were the names changed? (37)

In this case we have followed the role that fixed air played in the downfall of the ancient belief that air is an element. In Lavoisier's new system of chemistry, fixed air took its place as a chemical compound with the name "carbonic acid gas." Today, we call this same substance carbon dioxide. This name reflects our belief that two atoms of oxygen are joined to one atom of carbon in this compound. This is an example of one of the numerous interpretations, based on many, many experiments and observations, that have been added to our understanding of the fixed air of Joseph Black.

EXPERIMENT 6. Burning Charcoal in Oxygen

Place an inverted collecting jar in a large beaker or trough filled with limewater. Using oxygen from a storage cylinder, collect enough oxygen in the jar to force out all but an inch of the limewater. Cover the mouth of the jar with a glass and turn right side up. Shake the jar vigorously. What happens?

Place the closed jar on a tabletop. Using forceps, hold a small piece of charcoal in a Bunsen flame until it glows red. Gently slide the jar cover open just far enough for the piece of charcoal to be inserted. Hold the piece of charcoal inside the jar with the forceps. The charcoal will glow very brightly until the oxygen inside the jar has been consumed. After the charcoal has ceased to glow brightly, remove it and replace the jar cover. Shake the closed jar vigorously. What happens now? Explain what you see. Does this prove that carbon dioxide is a product of burning charcoal?

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36. What is a law in science? How is it different from a theory?

37. The materials of the physical world do not change, but the names given to these materials do. Why and how does this happen?

ADDITIONAL ACTIVITIES

ACTIVITY 1
Scientists and Nations

Here, listed by the countries in which they lived, are the scientists who made contributions to our knowledge of the atmosphere up to the time of Joseph Black.

Ancient Greece—Strato of Lampsacus

Belgium—Jan Baptista van Helmont

England—Robert Boyle, Stephen Hales, Robert Hooke, John Mayow

France—Edme Mariotte, Blaise Pascal, Jean Rey

Germany—Otto von Guericke

Italy—Evangelista Torricelli

Members of the class may wish to use this list and the list of participants in this case (found on the back of this booklet's title page) as takeoff points for special reports. In your library research and your report about one of these men, you will want to find out and discuss the answers to the following questions: Who was the man? What did he learn about the atmosphere? What else did he achieve in science and outside science?

From the list of countries above you can see that science is an international activity. This fact suggests other subjects from which you might choose a topic for a written report. How did these men, some living great distances from one another and speaking different languages, learn of each other's work? How do American scientists today learn of the work of foreign scientists? Are there barriers other than language to efficient international communication between scientists? Write an essay discussing these problems.

Finally, isn't there something peculiar about the above list? Although there are representatives of six nations on the list, there were certainly many more countries in the world, even in these earlier times. Why aren't scientists listed from these many other countries? (The list is a fairly thorough one for the period, so incompleteness isn't the answer.) With the help of the library card file and your school librarian, you may be able to locate books discussing the social, cultural, and intellectual histories of such countries as Greece, England, France, and Italy during the periods when the scientists listed above were alive. See whether you can discover from these books what factors operating in a particular country at a particular time are likely to produce a large number of scientists and scientific discoveries. Write an essay discussing your personal generalizations on the subject and any evidence you have to back up these generalizations. Why is it important to us today to know what factors help a nation produce many scientists and scientific ideas?

ACTIVITY 2
Experiments on Magnesia Alba

Black's directions for his pioneering quantitative experiments are clear enough to allow you to repeat some of them for yourself. If you have no magnesia alba available, magnesium carbonate will give similar results. In the system of apothecary's weights that Black used, the grain (.0648 gm) is the smallest unit. Twenty grains make 1 scruple (1.296 gm); 3 scruples make 1 dram or drachm (3.8879 gm); 8 drams make 1 ounce (31.1035 gm). The description of the following two experiments is taken from Black's *Dissertatio* (University of Edinburgh, 1754).

> "**Experiment XIII.** An ounce [31.1 gm] of Magnesia [alba] was heated, in a crucible covered with a lid, for about an hour, at a temperature sufficient for the fusion of copper; when the crucible had been cooled the Magnesia weighed three drachms one scruple." [What is the percent of weight lost?]
>
> "**Experiment XX.** I put three ounces of Magnesia [alba] in a glass retort, with a receiver attached, and placed on sand: I then applied fire, which was gradually increased until the Magnesia [alba] was just obscurely red hot. When everything was again cold, the Magnesia weighed one ounce three drachms and a half: it still effervesced strongly when put into acids, although not so much as before. In the receiver I found a little whitish water, weighing five drachms: this . . . changed the colour of violets to green, . . . yet when mixed with acids showed very little action. . . . [What do you get in the receiver?]
>
> "We saw (Exper. XIII) that Magnesia [alba] lost a very large part of its weight when heated. By this experiment, therefore, I wished to know what it was that it had lost. In this case the heat applied was much less than that required for its complete burning, and so it still effervesced pretty strongly with acids, and I could not avoid this, for I had not the proper apparatus for the purpose . . . [Hope you don't have the same trouble.] The weight of the liquid caught in the receiver was not the half of that lost . . . [Is this correct?]

