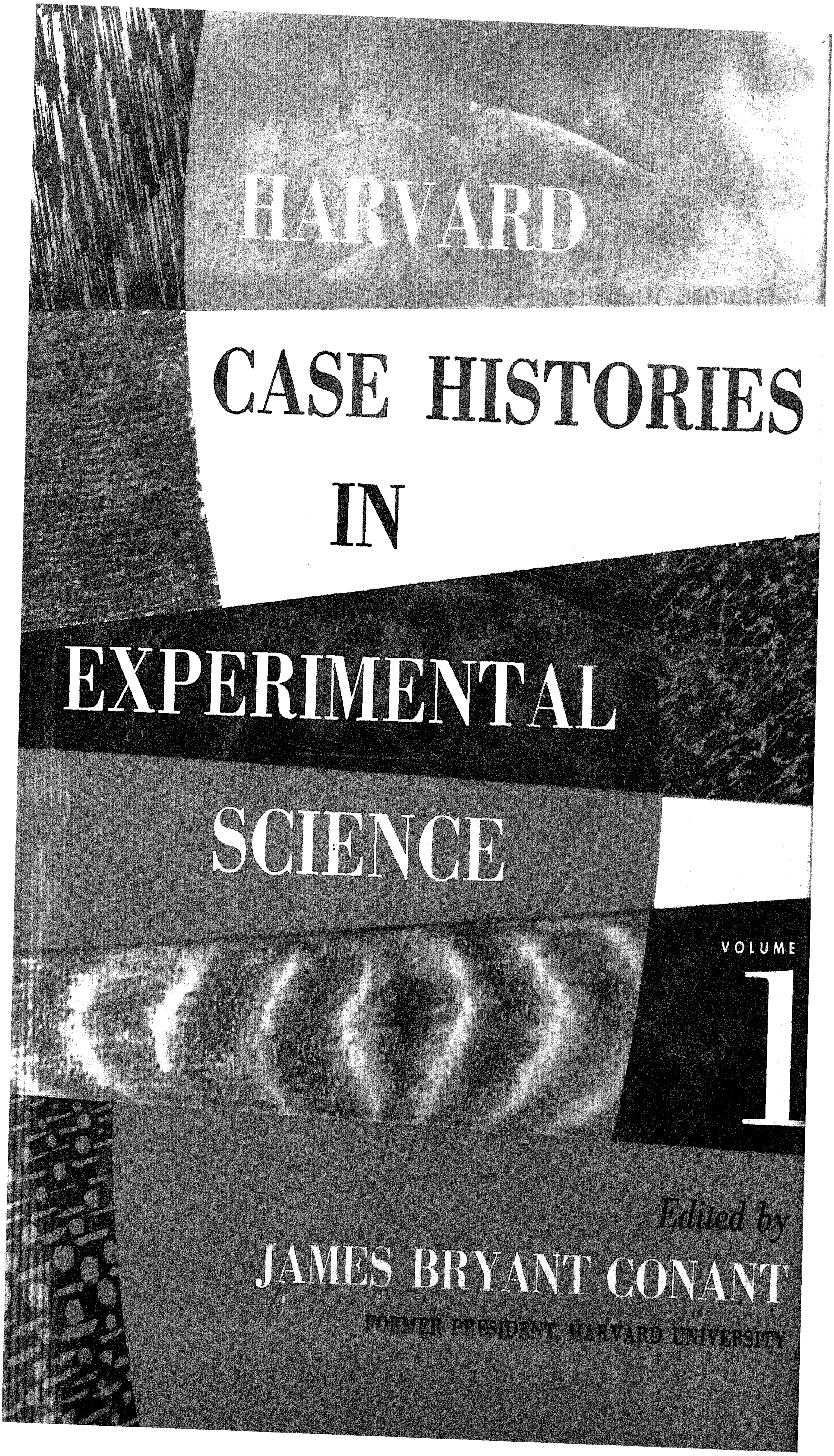

HARVARD
CASE HISTORIES IN EXPERIMENTAL SCIENCE

VOLUME
1

Edited by
JAMES BRYANT CONANT
FORMER PRESIDENT, HARVARD UNIVERSITY

HARVARD CASE HISTORIES
IN EXPERIMENTAL SCIENCE

edited and with a foreword by
James Bryant Conant

These volumes of the HARVARD CASE HISTORIES IN EXPERIMENTAL SCIENCE are designed to help the general reader relate developments in the natural sciences to those in the other fields of human activity.

No matter what his education and intelligence, the reader without research experience finds himself at a loss when required to evaluate the work of scientists, not because of his lack of scientific knowledge but because he has no sound general understanding of what science can or cannot accomplish. These narrative histories of great experiments help fill this gap by supplying what Dr. Conant describes as the "feel" for "the tactics and strategy of science."

Familiarity with the cases outlined in these volumes can lead the reader to a better understanding both of modern science and of modern technology. And attention paid to the kinds of difficulties that have arisen in the past over the testing of new concepts gives insight into what is happening in the laboratories of physics and chemistry today.

Edited and with a foreword by James B. Conant, distinguished scientist, teacher and diplomat, these histories were first prepared for students in the humanities and social sciences at Harvard College. They are now offered to a wider public in the belief that a detailed knowledge of a few epoch-making advances in science will provide a key to a better comprehension of the modern world.

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HARVARD CASE HISTORIES IN EXPERIMENTAL SCIENCE
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Introduction

The Harvard Case Histories in Experimental Science were designed primarily for students majoring in the humanities or the social sciences. Such students require an understanding of science that will help them to relate developments in the natural sciences to those in the other fields of human activity. To do so demands an understanding both of the methods of experimental science and of the growth of scientific research as an organized activity of society. Experience shows that a man who has been a successful investigator in any field of experimental science approaches a problem in pure or applied science, even in an area in which he is quite ignorant, with a special point of view. One may designate this point of view "understanding science"; it is independent of a knowledge of the scientific facts or techniques in the new area. Even a highly educated and intelligent citizen without research experience will almost always fail to grasp the essentials in a discussion that takes place among scientists concerned with a projected inquiry. This will be so not because of the layman's lack of scientific knowledge or his failure to comprehend the technical jargon of the scientist; it will be to a large degree because of his fundamental ignorance of what science can or cannot accomplish, and his subsequent bewilderment in the course of a discussion outlining a plan for a future investigation. He has no "feel" for what we may call "the tactics and strategy of science."

The present two-volume publication of the series was planned in order to make this material available to the general reading public. A citizen, a businessman, a public servant, a lawyer, a teacher, or a writer, may be called upon at some time to evaluate the work of scientists and to consider the ways in which such work can be organized and financed. He may wish also to consider to what degree systematic investigations more or less analogous to those that have been successful in the physical sciences may be fruitful in other fields. Although the first cases are concerned almost exclusively with the physical sciences, an understanding of the variety of methods by which these sciences have advanced will provide some basis, it is hoped, from which the citizen can appraise proposals for research and its applications in the biological and social sciences.

1. UNDERSTANDING SCIENCE

In order to appreciate the methods of the experimental sciences it is necessary to master a certain amount of technical subject matter within the fields of physics and chemistry although no one can prescribe the particular topics to be studied. It is quite clear that one need not attempt the task of surveying all physics or chemistry, nor is it necessary to memorize comprehensive factual information about the scientific basis of our modern technological civilization. If one understands the nature of modern science, such factual information can when needed be readily acquired by consulting appropriate books and articles.

A direct study of the methods of modern science presents great difficulties. A visitor to a laboratory, unless he is himself a scientist, will find it almost impossible to understand the work in progress; he will comprehend neither the objectives nor the implications of the measurements and observations that the investigator is making. To be sure, he may be able to appreciate in a general way the nature of the problem that is under investigation; he may well realize that the questions raised by those who planned the experiment are of importance — either for immediate practical reasons or as part of the general advance of science. But unless he himself has had considerable experience with scientific research, he will be baffled by what he sees or hears, for almost without exception research problems today are concerned with areas of science where there is a large accumulated background of technical information. To be able to follow the new work one must have studied the advance of the science thoroughly, which usually means mastering a considerable amount of mathematics as well as physics or chemistry or biology.

