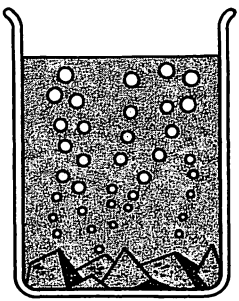
HISTORY OF SCIENCE CASES
FOR HIGH SCHOOLS

Case 8

THE CHEMISTRY OF FIXED AIR



Prepared by LEO. E. KLOPFER

THE CHEMISTRY OF FIXED AIR

Prepared by...
LEO. E. KLOPFER

Graduate School of Education, Harvard University
Cambridge 38, Massachusetts

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INTRODUCTION

In this HISTORY OF SCIENCE CASE, we shall 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 role of scientists as people and the personal characteristics of scientists
- the interplay of social, economic, technological, and psychological factors with the progress of science
- the importance of accurate and accessible records, constantly-improved instruments, and free communication

Proper study of this CASE consists of more than simply reading this little booklet. In the narrative outline, which follows this introduction, you will find numerous comments and questions in the margins. These marginal notes are intended to stimulate your thinking and to guide discussion on the points illustrated by the CASE. Space is provided on the left-hand pages for you to write answers to the questions which appear in the marginal notes . . . A most important part of the study of this CASE are the experiments and exercises which are suggested in this booklet, following the narrative outline. You should try to complete as many of these exercises as possible, so that you may get a real "feel" for the situations faced by scientists in creating science. Your teacher may suggest additional exercises and experiments that you can work on in connection with this CASE. On the last page of this booklet, you will find some reading suggestions of books and articles relating to the story of this particular CASE.

Some students will think that this CASE is out of date, because the story is set in the scientific past.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 which are featured in this CASE hold just as cogently in the present as they did in the past. The methods of scientific investigation are much the same today as they have been for several hundred years; similar non-scientific factors now interact with the progress of science as they did then; the character and personalities of scientists are always paramount factors when we think about science; adequate recording, free communication, and improved instrumentation continue as vital needs. These aspects of science held true yesterday, hold true today, and will hold true tomorrow.

As you study this CASE and work through the exercises, you will learn a great deal about scientists and about what goes on in science.

L.E.K.

The principal people you will meet in this CASE are --

Stephen Hales	English botanist and chemist. Born September 1677 at Bekesbourne, Kent. Died 4 January 1761 at Teddington, Middlesex.
Joseph Black	Scottish physician and chemist. Born 16 April 1728 at Bordeaux, France. Died 6 December 1799 at Edinburgh.
Henry Cavendish	English physicist and chemist. Born 10 October 1731 at Nice, France. Died 24 February 1810 at Clapham, London.
Joseph Priestly	English minister and chemist. Born 13 March 1733 at Fieldhead, Yorks. Died 6 February 1804 at Northumberland, Pennsylvania.
Antoine Laurent Lavoisier	French chemist. Born 26 August 1743 at Paris. Died 8 May 1794 at Paris.

[Use these left-hand pages to take notes and to write out your answers to the questions suggested in the margins of the text.]

Has the physical world really remained the same over the past 200 years? How do we know that nature remains constant through time? -- Do the names and terms men use to describe the world change our view of the world?

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

THE CHEMISTRY OF FIXED AIR

What is "fixed air"? . . . It is a dense, colorless, odorless gas which today's chemists call "carbon dioxide." It was given the name "fixed air," for good reasons, by Joseph Black, a Scottish medical doctor and professor of chemistry, the first to carefully study this material at about the middle of the 18th century. Black's study opened up a new and fruitful line of investigation that was to lead to the fresh concepts of modern chemistry.

The chemical terms which Professor Black taught to his students during most of his career may seem strange and unfamiliar to you, because, in this Case, we are dealing with an era before the introduction and general acceptance of the chemical terminology which 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; (-- do I hear any cheers??? --) he says nothing about atoms or molecules. These present-day names and ideas had not been invented when Black began his researches. Yet, we must remember that Black studied essentially the same physical world that we live in today. The materials he worked with and their behavior have remained the same; only the man-made labels attached to the materials and the chemists' concepts that describe their behavior have changed . . . Let us see, as we study this Case, what Black and his contemporaries learned about the properties of fixed air and its chemical behavior . . .