"What then is it that has disappeared? Perhaps some water, but more seems to be air; a great deal of air must have remained with the Magnesia [alba], for, after the loss of so much, it still gives off air on the addition of acids. The qualities of the water may perhaps be a little due to Magnesia carried over by the heat with the air and water." [Note the similarity between magnesia alba and limestone.]

ACTIVITY 3
Modern Terminology

Now that you have followed Black's explanation of the chemical behavior of limestone, quicklime, slaked lime, and limewater using his "theory of lime," you may wish to look at the same series of reactions by using modern chemical terminology. To do this, rewrite Reactions 1 to 4 on page 15 but this time use the modern names and formulas found in the glossary at the bottom of this page. With this glossary, **Reaction 1,** for example, would be written thus:

calcium carbonate → calcium oxide + carbon dioxide

$$CaCO_3 \rightarrow CaO + CO_2$$

Now, you do the next three:

Reaction 2—

Reaction 3—

Reaction 4—

GLOSSARY OF NAMES — THEN AND NOW

Black's Name	Modern Name	Modern Formula
fixed air	carbon dioxide	CO_2
limestone, chalk, marble (also called "calcareous earth in its natural state")	calcium carbonate	$CaCO_3$
quicklime	calcium oxide	CaO
slaked lime	calcium hydroxide	$Ca(OH)_2$
limewater	calcium hydroxide solution	$[Ca(OH)_2 + H_2O]$
vitriolic acid	sulfuric acid	H_2SO_4
magnesia alba	(chiefly) magnesium carbonate	$MgCO_3$
mild vegetable alkali	potassium carbonate	K_2CO_3
lye	sodium hydroxide	$NaOH$
alkaline solution (a solution of lye)	sodium hydroxide solution	$[NaOH + H_2O]$

Notice that the glossary also includes the modern equivalents of five other terms used by Black elsewhere in this case. If you wish to understand the chemistry of fixed air in modern terminology, it will be helpful if you write the appropriate word (or formula) equation as indicated in the glossary for each reaction that is discussed.

ACTIVITY 4
Density of Fixed Air

Cavendish's value, given on page 18, for the density of fixed air at 45°F was 1.57 times the density of common (atmospheric) air. The purpose of this activity is to make an estimate of Cavendish's skill as an experimenter. Of course, you could check his measurement of the relative density of fixed air in a modern handbook, but you will learn more about the skill involved in making such a measurement by trying it yourself. In this way, too, you can match your own skill as an experimenter with that of Cavendish.

To make his determination, Cavendish first weighed the empty bladder of an ox. He then filled the bladder with common air and weighed it. Emptying the bladder, he filled it a second time to the same distention—this time with fixed air. He again weighed the bladder, and the difference in weight of the full bladder in these two trials (minus the weight of the empty bladder) gave him the figures he needed to find the relative density of fixed air.

For your determination, you might use a rubber balloon or a basketball bladder. (Or is there an advantage in using a milk carton or plastic bottle that is more rigid and can be cut up to find its empty weight?) The details of the determination are left to your ingenuity.

What value do you get for the relative density of fixed air? How good was Cavendish?

ACTIVITY 5
Making Your Own Soda Water

This experiment is based on the *Directions for Impregnating Water with Fixed Air* of Joseph Priestley (London, 1772). You will need a generating flask fitted with a two-hole rubber stopper, a delivery tube leading into a basin of water (or pneumatic trough), and a collecting bottle for each bottle of soda water you wish to make. You will also need flavoring syrup of your choice and the chemicals for generating fixed air. Sodium carbonate and dilute hydrochloric acid is a good combination, or you could use baking soda and lemon juice.

Fill the collecting bottle with *cold* water and invert it in the basin of water. Attach the delivery tube to one hole of the stopper of your generating flask. (The other hole is left open to control the flow of gas.) Place the sodium carbonate (or baking soda) in the generating flask and add a small amount of acid (or lemon juice). Put the stopper on the flask, holding your finger over the open hole. After the first bubbles of atmospheric air come over, place the mouth of the delivery tube in the collecting bottle. Bubble the fixed air into the bottle until the bottle is half full. You can stop the flow of fixed air to the collecting bottle by removing your finger from the open hole of the generating flask stopper.

Keeping the mouth of the collecting bottle under water, shake it vigorously until the fixed air dissolves. Replace your finger over the open hole of the generating flask stopper, and again bubble the fixed air into the same collecting bottle until it is half full. Stop the flow of fixed air, and again shake the collecting bottle with its mouth immersed to dissolve the fixed air. Repeat the bubbling and shaking operation two more times.

Remove the collecting bottle of water impregnated with fixed air. Is it an acidic solution? How did you determine the answer?