Modern science has become so complicated that today methods of research cannot be studied by looking over the shoulder of the scientist at work. If one could transport a visitor, however, to a laboratory where significant results were being obtained at an early stage in the history of a particular science, the situation would be far different. For when a science is in its infancy, and a new field is opened by a great pioneer, the relevant information of the past can be summed up in a relatively brief compass. Indeed, if the methods of experimental science are being successfully applied for the first time to a problem of importance, the scientist's knowledge would not be much greater than that of his inquiring guest. Briefly, and in simple language, he could explain the new experiment. Then as from day to day results were obtained and further experiments planned the visitor would see unfolding before him a new field. However, such periods in the history of science are relatively few, and it would be a fortunate visitor indeed who could spend some time merely as a witness of the events. For he would have the pleasure of knowing not only that he had been present at one of the critical battles in the forward march of science, but that he had had a unique opportunity of learning at first hand about the methods of science.

2. THE USE OF CASE HISTORIES

The purpose of the case histories presented in this series is to assist the reader in recapturing the experience of those who once participated in exciting events in scientific history. The study of a case may be to some degree the equivalent of the magical operation suggested in the preceding paragraph, namely, that of transporting an uninformed layman to the scene of a revolutionary advance in science. To be sure, usually more than one investigator or laboratory is involved and the period of time is at least several years; for, however significant a single experiment may seem in retrospect, no important step forward in experimental science rests solely on the record of any single investigator's observations. Rather, the interplay of ideas of several men, arguments about experiments and their interpretation between workers in different laboratories, often mark the decisive turn in scientific thinking. However, by the intensive study of the actual work of some of the great investigators of the past (and less in detail, the work of their contemporaries), the methods then employed stand out clearly.

Some of the cases in this series present the work of men who lived over three hundred years ago; others are drawn from the eighteenth and nineteenth centuries. But irrespective of their dates, the examples presented illustrate the methods of modern science. Familiarity with those methods will increase the ease of understanding of the work of scientists today; as one consequence, popular accounts of scientific progress can be read with more appreciation. If one is face to face with problems of financing or organizing research, a critical but sympathetic attitude toward experimental investigation is a prerequisite for an intelligent examination. The occasion may arise in connection with private industry, the expenditure of public money, or a philanthropic enterprise related to medicine and public health. Almost all that a trained scientist has to go on when he passes judgment on the prospects of a new venture far removed from his own specialty is his knowledge of the methods by which science has progressed in his own experience. To a considerable degree a nonscientist may come to have a similar basis for his opinions. An intimate acquaintance with a relatively few historic cases should assist him in finding his way through the complexities of modern investigation as he listens to those who tell him what is being proposed.

3. CONCERNING THE METHODS OF SCIENCE

Science I have defined as a series of concepts or conceptual schemes arising out of experiment and observation and leading to new experiments and new observations. From the experimental work and careful observations of nature come the scientific facts that are tied together by the concepts and conceptual schemes of modern science. The rather sudden burst of interest in the new "experimental philosophy" in the seventeenth century is historically related to a new interest on the part of thoughtful men in practical matters ranging from medicine through mining to the ballistics of cannon balls. But while the problems were often suggested by the interest of learned men in the practical arts, the development of science involved something more than the type of experimentation by which the practical arts had been developing for centuries. The method of reasoning employed in mathematics (for example, in geometry), commonly called deductive reasoning, had to be combined with the methods of experimentation that came from the practical arts before science could progress rapidly. The interaction of these two streams of human activity was largely responsible for the development of physics and chemistry; the focus of attention was shifted from an immediate task of improving a machine or a process to a curiosity about the phenomena in question. New ideas or concepts began to be as important as new inventions, and their interweaving began to produce conceptual fabrics whose various threads gained support from one another as well as from the direct results of experiment and observation.

Concepts and Conceptual Schemes. The cases presented in this series illustrate some of the many ways in which the new ideas (concepts) have arisen from observation and experiment and the consequences they have entailed. In more than one case we shall see a new conceptual scheme (theory) replacing an older one, or two rival schemes in conflict. The transition to a new theory is seldom easy; old ideas are apt to be tenacious. Looking back at the history of any branch of science we can see that a new conceptual scheme (theory) comes to be accepted because it is at least as satisfactory as the older one in relating all the known facts in a simple way and because it proves to be more fruitful of new experiments. The latter outcome is clearly a matter for the future, so that there can be no way to determine in advance whether a new concept or conceptual scheme will prove acceptable in this double sense; nor can one foretell how soon the next major advance will occur. A study of these cases makes it clear that there is no such thing as *the* scientific method, that there is no single type of conceptual scheme and no set of rules specifying how the next advance will be made through the jungle of facts that are presented by the practical arts on the one hand and by the experimentation and observation of scientists on the other.

Speculative Ideas and Broad Working Hypotheses. The relation between a speculative idea and a broad working hypothesis that becomes a wide conceptual scheme is of interest. A good example is furnished by the history of the atomic theory. The notion that there are fundamental units — ultimate particles — of which matter is composed goes back to ancient times. But expressed merely in general terms this is a speculative idea until it forms the basis of a broad working hypothesis from which consequences can be deduced that are capable of experimental test. This particular speculative idea became in Dalton's hands a broad working hypothesis and came to be a new conceptual scheme only after he had shown, about 1800, how fruitful it was in connection with the quantitative chemical experimentation that had been initiated by the chemical revolution.

Dalton's atomic theory is an instance where we can trace the origin of a conceptual scheme; in other cases we are uncertain how the idea came to the proponent's mind. Thus Torricelli seems to have been the first to suggest that we live in a "sea of air" that exerts a pressure analogous in many ways to the pressure of water on submerged objects; yet we have insufficient knowledge to say what led him to this idea. His famous experiment with a column of mercury, in which he made the first barometer, may have been the point of departure or it may have been a case of testing a deduction from a broad working hypothesis, arrived at by means that history does not record. At all events, from that time on a number of deduced consequences led to experiments nearly all of which were consistent with the ideas of Torricelli, and his hypothesis quickly attained the status of a new conceptual scheme.

The cases presented in this series emphasize the prime importance of a broad working hypothesis that eventually becomes a new conceptual scheme. They illustrate the variety of mental processes by which the pioneers of science developed their new ideas. But it must be emphasized that great working hypotheses have in the past often originated in the minds of these scientific pioneers as a result of mental processes that can best be described by such words as "inspired guess," "intuitive hunch," or "brilliant flash of imagination." The origins of the working hypotheses are to be found almost without exception in previous speculative ideas or in the previously known observations or experimental results. Only rarely, however, do these broad working hypotheses seem to have been the product of a careful examination of all the facts and a logical analysis of various ways of formulating a new principle.

The Testing of Deductions from Conceptual Schemes. When first put forward, a new conceptual scheme may be no more than a working hypothesis on a grand scale. From it we can deduce, however, many *consequences,* each of which can be tested by experiment. If these tests confirm the deductions in a number of instances, the accumulating evidence tends to confirm the broad working hypothesis and the hypothesis may soon come to be accepted as a new conceptual scheme; its subsequent life may be short or long, for from it new consequences are constantly being deduced that can be verified or not by experimental test.