In 1735, Joseph Black, as a young medical student at the University of Edinburgh, was carrying out a systematic chemical investigation in preparation for his doctoral thesis. One of his experiments particularly fascinated him, as he tells us in a letter of 3 January 1754 to his former teacher and friend, Professor Edmund Cullen at the University of Glasgow:

What is a "doctoral thesis"? Do scientists write them today?

Black forgot to write to Dr. Cullen. -- Are scientists generally absent-minded?

What do you know about living conditions in the 18th century? -- What kinds of houses did people live in? How did they heat them? What sort of manufactured goods and materials were available? What sources of power were used?

What is an element? -- Certainly, if air was considered an element, the term "element" did not mean the same as what we understand by the term "chemical element" today. What <u>did</u> "element" mean?

Who provides the special equipment needed for scientific work? (Incidentally, who pays for it?)

Is Hale's statement about the atmosphere a description or a concept? -- Before answering this question, you should explain what is meant by "concept." -- Is it ever possible to give a description which doesn't involve some concept? Try it.

> 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 acid at the bottom of a large cylindrical glass; the strong effervescence 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." (You can easily prepare this "air" as Black did and observe its characteristic properties; see Exercise 1, page 24.)

Are scientists "absent-minded"?

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 take a brief look at the chemical ideas about the atmosphere prevailing in the middle of the 18th century and at Joseph Black's earlier career.

What do you know about living conditions in the 18th century?

The atmosphere that surrounds our earth had been a subject of experimentation and speculation for many centuries. Numerous investigators in different countries had given their attention to its problems, so that a sizable amount of scientific knowledge about the atmosphere was at hand by the middle of the 18th century. (See Exercise 2, page 24.) The atmosphere was generally regarded as a chaotic mixture of elementary particles of air with various impurities floating in it. Air was thought of as an element that was "permanently elastic," or as we would say, the element air always exists in a gaseous state. Stephen Hales, who perfected the apparatus which is usually used even today for studying gases, summarized the prevailing ideas in his book, <u>Vegetable Staticks</u>, published in 1727:

Science is not confined to any nation or group.

Scientists build on the work of those who have gone before.

What is an element?

Special equipment is needed for experimentation. Who provides it?

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

Is Hales' statement about air a description or a concept?

Can you explain why the dogs died in the Grotto del Lane? Why didn't men die also?

Have you ever observed such a puzzling event? How may "puzzling events" lead to scientific discoveries?

Why did chemists fail to make tests on the air which bubbled out of the metals and limestone?

How could Hales have found out what the properties of the air he obtained were? Why didn't he do this? Suggest two or more different reasons.

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

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

Since air was believed to be an element, there were some observations which puzzled the chemists. For example, there was a well-known grotto near Naples in Italy where it had frequently been observed that dogs who 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 here that the site was given the name "Grotto del Cane." Another observation that puzzled the chemists was the vigorous effervesence of air when acid was poured on certain metals or on limestone. Most chemists looked on this phenomenon as a kind of boiling off of a modified form of the element air, but they did not further test the air that was given off. Stephen Hales also collected and measured the amounts of air given off when many different vegetable and mineral substances were heated, but he did not investigate the properties of the air he obtained.

Can you explain why the dogs died?

Have you ever observed such a puzzling event?

Why did chemists fail to make tests on the air which bubbled out of the metals and limestone?

How could Hales have found out what the properties of his air were? Why didn't he do this?

It was Joseph Black's good fortune that the air in which he became interested had properties which were strikingly different from those of atmospheric air. Such was the air that effervesced when an acid was poured on limestone. Limestone also gives off air when it is strongly heated to produce quicklime. The roasting of limestone in lime-kilns had been carried out for centuries as a commercial process for making quicklime for use in construction. It was known that the limestone lost as much as forty per-cent of its weight in the heating, but the reasons for this weight loss were not experimentally investigated. It was also known that, although limestone is insoluble in water, quicklime reacts vigorously with water, in the manner that Professor Black described to his students:

Does luck play an important role in scientific discovery?