Add flavoring to taste, and drink.

ACTIVITY 6
Black's Comments on Lavoisier's Names

The name "carbonic acid gas" to replace "fixed air" was only a small part of Lavoisier's new system of nomenclature. In his later lectures Black made the following remarks about Lavoisier's new terminology.

"By a most sagacious and careful consideration of those discoveries, Mr. Lavoisier formed an opinion concerning the composition of bodies, and principles by which this composition was effected, which comprehended the whole of chemistry . . . This philosopher, therefore, associated several other eminent chemists in his labours, and the study soon acquired, in their hands, very great improvements. Assembled in Paris in 1787, and, confident of the superiority of what they called *French Chemistry* over all former doctrines and theories, they adopted a plan by which they hoped to give universal currency and authority. They hoped to effect this by means of a nomenclature, so adapted to their system, that the very denominations of the different objects should imply the doctrines of their theories; so that, by using this language, it should scarcely be possible to think on chemical subjects in a way different from their theories."

a) What does Black mean by his last remark? Is it a just evaluation?

b) What was your personal experience in studying this case? Did you find it difficult to think of chemical problems in terms other than those to which you are accustomed?

c) Does this mean that a scientist's investigations may be limited, in an unconscious way, by the terminology he adopts?

d) Is there any connection between Black's remark and the fact that significant pioneering work in the physical sciences is frequently done by relatively young, inexperienced men?

READING SUGGESTIONS

- Black, Joseph. **Experiments upon Magnesia Alba, Quicklime and some other Alkaline Substances** (1755). Alembic Club Reprint No. 1 (Edinburgh: E. & S. Livingstone; Baltimore: Williams and Wilkins Co., 1906). The reprint edition is available in many public and university libraries.

- Holmyard, E. J. **Makers of Chemistry.** New York: Oxford Univ. Press, 1931. Pp. 119–216.

- Jaffe, Bernard. **Crucibles** (chapters on Priestley, Cavendish, Lavoisier). New York: Fawcett, 1957.

- Klopfer, Leo. E. "The Mysterious Air," in **Current Science,** Vol. 48, Nov. 26–30, 1962, pp. 83–86.

- McKie, Douglas. **Antoine Lavoisier: Scientist, Economist, Social Reformer.** New York: Collier Books, 1961.

- Parington, J. R. **A Short History of Chemistry,** 3d ed. (Chapter V, "Early Studies on Combustion and the Nature of the Atmosphere"; Chapter VI, "Discovery of Gases"; Chapter VII, "Lavoisier and the Foundation of Modern Chemistry.") New York: Harper, 1960.

- Editors of **Scientific American.** "Priestley" and "Lavoisier," in **Lives in Science,** New York: Simon & Schuster, 1957. Pp. 87, 97.

SOURCES OF QUOTATIONS

PAGES	
4	As quoted in Bern Dibner, *Early Electrical Machines* (Norwalk, Conn.: Burndy Library, 1957), p. 26.
6, 8	Robert Whytt, *An Essay on the Vital and Other Involuntary Motions of Animals* (Edinburgh, 1751), pp. 387–388, 427, 261, 11–12.
10, 12, 14, 16, 18	Luigi Galvani, *Commentary on the Effects of Electricity on Muscular Motion* (Norwalk, Conn.: Burndy Library, 1953). Translated by Margaret Glover Foley from Galvani's original book in Latin, *De viribus electricitatis in motu musculari commentarius* (1791).
18	Summary of Galvani's theory from "Galvani and the Pre-Galvanian Electrophysiologists," by Hebbel E. Hoff, *Annals of Science,* 1936, p. 159. By permission of Taylor and Francis, Ltd.
20	Charles H. Wilkinson, *Elements of Galvanism* (London: John Murray, 1804), Vol. I, pp. 92–95. (Adapted.) A translation of a letter by Alessandro Volta to the editors of the *Philosophical and Medical Journal of Leipsick* (1793).
22, 25	Bern Dibner, *Galvani-Volta* (Norwalk, Conn.: Burndy Library, 1952), p. 50. Translated by Mario Tchou from the anonymous book, *Dell' Uso e dell' Attività dell' Arco Conduttore nelle contrazione dei Muscoli* (Bologna, 1794).
24	Quoted by I. Bernard Cohen in his introduction to Luigi Galvani's *Commentary on the Effects of Electricity on Muscular Motion* (Burndy Library, 1953), p. 33. Originally printed in Volta's *Opere*, Vol. I, pp. 203–208.
26	Bern Dibner, *Galvani-Volta* (Norwalk, Conn.: Burndy Library, 1952), pp. 42, 46–48. Reproduction of the English translation, from *The Philosophical Magazine* of September 1800, of the paper in French by Alessandro Volta, "On the Electricity excited by mere Contact of conducting Substances of different kinds," *Philosophical Transactions,* **90**: 403–431 (1800).

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