While the modes of formulating broad working hypotheses are so varied as to defy generalization, the procedures by which these hypotheses are tested conform to a fairly consistent pattern. One is tempted, therefore, to represent the process of testing a broad conceptual scheme by a diagram. Unfortunately, however, the interrelations are so complex as to make a diagram more confusing than helpful. While our purpose would be defeated in the distortion necessary to compress a case history into a single diagram, we can perhaps suggest by a particular example, drawn from *part* of one case, the type of process involved in the experimental testing of broad conceptual schemes. Thus, at one stage in the development of pneumatics, Pascal deduced from Torricelli's idea of a sea of air the consequence that the air pressure should be less on a mountain top than at the base. This deduction could be expressed in some such words as these: if the Torricellian experiment is performed at such and such a place the height of the mercury column will be greater than on the same day at a nearby spot high up on a mountain. This prediction is susceptible of a test which yields a yes or no answer.

As the cases illustrate, however, there are often many slips in the argument at this point; unconscious assumptions are often involved that turn out to have been unwarranted. In general, the complete pattern of deduction linking the broad working hypotheses to the experimental tests proves far from simple. Thus, in the example just cited, the tacit assumption is clearly being made that the laws of liquid pressure and the density of mercury (and probably several other such things as well) are not themselves appreciably different at different altitudes; these assumptions find their ultimate justification (for the purposes of *this* experiment, at least) in other broad conceptual schemes such as make up the laws of hydrostatics. It is the multiplicity, the complexity, and indeed often the vagueness of this sort of interconnection that is ignored in many oversimplified discussions of "*the* scientific method."

Experimentation. The experiments performed to test deductions from broad working hypotheses involve in the last analysis a type of activity with which everyone is familiar. Examples of experimentation in everyday life come readily to mind. Whenever one has a choice of alternative ways of trying to solve a problem, decides on one, and then says in essence "let's try it and see," he is getting ready to perform an experiment. Framing various possibilities as to what is wrong with an automobile engine when the car is stalled is usually a preliminary to carrying out an actual trial, an experiment. Similarly, if a man is trying to locate a broken wire, a blown-out fuse, or a bad tube in a radio set, he usually turns over in his mind a number of tests that could be made and then tries first one and then another. He is guided in the formulation of his trials (experiments) by his knowledge of the automobile or the radio set in question and his general information about the behavior of these machines. When he finally carries out the experiment he is, however, testing the validity of a very *limited working hypothesis.* A simple and perhaps trivial example of the testing of a limited working hypothesis is when a person trying to unlock a door puts in the lock a hitherto untried key and says to himself, "if this key fits the lock, then the lock will spring when I turn the key." The trial either validates or negates the limited working hypothesis; the same is true of the final step in most experiments in science.

The difference between experimentation in everyday life and experimentation in science lies primarily in the fact that in the one case common-sense assumptions and practical experience determine the nature of the experiment; in the other, a series of connecting links usually relates some deductions of a broad working hypothesis with the final limited working hypothesis involved in the specific experiment. This will be more evident as one studies the cases. The steps by which practical men throughout the ages have improved the practical arts have also involved experimentation. Here, as in everyday life, however, the experiment is in almost every case planned in terms of common-sense assumptions and practical experience, not in terms of broad generalizations or conceptual schemes. Furthermore, as was pointed out in the opening paragraph of this section, experimentation in the practical arts always has a practical objective. Experimental science was the consequence of the combination of the ancient art of experimentation with the type of thinking that employs general ideas and deductive reasoning. Experimentation by itself does not produce science, although it is an essential element in advance in many fields of science.

The progress of science in many areas has depended on the overcoming of experimental difficulties, in part by the invention of new instruments and the discovery of new materials. A study of the types of difficulties that have arisen in the past and how they have interfered with the testing of new concepts and conceptual schemes throws light on what is going on in the laboratories of physics and chemistry today. Furthermore, in formulating problems according to certain conceptual schemes, and particularly in planning the experimental tests, it became necessary as science advanced to make precise and accurate many vague common-sense ideas, notably those connected with measurement. Old ideas were clarified or new ones introduced. These are the new concepts that are often quite as important as the broad conceptual schemes; for example, pressure, acceleration, mass, temperature, atom, are words that have now precise scientific meanings. At the time the new ideas were advanced that are considered in the case histories from the seventeenth, eighteenth, and nineteenth centuries, they were as novel as are in our own times the ideas of neutrinos and mesons in the field of nuclear physics.

A close attention to the difficulties that have beset investigators in getting clean-cut answers to apparently simple questions will suggest some of the complexities of research today. And the broader hypotheses must remain speculative ideas until one can by the processes indicated succeed in relating them to experiments.

4. THE ADVANCE OF SCIENCE AND PROGRESS IN THE PRACTICAL ARTS

The relation between advances in the practical arts (such as mining, agriculture, manufacturing) and progress in science is more complicated than at first sight appears. To appreciate the present situation, it is helpful to have some knowledge of the history of these two branches of human endeavor and of their interaction. For many generations after the new experimental philosophy was put forward by a few amateurs in the seventeenth century, the direct impact of science on the practical arts was almost negligible. This was the consequence not of any lack of interest in practical affairs on the part of the early scientists but of the fragmentary nature of the knowledge they acquired and the inadequacy of the conceptual schemes they elaborated. The advances in the practical arts of mining, metal making, agriculture, food processing, and medicine in the eighteenth and early nineteenth centuries were made without any very direct benefit of science. (The art of navigation is an exception to this statement.)

The ancient method of experiment, the use of the "let's-try-it-and-see" type of reasoning in solving immediate practical problems, has led over the centuries to amazing results. This process of advance is often called *pure empiricism,* there being no wide generalization to guide the inventor. Even today in the mid-twentieth century when science has penetrated so deeply into industry, there is still a great deal of empiricism in a practical art such as steel making. Even when no practical aim is involved, the practical methods of a science may contain many recipes and rules that have no relation to theory; in other words, there is some empiricism in almost all scientific procedures even now. It is often convenient to speak of the "degree of empiricism" in a given industrial process or branch of science. Where wide generalizations and theory enable one to calculate in advance the results of an experiment or to design a machine (a microscope or a telescope, for example), we may say that the degree of empiricism is low or that the theoretical component of the knowledge is large. On the other hand, if the conditions for satisfactory operation of a machine, a process, or an instrument are based only on cut-and-try experimentation (as is true in some branches of chemistry), we may say that the degree of empiricism in that branch of science is still high or that the theoretical component is small.

5. PURE AND APPLIED SCIENCE

Applied research may be defined as research directed to the end of reducing the degree of empiricism or increasing the theoretical component in a practical art. Activities concerned solely with developing and improving our conceptual schemes and filling in gaps in our systematic knowledge may be defined as pure science. Modern science is a fabric the texture of which is composed of many interrelated concepts and conceptual schemes. Today the validity of each conceptual scheme must be tested in the light of our total knowledge. The cases presented in this series fall in the category of pure science; they are nevertheless concerned for the most part with episodes in the history of science that eventually had great influence on applied science. The conceptual schemes elaborated by scientists have been fundamental to further discoveries and to the formulation of the ideas that are the fabric of modern science. With the aid of the concepts and theories developed over the past three hundred years, and drawing on the sytematic knowledge accumulated during that period, the applied scientist today can improve the industrial arts and invent new processes, products, and machines far more readily than could his predecessors of the seventeenth and eighteenth centuries. Science today is closely connected with technology because theory and the practical arts have become closely interwoven. The degree of empiricism has been lowered on almost every hand and is being still further reduced by the activity of investigators in laboratories of both pure and applied science. The applied scientist or engineer can now engage in what was once an activity of those inventors who proceeded largely empirically. The analysis of experimental science presented in this introduction and a study of the cases outlined in this series may lead the layman to a better understanding both of modern science and of modern technology. It was with this hope in mind that the present edition has been prepared. If the reader is stimulated to read further in the history of science and to follow current developments in some field through articles and books prepared for the general reader, our aim will have been achieved.