What is the difference between science and technology?

Woe to limestone mountains if limestone were soluble!

> 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

What does the fact that lime water turns litmus dye blue mean to a chemist? What is the value of <u>any</u> indicator?

How do you interpret these observations on lime water at this point? (We shall come to Black's interpretation in a few pages.)

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

Can you suggest some reasons why Black was seeking a medical degree in 1752, although he was interested in chemistry?

> 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 experiment, see Exercise 3, page 24.)

Now, slaked lime is itself slightly soluble in water, yielding a colorless, transparent solution called "lime water." Lime water has a bitter taste and turns litmus dye blue. Lime water may be preserved in closed bottles,

What does this fact mean to a chemist?

> 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 limewater, and at last becomes a mere insipid water. The crusty matter itself, on examination, proves a mild calcereous earth, like the [limestone] in its natural state. (See Exercise 4, page 25.)

How do you interpret these observations?

During the 1740's, the decade of Joseph Black's studies at the University of Glasgow, another remarkable property was assigned to lime water. Many physicians in England and Scotland believed that lime water was an effective remedy for kidney stones and gall stones and that it would dissolve these concretions out of the human urinary track. 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 lime water and to an explanation of the broader problem of the chemical behavior of lime water, slaked lime, quicklime, and limestone.

Are scientists concerned with people's health?

Can you suggest why Black was seeking a medical degree instead of a degree in chemistry?

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

The title of Black's thesis may be translated as: Inaugural Dissertation in Medicine on the Acid Humours 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?

Is it usual for medical doctors to do research in chemistry today? If not, why not?

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

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:

> 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.

Is Black's action really "proper"? Was he behaving like a coward?

Thus, the young medical student prudently abandoned a topic about which his professors, who would have to approve and pass his thesis, had a disagreement, and selected a non-controversial subject. Black's thesis was devoted to the acidity of the stomach and a little-known, anti-acid material, magnesia alba, whose chemical properties he investigated. The thesis, titled Dissertatio medica inauguralis, de humore a cibis orto, et magnesia alba, was accepted and Black received his medical degree on 11 June 1754. Soon thereafter, he returned to his earlier investigation and, although he was also practicing medicine at the same time, developed a thorough explanation of the chemistry of limestone and its derived materials within the next year. Black described his researches in a paper read to the Philosophical Society of Edinburgh on 5 June 1755. This paper "Experiments upon Magnesia Alba, Quicklime, and Some other Alcaline Substances," has become famous as the first model of a careful quantitative investigation in the field of chemistry. (See Exercise 5, page 25.)

Why was the thesis in Latin?

Is it usual for medical doctors to do research in chemistry today?

Scientific societies promote the progress of science.

Are quantitative investigations better than qualitative ones?

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

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

What is an "alkaline substance"? How could you identify one?

Does progress in science depend on innovations? -- We'll be sporting and give you the answer to this one, but we have a more interesting question for you to answer right after.

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

If this is so, what kind of person is most needed in science? Or, are many kinds of people needed in science?

Do you see the reason for calling it "fixed air"?

> 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.

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

> 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, . . .

What is an "alkaline substance"?

Following this reasoning, Black introduced his bold innovation which marks the downfall of the prevailing idea of the air of the atmosphere being considered an element.

Does progress in science depend on innovations?

> 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.

Do you see the the reason for calling it "fixed air"?

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 lime water. On the next two pages we shall see what Black's explanation was.

[Continue reading on page 12.]

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 were not used by Black, but are supplied through the courtesy of the editor of this Case.) The three symbols we shall use and the properties of each material are --

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

By reading Black's description below and on the next page, you can fill in the pertinent properties of fixed air and water that have been omitted. Also, in the right-hand column below, you should be able to write the "formula" for each material and an "equation" for each reaction using our three symbols.