JAMES B. CONANT

New York City
August 1, 1957

CASE 1

Robert Boyle's Experiments in Pneumatics

EDITED BY

JAMES BRYANT CONANT

CASE 1

Robert Boyle's Experiments in Pneumatics

INTRODUCTION

If, in the last quarter of the seventeenth century, a well-educated person in England or France had been asked why water rises in a suction pump, the answer would have been in terms familiar to our ears. Phrases such as "pressure of the atmosphere," "creation of a vacuum," "air pressure dependent on the height above sea level" would have been used 250 years ago much as we use them in our own time. But if we jump back in our imagination a little more than three centuries, say to 1620, the picture changes. We have clear evidence from the printed records of those days that no such explanation of the action of suction pumps was available even to the most learned and clear-headed men of that time. People were talking in terms of "nature's abhorring a vacuum" and were unable to account for the fact that at sea level a suction pump will not raise water more than about 34 feet.

The radical change that took place between the first and last quarters of the seventeenth century was not confined to discussions of the action of pumps. During the fifty years in question there was a rapid development of what we now call science and was then known as "experimental philosophy." This changed attitude and the process by which the new knowledge was obtained are very well illustrated by a study of seventeenth-century experiments with air and the effect of air pressure on liquids. This subject was called in those days pneumatics. By tracing the growth of the new ideas (concepts) by which ever since that time people have explained a variety of phenomena, we obtain a "case history" of the way in which the experimental sciences developed.

For convenience, the study of pneumatics between 1630 and 1680 may be thought of in terms of the following subdivisions:

(i) Torricelli's experiment with a column of mercury, which included the invention of the barometer and his formulation of the conceptual scheme of a "sea of air" surrounding the earth;

(ii) Pascal's repetition of the Torricellian experiment and his instigation of the measurement of the barometric height at the foot and on the top of a mountain, in 1648;

(iii) Experiments with pumps to produce a vacuum, by von Guericke and by Boyle, 1650–1660;

(iv) Examination by Boyle of the phenomena accessible for study by means of a vacuum pump, including the search for a "more subtle fluid" than air, 1660–1680;

(v) A study of the compressibility of air as compared with that of water, including the discovery of Boyle's Law, 1660–1680.

Evangelista Torricelli (1608–1647), an Italian mathematician, was strongly influenced by the writings on mechanics of the Italian physicist Galileo. He worked on projectile motion and hydrodynamics, but is probably best known for the experiment that bears his name.

Blaise Pascal (1623–1662) is at least as well known for his philosophic writings and his work in mathematics as for his contributions to pneumatics. A mathematical theorem that bears his name was published when he was sixteen, and by the age of 31 he had assisted in establishing the mathematical theory of probability. He renounced scientific activity shortly thereafter, and during the last eight years of his life he was associated with the religious group known as the Jansenists.

Otto von Guericke (1602–1686), mayor of Magdeburg and a military engineer, performed many experiments similar to those of Boyle, and at about the same time. He built a water barometer some three stories high, and observed the variations of the height of the water from day to day.

Robert Boyle (1627–1691) is the central figure in this case. The seventh and last son of the "great" Earl of Cork, Boyle was a man of wealth who devoted his life to religion and science. Too young to have taken part in the Civil War in England in the middle of the seventeenth century, he resided in Oxford at the time when the Puritan element was in the ascendancy in the University. It was the gathering of amateur scientists in Oxford in the 1650's that led to the formation of the Royal Society in 1660, after the Restoration.

In Section 6 we shall consider briefly the relation of science to the practical arts in the seventeenth century. We shall see that the interest in pneumatics was connected to some degree with a concern of learned men with the performance of the common suction pump for raising water. The fact that water would not rise above a certain height in such a pump was almost certainly known to Torricelli, and it may well be that pondering on this phenomenon led him directly to his experiment with a liquid about 14 times as heavy as water, namely, liquid mercury. From this line of thinking may have developed the idea that a column of mercury only about 1/14 as high as the column of water could be supported by atmospheric pressure. Quite apart from the new interest in technologic matters, interest in pneumatics was also probably increased by the publication in 1575 of a Latin translation of an Alexandrian writer, Hero, on this subject. This new edition of an ancient treatise was well known by the beginning of the seventeenth century and called to peoples' minds many phenomena, including the action of a siphon and the fact that a liquid cannot flow from a closed vessel unless air can get in.

We can start our Case by considering the performance of the following experiment by Torricelli in 1643. Taking a glass tube (see Fig. 1) somewhat less than an inch in diameter and about a yard long, with one end closed, he filled the tube with mercury. Then, placing a finger over the open upper end, he inverted the tube so that the open end was immersed in an open dish of mercury. When he removed his finger from the open end, the mercury in the tube fell until the top of the mercury column was about 30 inches above the level of the mercury in the open dish. Between the top of the mercury column and the upper end of the tube was an empty space, which became known as a Torricellian vacuum. We shall see Boyle referring to this experiment as the experiment of *Torricellius*, or as the experiment *de vacuo.*[1]

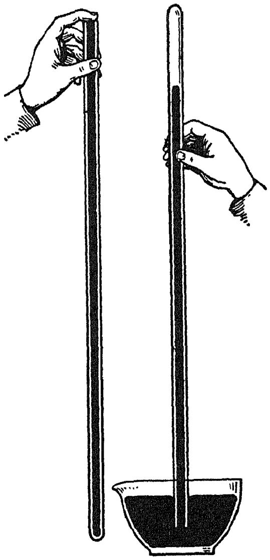

FIG. 1. Torricelli's experiment with a column of mercury in a tube longer than 30 inches.

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[1] A group in Florence, members of a scientific society called the Accademia del Cimento (Academy of Experiment), continued experiments with vacuum after Torricelli's death. They soon contrived to have the top of the tube consist of a

What led Torricelli to perform this famous experiment we cannot say. It may have been an accidental discovery, the consequence of an interest in the flow of liquids from small orifices; we know that Torricelli had been experimenting in this field. But more probably it was the act of an investigator who wished to test a deduction from a new idea — a working hypothesis on a grand scale. For in the earliest account[2] of the experiment that we have in Torricelli's own words, there is clearly set forth the new conceptual scheme. What most of us today regard as a fact, namely, that the earth is surrounded by a sea of air that exerts pressure, was in the 1640's a new conceptual scheme that had still to weather a series of experimental tests before it would be generally adopted.

Torricelli would never have been able to formulate his ideas as clearly as he did, however, if it had not been for earlier work of those who were concerned with the pressure of *liquids*. The subject is known as hydrostatics and the enunciation of the general principles involved goes back as far as Archimedes (B.C. 287?–212). Thanks to clear-headed writers in the sixteenth century, and in particular to Simon Stevin of Bruges (1548–1620), Torricelli and many of his contemporaries were familiar with such concepts as "pressure," which is force per unit area of surface, and "equilibrium." They knew that the pressure on the bottom of a vessel filled with a liquid depended on the height of the liquid in the vessel but not on its volume or its shape [Fig. 2*(a)*]. They realized that if the stopcock joining two vessels, one containing water, the other empty of water and open to the air, is quickly opened, the water will flow from one to the other, and soon the heights of the liquid will be the same [Fig. 2*(b)*]; the system is then in equilibrium. But for a few seconds before equilibrium is reached, the liquid may surge back and forth a little. The principles relating pressure and height of liquid were applicable only in the equilibrium state.

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bulb in which various devices could be placed. The whole could then be filled with mercury and inverted in the usual way, so that the device would be in a Torricellian vacuum. The results of these experiments were not published until after the publication of Boyle's first book, but he must have heard of them by word of mouth or by letter. We shall see that, although many of the experiments performed *in vacuo* by Boyle and by von Guericke could also be performed in a Torricellian vacuum, by using a vacuum produced by an air pump they were able to work on a larger scale and in a less awkward way.

[2] A letter from Torricelli to Cardinal Ricci, dated Florence, June 11, 1644. For an English translation, see *The Physical Treatises of Pascal*, translated by I. H. B. and A. G. H. Spiers (Columbia University Press, New York, 1937), pp. 163–170. Students of this case are strongly urged to read this exchange of letters between Torricelli and Ricci.

Armed with these concepts of hydrostatics, Torricelli and, after him, Pascal could formulate ideas about a sea of air. They could easily answer doubting Thomases who asked why the barometer did not fall if it were placed inside a large glass vessel that was sealed off from the surrounding air (Fig. 3). (This is one of the first objections on record to Torricelli's new idea of a sea of air. The answer was of course that the pressure inside the enclosing vessel was the same as the atmospheric pressure when the vessel was first closed off. There would be no change of pressure on the outer surface of the mercury of the barometer unless some of the air was removed. And it was precisely this that Boyle set out to accomplish!)

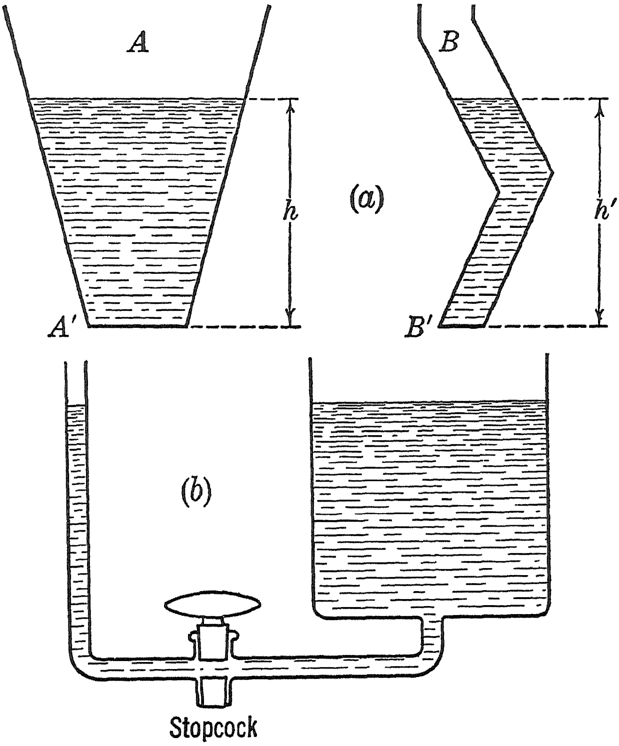

FIG. 2. Diagrams to illustrate the principles of hydrostatics known to Torricelli and his contemporaries: (*a*) in a homogeneous body of liquid, the pressure (force per unit area) at a given point depends on the depth below the surface; if the liquids in *A* and *B* are the same and homogeneous, the pressures at *A'* and *B'* are the same if $h = h'$; (*b*) in equilibrium, the levels of the liquids in connecting vessels are the same whatever the shapes of the vessels.

Pascal saw that from Torricelli's new conceptual scheme one could draw a logical conclusion susceptible of experimental test. For if the mercury column in Torricelli's new instrument — the barometer — were held up by the pressure of a sea of air, this pressure should be less above the earth's surface than at sea level. Just as the hydrostatic pressure in the ocean diminishes as a diver ascends from the bottom of a harbor toward the surface, so the pressure of the air should diminish as one ascends a mountain. From this line of reasoning came an experiment performed on the Puy-de-Dôme, a mountain in central France. Translating Pascal's deduction into specific experimental terms, one could say that the height of the mercury in a Torricellian experiment performed high on the mountain should be considerably less than if the experiment were conducted at the foot. The experiment was performed in 1648 by Pascal's brother-in-law, Perier,[3] and the deduction was confirmed. One cannot help, however, but be somewhat skeptical of the high degree of accuracy reported by Perier. To be able to repeat the Torricellian experiment so that there was less than a twelfth of an inch (one "line") difference in successive readings, as Perier claimed, is remarkable. The accidental intrusion of a slight amount of air is very difficult to avoid.

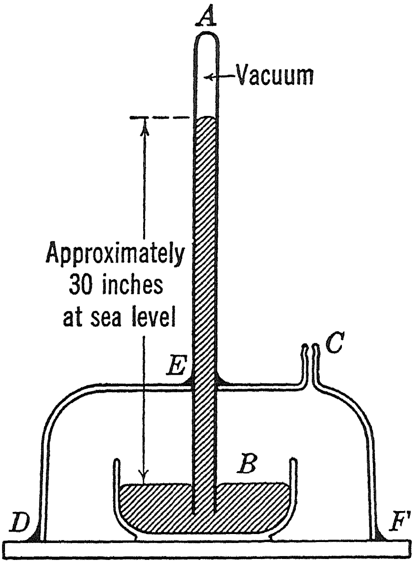

Fig. 3. Diagram of a barometer, with the reservoir *B* enclosed in a vessel *DEF*. Will the mercury in tube *A* fall into the reservoir *B* if the orifice *C* is sealed?

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[3] For an English translation of Perier's report, see *The Physical Treatises of Pascal*, pp. 97–120, and also preface, pp. ix–xxiv. This material can be read with profit by the student of this case, and is strongly recommended.

This report of Perier's was written, it must be remembered, before standards of accurate reporting in science had been established. The contrast with Boyle's procedures is striking. It may be that Perier, persuaded of the reality of the large differences in height of the mercury column at the top and bottom of the mountain, succumbed to the temptation of making his argument appear convincing by recording exact reproducibility of his results on repeated trials.

Robert Boyle heard of these experiments of Perier's in the 1650's, although the formal publication of Pascal's treatise dealing with hydrostatics and pneumatics was delayed until 1663. Boyle also knew of the air pump that had been constructed by Otto von Guericke and had heard of the Florentine method of performing experiments in a vacuum. (See footnote 1. The first full account of these experiments of the members of the Accademia del Cimento, however, was not published until 1667; von Guericke's pump was described briefly in a book by K. Schott in 1657.) Boyle saw the importance of having a more convenient method of removing the air from a glass globe in which various pieces of apparatus could be placed. In particular, he was interested in testing one of the deductions from Torricelli's conceptual scheme, namely, that if the air is removed from above the mercury reservoir of a barometer, the mercury column will fall. In other words, he desired to have an instrument with which he could evacuate the vessel *DEF* in Fig. 3 (with *C* closed).

The following sections of the Case History deal with (i) the construction of Boyle's pump; (ii) the experiment for which it was particularly designed; (iii) certain experiments on the transmission of sound which illustrate some of the many experiments Boyle was able to perform with his new pump; (iv) Boyle's search for a more subtle fluid; (v) his discovery, as a consequence of a controversy about the validity of his ideas, of what is now known as Boyle's law.

Boyle's work in pneumatics is an excellent illustration of the significance of improvement in experimental equipment for the advance of science. His improved pump made possible the exploration of a wide field of study; it was for his day the equivalent of the x-ray tubes of the late nineteenth century, the cyclotron of the twentieth century and perhaps even the experimental "piles" that since 1945 have produced radioactive isotopes as a consequence of the release of "atomic" energy. Boyle's experiments offered many instances of the care with which an experimenter in a new field must operate in order to obtain significant results. Mechanical difficulties must be overcome and this is by no means easy; moreover, new instruments must be invented, such as a gauge for showing the pressure in an evacuated vessel.

A careful analysis of Boyle's reports of his experiments will bring out the distinction between the limited working hypothesis and its verification or negation on the one hand, and the broad working hypotheses which, if successful, as will be seen, will soon become new conceptual schemes. Of the latter we note in this case four in particular: first, the "sea of air" hypothesis originating with Torricelli; second, the concept of air as an elastic fluid, or in Boyle's words, that air has a spring; third, that sound is transmitted by air; fourth, one that was not successful, namely, that there is a subtle fluid which pervades all space.