Black's Theory of Lime:

> 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 earth in its natural state; that this earth is expelled by the heat; [1] and that the solubility in water, and the remarkable acrimony 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 calcereous earth, in which it is saturated and neutralized by the [fixed] air combined with it.

Formula for limestone:

Equation for reaction [1]:

Black explains the formation of slaked lime from quicklime by relating this reaction to the formation of crystals by chemical salts. (See Exercise 6, page 25.)

> The calcereous 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 salts, -- 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 or liquid, in which the salt is dissolved in the water ; . . .

Formula for quicklime:

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

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. [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. [3]

Formula for slaked lime:

Equation for reaction[2]:

Formula for lime water:

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 calcereous earth [which is limestone]. [4] (See Exercise 7, page 26.)

Equation for reaction[3]:

Equation for reaction[4]:

[And so, the cyle is completed.]

Black well realized the significance of his discovery of fixed air for the downfall of the belief that atmospheric air is an element. As he later told his students:

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

> 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 . . .
>
> 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.

Scientists today often do not have enough time for research also.

Nevertheless, Black was able to carry out some experiments on the properties of fixed air, although the major work fell to other investigators. For instance, in the year 1756, Black found

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

> . . . 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, . . . 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.

Is this supposition correct? (**)

Have you ever tried this standard test for fixed air? (**)

Does a scientist investigate every problem from the beginning? (**)

[**Answer these questions on page 14; the story continues on page 15.]

How did others find out about Black's work? -- List five possible ways?

Is Black's supposition that fixed air is deadly to all animals that breathe it correct? -- Give two reasons why fixed air might act in this way.

Have you ever tried the standard test for fixed air? -- Here is a variation: Measure out 5 ml of lime water 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 of limestone? Now, do some exercise that makes you pretty tired. Stumble over to your second test tube of lime water and blow into it through the glass tubing. 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?

Does a scientist investigate every problem from the beginning? Explain.

What happened to the lime water? Explain, using Black's theory of lime.

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

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

What is the Royal Society of London? What does it do?

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

How could Cavendish find out that both inflammable air and fixed air were 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 limewater. 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.

A scientist's life is not dull.

What happened?

In the evening of the same day that I discovered that it was fixed air that excaped from fermenting liquors, I made an experiment which satisfied me [that fixed air was produced when charcoal burns]. 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 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.

Scientists work with mind and hand.

Does this experiment explain the nature of burning?

After the pioneering work of Black, the next scientists to carry on a thorough investigation of the properties of fixed air was Henry Cavendish, who also made the effective discovery of another new gas which he called "inflammable air" (and we call "hydrogen" today). Cavendish had read Black's experiments on magnesia alba and lime and was thereby led to further study of the gases effervescing from solids. Cavendish read two papers reporting his experiments with fixed air to the Royal Society of London on 6 and 13 November 1766. These papers were later published in volume 56 of the Philosophical Transactions. In a series of careful experiments, Cavendish tested the gas given off by fermenting brown sugar in water and by fermenting apple juice.

What was the significance of this discovery? Why did he choose this name?

What is the Royal Society of London?

Was this a new scientific journal? What was its purpose?

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.

Is this correct? (See Exercise 8, page 26.)

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.

How could Cavendish find this out?

What is meant by "density"? How does Cavendish's value for the density of fixed air compare with modern values? -- How good an experimenter was Cavendish?

Summarize the physical and chemical properties of fixed air which were discovered by Black and Cavendish. (There are at least ten.) Mark each physical property with a "P" and each chemical property with a "C".

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.

Cavendish determined the amount of fixed air which would dissolve in water at different temperatures, finding that it was more soluble in cold water than in hot water. He learned that water loses its dissolved fixed air when boiled and when exposed to the atmosphere. 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. This high density of fixed air and the fact that it is injurious to life finally provided an explanation for the strange happenings at the Grotto del Cane. As Joseph Black explained it to his students:

How does this compare with modern values? How good an experimenter was Cavendish?

> 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 goes 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.