The *limited* working hypotheses are as numerous as the experiments. When Boyle built his engine he set out to test one deduction from Torricelli's broad hypothesis. When he had his apparatus all arranged he reasoned somewhat as follows: "If I now operate the pump, then the mercury column in the Torricellian tube should fall." This, be it noted, is a hypothesis strictly limited to that particular experiment. He proceeded with the experiment and the results were as predicted. He employed a similar "if . . . then" type of statement when he considered introducing air into the receiver; the mercury rose, as predicted. The student will find it profitable to identify a number of similar instances of this use of the limited working hypothesis in the experiments on sound and in Boyle's search for a subtle fluid. The connection between these limited working hypotheses and the broader idea that is being tested often involves a number of assumptions, sometimes not made explicit by Boyle. This is particularly clear in the experiments recorded in Sec. 4. Boyle's experiments did not disprove the existence of a subtle fluid in general. They could only test the presence in the air he examined of a specific fluid, more subtle than air, but having certain properties. These properties were such as to cause an effect on the instruments he manipulated in a vacuum (see pp. 39–48) if the subtle fluid were present.

The experiments that Boyle performed in his search for a subtle fluid may seem naïve and foolish to us, but a little thought will make it clear that they were well conceived to test a real possibility. For all the seventeenth-century investigators knew, air might have been composed of two or more materials differing in their ability to pass through very fine holes; such a difference is taken advantage of whenever we strain out a finely divided solid from a liquid, for example. Indeed, we now know that there is a very slight difference in the rate at which the constituent gases of the atmosphere (chiefly oxygen and nitrogen) flow through a tube of very small diameter. But this difference is so slight that it is not reflected in any behavior of air in experiments that could be performed with the equipment available in the seventeenth or even the eighteenth century. The great difference in "subtlety" for which Boyle was looking does not exist in any mixture of gases. It is in the nature of a gas that there can be no gross nonhomogeneity in the mixture, such as occurs in a suspension of fine particles of clay in water or even in water solutions of the materials that are present in blood or milk. More than a century elapsed, however, before it became obvious that such was indeed the case. And it was almost two centuries before the conceptual scheme was developed which we now use in all our explanations of the behavior of air and other gases (the kinetic theory of gases).

In reading the original records of the seventeenth-century investigators, the student will wish to have firmly in mind the simple ideas about atmospheric pressure that are almost common knowledge today. There are one or two less obvious points that now seem clear to us but long were puzzles to those who studied pneumatics in the seventeenth and eighteenth centuries. The first concerns the presence of water vapor in the atmosphere; the second, the evaporation of liquids both below the temperature at which they boil and during the process of boiling itself. Since the first notions that developed about the evaporation of water into the atmosphere were either wrong or confused, we are omitting the seventeenth-century experiments dealing with this subject.

At first Boyle was confused by the fact that water contains dissolved air, but he eventually came to understand the relation between boiling point and the pressure of the surrounding atmosphere; indeed, he invented an apparatus for distilling *in vacuo*. The question of the chemical homogeneity of the atmosphere had to be explored before a satisfactory picture could be developed and the relation of liquid water to water vapor properly understood. This hiatus must be mentioned, for today every reader of the weather reports is familiar not only with variations in atmospheric pressure but also with the degree of humidity on a given day. For a long time little or no sense could be made of the fluctuations in the barometer because it was believed that these fluctuations were directly related to what we now call humidity (that is, the relative amount of water vapor in the air). The student will naturally wonder what Boyle and his contemporaries made of their observations of the changes in the atmospheric pressure and of the behavior of water in the vacuum that they produced. Boyle and his contemporaries studied these phenomena but came to no satisfactory and enduring conclusions. This serves to illustrate the slow stages by which science often advances.

1. THE AIR PUMP OR VACUUM PUMP AS A NEW SCIENTIFIC INSTRUMENT

There were three models of Boyle's "pneumatical engine," as he called his pump for producing a vacuum. The first, described in a book published in 1660 (dated December 20, 1659), is shown in Figs.

4 and 5; a second is described in another book dated March 24, 1667 and published in 1669; and a third was described in a volume published in 1680. In the construction of the first two of these engines Robert Hooke played an important and perhaps determining role; the third was designed by Denis Papin in 1676 and was brought with him from France in the same year that he joined Boyle. As compared with the first air pump of von Guericke, Boyle's first model was far more convenient for those who wished to perform experiments *in vacuo*. The opening at the top of the glass bulb was the important new addition. The second model of Boyle's engine (Fig. 7) allowed various types of receivers to be evacuated, such as those shown in Fig. 8. Much larger equipment could be placed *in vacuo* than with the first model. The experiments were correspondingly more ambitious. The third model was more rapid in its action because it had two plungers and two pistons and was operated by foot power. The valves were automatic. Boyle likewise devised methods of measuring the diminished pressure by means of what are now called vacuum gauges; he also built compression pumps that enabled him to study air under pressure.

Boyle's public announcement of the construction of his first pump and the description of the experiments he performed were given in his book of 1660, carrying the title page:

NEW
EXPERIMENTS
Physico-Mechanicall,
Touching
The SPRING of the AIR,
and its EFFECTS,
(Made, for the most part, in a New
PNEUMATICAL ENGINE)
Written by way of LETTER
To the Right Honorable *Charles*
Lord Vicount of *Dungarvan,*
Eldest Son to the EARL of *CORKE.*

The first sections of the preface are of some general interest even today and therefore are given below:[4]

To the Reader

Although the following treatise being far more prolix than becomes a letter, and than I at first intended it, I am very unwilling to encrease

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[4] All quotations of Robert Boyle's writings are taken from a late edition of his collected writings, *The Works of the Honourable Robert Boyle* (London, 1772).

the already excessive bulk of the book by a preface; yet there are some particulars, that I think myself obliged to take notice of to the reader, as things that will either concern him to know, or me to have known.

In the first place then: If it be demanded why I publish to the world a letter, which, by its style and divers passages, appears to have been written as well for, as to a particular person; I have chiefly these two things to answer; the one, that the experiments therein related, having been many of them tried in the presence of ingenious men, and by that means having made some noise among the Virtuosi (insomuch that some of them have been sent into foreign countries, where they have had the luck not to be despised) I could not, without quite tiring more than one amanuensis, give out half as many copies of them as were so earnestly desired, that I could not civilly refuse them. The other, that intelligent persons in matters of this kind persuade me, that the publication of what I had observed touching the nature of the air, would not be useless to the world; and that in an age so taken with novelties as is ours, these new experiments would be grateful to the lovers of free and real learning: so that I might at once comply with my grand design of promoting experimental and useful philosophy, and obtain the great satisfaction of giving some to ingenious men; the hope of which is, I confess, a temptation, that I cannot easily resist.

Of my being somewhat prolix in many of my experiments, I have these reasons to render: that some of them being altogether new, seemed to need the being circumstantially related, to keep the reader from distrusting them: that divers circumstances I did here and there set down for fear of forgetting them, when I may hereafter have occasion to make use of them in my other writings: that in divers cases I thought it necessary to deliver things circumstantially, that the person I addressed them to might, without mistake, and with as little trouble as is possible, be able to repeat such unusual experiments: and that after I consented to let my observations be made public, the most ordinary reason of my prolixity was, that foreseeing, that such a trouble as I met with in making those trials carefully, and the great expence of time that they necessarily require (not to mention the charges of making the engine, and employing a man to manage it) will probably keep most men from trying again these experiments, I thought I might do the generality of my readers no unacceptable piece of service, by so punctually relating what I carefully observed, that they may look upon these narratives as standing records in our new pneumatics, and need not reiterate themselves an experiment to have as distinct an idea of it, as may suffice them to ground their reflexions and speculations upon. . . .