The explanation is easy when a great deal is known!

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. He reported:

> 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.

Can you explain why lye absorbs fixed air?

The collection of gases over quicksilver or mercury was to prove highly useful in the later work of Priestley and Lavoisier.

Following the publication of Cavendish's work, quite a number of chemists became interested in the study of gases, for it was now clear that

Can you explain why Sweden, a comparatively small country, has made many contributions to science? What are some of the factors at play within a given country that will produce a sizable number of scientists?

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

Two (or sometimes more) scientists working independently often make the same discovery at about the same time. Why do such simultaneous discoveries often occur in science? -- Does this tell you anything about the possibilities of keeping scientific "secrets" for any length of time?

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?

there were many different kinds of "air" which could be distinguished by appropriate tests. Among the investigators who were attracted to the new "pneumatic chemistry," we may mention two men who did their work in Sweden. Torbern Olof Bergman, professor of physics at the University of Uppsala, continued the study of water solutions of fixed air and learned that these solutions are acidic. Karl Wilhelm Scheele, an apothecary, studied the chemistry of combustion and also brought to light many new substances. He discovered a new gas which he called "fire air" (and we call "oxygen" today) at about the same time that Joseph Priestley independently discovered the same gas in England.

Techniques and ideas go hand-in-hand.

Can you explain why Sweden, a small country, has made many contributions to science?

How could Bergman find this out?

Why do simultaneous discoveries often occur in science?

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:

> It was in consequence of living for some time in the neighborhood 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; . . .

Priestley's independent work is quite similar to Black's.

Priestley made use of this ready source of fixed air for many experiments. Among 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 of <u>Directions for Impregnating Water with Fixed Air</u> for the British navy in 1772. (You too can make your own soda water; see Exercise 9, page 27.)

What do you imagine the navy did with the soda water?

Having become adept in pneumatic chemistry with his work on fixed air, Priestley prepared and studied the properties of many more gases. He collected and handled those gases which were soluble in water over mercury, as had been suggested by the work of Cavendish. Among the

Can you guess our present-day names for these gases? -- [This is a tough riddle. HINT: Priestley's names are all connected with what is formed when the gas is dissolved in water.]

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

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

Why does Priestley refer to these scientists as "philosophers"? Are scientists also philosophers?

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

Was this "Academie" a French school? What was its purpose?

gases which Priestley first prepared were, as he called them, "alkaline air," "marine acid air," "vitriolic acid air," and "nitrous air." Probably his most important discovery, however, was made when Priestley placed a sample of red "mercurious calcinatus per se" (--Our name for this substance is merçuric oxide.--) in a bottle of mercury that was inverted in a basin of mercury and heated the red powder by means of a large lens.

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

An ingeneous technique. What advantages does it have?

> With this apparatus , . . . on the 1st of August, 1774, I endeavored 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 about 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 surprised 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.

What does this show?

Priestley had found Scheele's "fire air."

In October 1774, Priestley visited Paris and had the opportunity of discussing his discovery with the chemists there.

> I frequently mentioned my surprise 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; . . .

"Philosophers"?

Afterwards, both Priestley and Lavoisier continued the investigation of the newly-discovered gas, but it was Antoine Laurent Lavoisier who derived the more far-reaching interpretations from his experiments. Lavoisier eventually came to consider this new 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 combine with oxygen when they burn. Lavoisier's theory was supported by a series of careful quantitative experiments, which were reported to the Academie des Sciences as he proceeded. In 1789, Lavoisier wrote about his ideas in his Traite Elementaire de Chemie (Elements of Chemistry), in which he tells us:

Facts plus ideas.

Does this theory sound familiar to you?

Was this "Academie" a French school?

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 3.

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

What scientific law is Lavoisier using here? --[HINT: Lavoisier established this law in chemistry.]

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

> 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 endeavor to determine, by experiments, the nature of the elastic fluids which compose the . . . air which we inhabit.

Compare Lavoisier's statement with that of Hales' on page 3.

> 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, . . .

Is this a description or a concept?

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?