Boyle's description of the construction of his engine is very long and rather tedious. A few paragraphs will illustrate the great detail with which he reported his work. In so doing, Boyle was setting the model for subsequent scientists. Unless experiments are reported in detail and with accuracy, other scientists are often unable to repeat the experiment in question. The more complicated the phenomena investigated, the more necessary it becomes to establish the practice of recording and reporting details of construction of the apparatus and the results obtained. Failure to adhere to these rules in the seventeenth and eighteenth centuries often made worthless the reports of many investigators. The published works of Stevin, Galileo, and Pascal (to name the more important of Boyle's predecessors), are written for the most part in the form of geometric propositions and it is often not clear whether the experiments described were actually carried out or are to be regarded as *possible* demonstrations.

The introduction of Boyle's book is in the form of a letter to his nephew, of which the first sections are printed below.

> Receiving in your last from *Paris* a desire, that I would add some more experiments to those I formerly sent you over; I could not be so much your servant as I am, without looking upon that desire as a command; and consequently, without thinking myself obliged to consider by what sort of experiments it might the most acceptably be obeyed. And at the same time, perceiving by letters from some other ingenious persons at *Paris*, that several of the Virtuosi there were very intent upon the examination of the interest of the air, in hindering the descent of the quicksilver, in the famous experiment touching a vacuum; I thought I could not comply with your desires in a more fit and seasonable manner, than by prosecuting and endeavouring to promote that noble experiment of *Torricellius* [see p. 5]; and by presenting your Lordship an account of my attempts to illustrate a subject, about which its being so much discoursed of where you are, together with your inbred curiosity, and love of experimental learning, made me suppose you sufficiently inquisitive.
>
> And though I pretend not to acquaint you, on this occasion, with any store of new discoveries, yet possibly I shall be so happy, as to assist you to know some things, which you did formerly but suppose; and shall present you, if not with new theories, at least with new proofs of such as are not yet become unquestionable. And if what I shall deliver hath the good fortune to encourage and assist you to prosecute the hints it will afford, I shall account myself, in paying of a duty to you, to have done a piece of service to the commonwealth of learning. Since it may highly conduce to the advancement of that experimental philosophy, the effectual pursuit of which requires as well a purse as a brain, to endear it to hopeful persons of your quality, who may accomplish many things, which others cannot but wish, or at most but design, by being able to employ the presents of fortune in the search of the mysteries of nature.
>
> And I am not faintly induced to make choice of this subject, rather than any of the expected chymical ones, to entertain your Lordship upon,

by these two considerations: the one, that the air being so necessary to human life, that not only the generality of men, but most other creatures that breathe, cannot live many minutes without it, any considerable discovery of its nature seems likely to prove of moment to mankind. And the other is, that the ambient air being that, whereto both our own bodies, and most of the others we deal with here below, are almost perpetually contiguous, not only its alterations have a notable and manifest share in those obvious effects, that men have already been invited to ascribe thereunto, (such as are the various distempers incident to human bodies, especially if crazy in the spring, the autumn, and also on most of the great and sudden changes of weather;) but likewise, the further discovery of the nature of the air will probably discover to us, that it concurs more or less to the exhibiting of many phænomena, in which it hath hitherto scarce been suspected to have any interest. So that a true account of any experiment that is new concerning a thing, wherewith we have such constant and necessary intercourse, may not only prove of some advantage to human life, but gratify philosophers, by promoting their speculations on a subject, which hath so much opportunity to solicit their curiosity. . . .

You may be pleased to remember, that a while before our separation in *England*, I told you of a book, that I had heard of, but not perused, published by the industrious Jesuit *Schottus*; wherein, it was said, he related how that ingenious gentleman, *Otto Gericke*, consul of *Magdeburg*, had lately practised in *Germany* a way of emptying glass vessels, by sucking out the air at the mouth of the vessel, plunged under water. And you may also perhaps remember, that I expressed myself much delighted with this experiment, since thereby the great force of the external air (either rushing in at the opened orifice of the emptied vessel, or violently forcing up the water into it) was rendered more obvious and conspicuous than in any experiment that I had formerly seen. And though it may appear by some of those writings I sometimes shewed your Lordship, that I had been solicitous to try things upon the same ground; yet in regard this gentleman was before-hand with me in producing such considerable effects by means of the exsuction of air, I think myself obliged to acknowledge the assistance and encouragement the report of his performances hath afforded me.

But as few inventions happen to be at first so complete, as not to be either blemished with some deficiencies needful to be remedied, or otherwise capable of improvement; so when the engine, we have been speaking of, comes to be more attentively considered, there will appear two very considerable things to be desired in it. For first, the wind-pump (as somebody not improperly calls it) is so contrived, that to evacuate the vessel, there is required the continual labour of two strong men for divers hours. And next (which is an imperfection of much greater moment) the receiver, or glass to be emptied, consisting of one entire and uninterrupted globe and neck of glass; the whole engine is so made, that things cannot be conveyed into it, whereon to try experiments: so that there seems but little (if any thing) more to be expected from it, than those very few phaenomena, that have been already observed by the author, and recorded by *Schottus*. Wherefore to remedy these inconveniences, I put both Mr. *G.* and *R. Hook* (who hath also the honour to be known to your Lordship, and was with me when I had these things under consideration) to contrive some air-pump, that might not, like the other, need to be kept under water (which on divers occasions is inconvenient) and might be more easily managed: and after an unsuccessful trial or two of ways proposed by others, the last-named person fitted me with a pump, anon to be described. And thus the first imperfection of the German engine was in good measure, though not perfectly remedied: and to supply the second defect, it was considered, that it would not perhaps prove impossible to leave in the glass to be emptied a hole large enough to put in a man's arm cloathed; and consequently other bodies, not bigger than it, or longer than the inside of the vessel. And this design seemed the more hopeful, because I remembered, that having several years before often made the experiment *de vacuo* [see p. 5] with my own hands; I had, to examine some conjectures that occurred to me about it, caused glasses to be made with a hole at that end, which uses to be sealed up, and had nevertheless been able, as occasion required, to make use of such tubes, as if no such holes had been left in them, by devising stopples for them, made of the common plaister called diachylon [a sealing wax]; which, I rightly enough guessed, would, by reason of the exquisite commixtion of its small parts, and closeness of its texture, deny all access to the external air. Wherefore, supposing that by the help of such plaisters carefully laid upon the commissures of the stopple and hole to be made in the receiver, the external air might be hindered from insinuating itself between them into the vessel, we caused several such glasses, as you will find described a little lower, to be blown at the glass-house. And though we could not get the workmen to blow any of them so large, or of so convenient a shape as we would fain have had; yet finding one to be tolerably fit, and less unfit than any of the rest, we were content to make use of it in that engine; of which, I suppose, you by this time expect a description in order to the recital of the phænomena exhibited by it.

To give your Lordship then, in the first place, some account of the engine itself; it consists of two principal parts; a glass vessel, and a pump to draw the air out of it [Figs. 4 and 5].

The former of these (which we, with the glass-men, shall often call a receiver, for its affinity to the large vessels of that name, used by chymists) consists of a glass with a wide hole at the top, of a cover to that hole, and of a stop-cock fastened to the end of the neck, at the bottom.

The shape of the glass, you will find expressed in the first figure of the annexed scheme. And for the size of it, it contained about 30 wine quarts, each of them containing near two pound (of 16 ounces to the pound) of water. We should have been better pleased with a more capacious vessel; but the glass-men professed themselves unable to blow a larger, of such a thickness and shape as was requisite to our purpose.