> 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. (For a similar experiment, which you can do, see Exercise 10, page 27.)

> 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 analysis.
What law is Lavoisier using here?

To replace the name "fixed air," Lavoisier chose the name "carbonic acid gas." Lavoisier's name for fixed air reflects his own ideas about the properties of this gas that forms an acid in water solution and is produced by the burning of carbon in oxygen.

What did Black think of Lavoisier's new name? -- See Exercise 11, page 27.

Thus, fixed air took its place as a chemical compound in Lavoisier's new system of chemistry. Today, we call this same material "carbon dioxide." This name reflects our belief that two atoms of oxygen are joined to one atom of carbon in this compound. Yes, still more interpretations, based on many, many experiments and observations, have been added to our understanding of the fixed air of Joseph Black.

Experiments and Exercises

YOUR Observations

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 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?

2. Science is an international activity. We can best recognize this when we see that many men in different countries frequently contribute to the development of a single field of investigation. Listed below are the names and nations of men who made some contribution to our knowledge of the atmosphere up to the time of Joseph Black. Who were these men? What did they learn about the atmosphere? What else did they achieve or discover? --- The answers to these questions will provide material for some good reports to your class. A visit to the library will help you.

Ancient Greece --	Strato of Lampsacus
Belgium --	Jan Baptista van Helmont
England --	Robert Boyle, Stephen Hales, Robert Hooke, John Mayow
France --	Edme Mariotte, Blaise Pacal, Jean Rey
Germany --	Otto von Guericke
Italy --	Evangelista Torricelli

   While you're at the library, you may also wish to find out more about the lives and achievements of the principal participants in this Case. Their names and nations are listed on the second page of the Introduction.

   Incidentally, isn't there something peculiar about the above list? Although there are representatives from five modern countries on the list, there are certainly more countries than five in the world. Yet, there are no representatives from these many other countries listed. Why not? (The list is a reasonable complete one for the period covered, so incompleteness isn't the reason.) Can you give some reasons why one country may produce a considerable number of scientists at a certain time while another does not?

3. Slaking of Quicklime. ::: First, you may prepare some quicklime by strongly heating powdered white chalk (or limestone). Place the chalk in an iron crucible over a Bunsen burner and keep it at red heat for about 30 minutes. What is the "air" that is given off? 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 it to cool.
   Half fill a 250 ml. beaker with fresh quicklime. (If you haven't prepared enough, obtain fresh quicklime from your instructor.) From 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 have you prepared now?

YOUR Observations

4. Lime Water. ::: The directions for this experiment are not very difficult. -- Pour about 50 ml. of lime water into a 100 ml. beaker. Test with litmus paper. Let the beaker of lime water stand undisturbed. Observe after a few hours, the next day, after two days, etc. The crust formed on the surface is limestone, but what is the liquid underneath? Test with litmus.

5. "Experiments upon Magnesia Alba." ::: Black's directions for his pioneering quantitative experiments are clear enough to allow you to repeat some of the experiments for yourself. If you have no magnesia alba available, magnesium carbonate will give similar results. The system of apothecaries weights, which Black used, has for its smallest unit the grain (equal to 0.0648 gm.), 20 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 descriptions of the following two experiments are taken from Black's Dissertatio.

> Experiment XIII. - An ounce of Magnesia [alba] was heated, [You]would use 31.1[gm.] 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 per cent 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 ... changes the colour of violets to green, ... [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.]

6. Crystals. ::: Black uses the analogy of the formation of crystals to explain the forming of slaked lime from quicklime. What he has in mind is the combination of water with an anhydrous salt to form a hydrated salt crystal. You can better understand this analogy if you have had some experience with forming crystals yourself . . . . A really fascinating project you can do is to learn how to grow crystals. An excellent handbook to help you with this project is Crystals and Crystal Growing by Alan Holden and Phylis Singer, (Anchor Science Study Series No. 57, Doubleday, 1960, $1.45). Have fun!

7. Now that you have followed Black's explanation of the chemical behavior of limestone, quicklime, slaked lime, and lime water 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 pages 11 and 12 as word (or formula) equations using the modern names. The following glossary will help you:

Black's Name	Modern Name and Formula	
fixed air	carbon dioxide	CO_2
limestone (chalk, marble) (also called: "calcereous earth in its natural state")	calcium carbonate	$CaCO_3$
quicklime	calcium oxide	CaO
slaked lime, lime water	calcium hydroxide	$Ca(OH)_2$
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)		

For example, reaction [1] on page 11 would be written as:

calcium carbonate → calcium oxide + carbon dioxide $CaCO_3 \rightarrow CaO + CO_2$

Now, you do the next three:

[2]
[3]
[4]

Notice that the above glossary also includes the modern equivalents of four other terms used by Black elsewhere in this Case. (See pages 3, 11, 13, 17.) If you wish to learn about the chemistry of fixed air in modern terminology, it will be helpful for you to write the appropriate word (or formula) equation for each reaction which is discussed.

8. Fermentation of Sugar. ::: You can check Cavendish's statement about the nature of "the air produced from the sugar by fermentation" by letting some sugar ferment and then collecting and testing the gas that is produced. One way of doing this is suggested by K. Laybourn and C. H. Bailey, Teaching Science to the Ordinary Pupil, page 154.

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 lime water 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 1 ounce of fresh brewer's 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 lime water? Is Cavendish correct?

YOUR Observations

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 that has been formed by fermentation? //Do not drink this mixture.//

9. Make Your Own Soda Water! ::: This experiment is based on the Direction for Impregnating Water with Fixed Air by Joseph Priestley. 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. Also, you will 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, to generate the fixed air.

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 on the stopper, holding your finger over the open hole. Discard the first bubbles of atmospheric air which come over. Then bubble the fixed air into your collecting bottle until it is half full. Remove your finger from the open hole of the generating flask stopper to stop the flow of fixed air to the collecting bottle. Keeping the mouth of the bottle under water, shake the collecting bottle 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 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? . . . Add flavoring to taste, and drink.

YOUR Observations

10. Burning Charcoal in Oxygen. ::: Half fill a battery jar or large beaker with lime water, and float a boat made out of aluminum foil in it. Prepare and collect oxygen in a wide-mouth collecting bottle. Put a cover glass on the inverted bottle of oxygen.

Using forceps, hold a small piece of charcoal in the Bunsen flame until it glows red. Put the glowing charcoal in the aluminum boat. Holding the bottle of oxygen with tongs, place it over the glowing charcoal. The charcoal burns vigorously. What happens to the water level in the bottle? What happens to the oxygen?

11. 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 and nomenclature. In his later lectures, Black made the following remarks about the new terminology:

"By a most sagacious and careful consideration of those discoveries, Mr. Lavoisier formed an opinion concerning the composition of bodies, and the 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 it 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."

What does Black mean by his last remark? Is it a just evaluation? . . . . What was your personal experience in studying this Case . . . . Did you find it hard to think of chemical problems in terms other than those to which you are accustomed? . . . . Does this mean that a scientist's investigations may be limited, in an unconscious way, by the terminology he adopts? . . . . 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?

Sources of Quotations

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page 3 — William Ramsay, The Gases of the Atmosphere; The History of Their Discovery, Fourth Edition, (London, 1915). Pages 36-37.

pages 5, 7, 11, 12, 13, 15, 17, and 27 — Joseph Black, Lectures on the Elements of Chemistry, Published from his manuscripts by John Robison, (Edinburgh, 1803). -- Quotations are taken from Volume II, pages 35-37, 47, 69-75, 92 and Volume I, page 489.

pages 15 and 17 — Henry Cavendish, "Three Papers, containing Experiments on Factitious Air," Philosophical Transactions, 56: 141-184, (1767). -- The quotations are from pages 181 and 160, respectively.

page 19 — Joseph Priestley, Experiments and Observations on Different Kinds of Air, (London, 1775). -- Quotations from Alembic Club Reprint No. 7, pages 8, 10, 11.

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Reading Suggestions

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