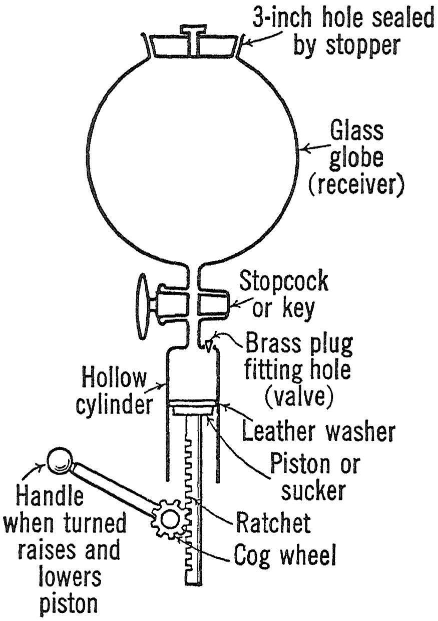

FIG. 4. Diagram of the first model of Boyle's air pump.

2. THE BEHAVIOR OF A TORRICELLIAN BAROMETER IN A VACUUM

The seventeenth experiment reported by Boyle in his volume of 1660 was the critical one for which he says he built the engine. No one had ever put this particular consequence of the new conceptual scheme to the experimental test. This experiment is, therefore, typical of a procedure repeatedly used with great effectiveness in the advance of the experimental sciences. From a new concept or conceptual scheme one can deduce that if the concept or set of concepts is a satisfactory scheme, then certain deductions follow that may be susceptible of experimental test.

Boyle saw that a new apparatus (von Guericke's pump), if *improved* and somewhat changed, would enable him to put to the experimental test another consequence of the new concepts about the atmosphere and its pressure. This he did in the manner described in the extract presented below. This combination of the possibilities inherent in a new type of machine — or a new chemical process — and the necessary consequences of a new concept has been one of the most fruitful sources of progress in the experimental sciences. For this reason, as a

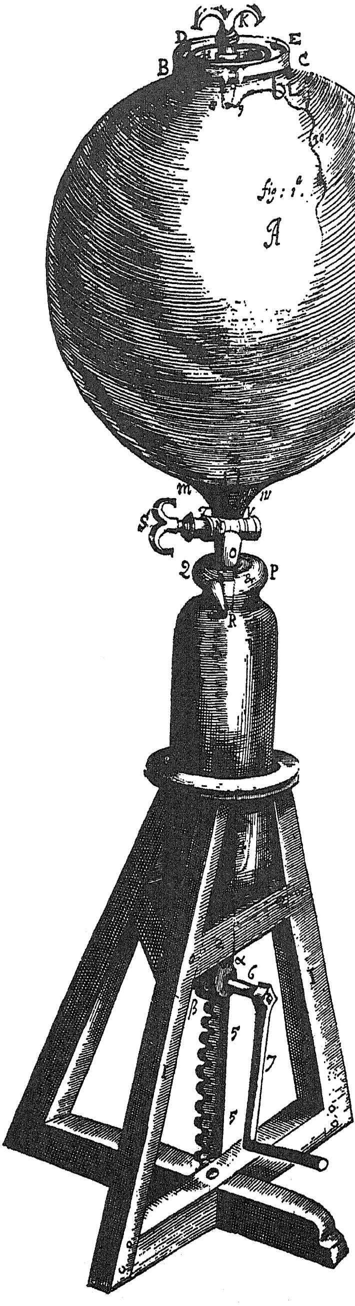

Fig. 5. Reproduction of a wood engraving of Boyle's first air pump, from his own book.

case in point, the details of Boyle's reasoning merit careful consideration by anyone who attempts to understand the methods of modern science.

Boyle's description of his seventeenth experiment now follows (the footnotes and the material enclosed in brackets have been added to assist the reader).

> Proceed we now to the mention of that experiment, whereof the satisfactory trial was the principal fruit I promised myself from our engine, it being then sufficiently known, that in the experiment *de vacuo*, the quicksilver in the tube is wont to remain elevated, above the surface of that whereon it leans, about 27 digits [about 29.5 inches, as Boyle explains later]. I considered, that, if the true and only reason why the quicksilver falls no lower, be, that at that altitude the mercurial cylinder in the tube is in an æquilibrium with the cylinder of air supposed to reach from the adjacent mercury to the top of the atmosphere [this is the conceptual scheme, suggested by Torricelli and elaborated by Pascal, that has been accepted ever since; note the use of the concept of equilibrium]; then if this experiment could be tried out of the atmosphere, the quicksilver in the tube would fall down to a level with that in the vessel, since then there would be no pressure upon the subjacent, to resist the weight of the incumbent mercury. Whence I inferred (as easily I might) that if the experiment could be tried in our engine, the quicksilver would subside below 27 digits, in proportion to the exsuction of air, that should be made out of the receiver. For, as when the air is shut into the receiver, it doth (according to what hath above been taught) continue there as strongly compressed, as it did whilst all the incumbent cylinder of the atmosphere leaned immediately upon it; because the glass, wherein it is penned up, hinders it to deliver itself, by an expansion of its parts, from the pressure wherewith it was shut up. So if we could perfectly draw the air out of the receiver, it would conduce as well to our purpose, as if we were allowed to try the experiment beyond the atmosphere.

It should be noted that throughout the descriptions of his experiments Boyle spells everything out in great detail. That the pressure within the glass receiver is just as great after the receiver is closed off as it was before is obvious today, but it was far from clear at first. One of the first objections (see p. 7 and Fig. 3) to Torricelli's new ideas was that if the weight of the air on the outside mercury was responsible for the mercury's standing about 30 inches in the Torricellian tube, then sealing the whole apparatus inside a box should cause the mercury to fall, since the weight of the air would then only be that of the small amount in the surrounding box (Fig. 3). The error here, as Torricelli showed, is a confusion of weight and pressure. Boyle had probably heard of these arguments but had probably not read the account of them that is now available to us.

Wherefore (after having surmounted some little difficulties, which occurred at the beginning) the experiment was made after this manner: we took a slender and very curiously blown cylinder of glass, of near three foot in length, and whose bore had in diameter a quarter of an inch, wanting a hair's breadth: this pipe being hermetically sealed at one end [i.e., the glass being melted together so that no air could subsequently leak in], was, at the other, filled with quicksilver, care being taken in the filling, that as few bubbles as was possible should be left in the mercury. Then the tube being stopt with the finger and inverted, was opened, according to the manner of the experiment, into a somewhat long and slender cylindrical box (instead of which we now are wont to use a glass of the same form) half filled with quicksilver: and so, the liquid metal being suffered to subside, and a piece of paper being pasted on level with its upper surface, the box and tube and all were by strings carefully let down into the receiver [through the opening at the top; see Fig. 6]: and then, by means of the hole formerly mentioned to be left in the cover, the said cover was slipt along as much of the tube as reached above the top of the receiver; and the interval, left betwixt the sides of the hole and those of the tube, was very exquisitely filled up with melted (but not over-hot) diachylon, and the round chink, betwixt the cover and the receiver, was likewise very carefully closed up: upon which closure there appeared not any change in the height of the mercurial cylinder, no more than if the interposed glass-receiver did not hinder the immediate pressure of the ambient atmosphere upon the inclosed air; which hereby appears to bear upon the mercury, rather by virtue of its spring than of its weight; since its weight cannot be supposed to amount to above two or three ounces, which is inconsiderable in comparison to such a cylinder of mercury as it would keep from subsiding.

All things being thus in a readiness, the sucker [Fig. 4] was drawn down; and, immediately upon the egress of a cylinder of air out of the receiver, the quicksilver in the tube did, according to expectation, subside: and notice being carefully taken (by a mark fastened to the outside) of the place where it stopt, we caused him that managed the pump to pump again, and marked how low the quicksilver fell at the second exsuction; but continuing this work, we were quickly hindered from accurately marking the stages made by the mercury, in its descent, because it soon sunk below the top of the receiver, so that we could henceforward mark it no other ways than by the eye. And thus, continuing the labour of pumping for about a quarter of an hour, we found ourselves unable to bring the quicksilver in the tube totally to subside; because, when the receiver was considerably emptied of its air, and consequently that little that remained grown unable to resist the irruption of the external, that air would (in spight of whatever we could do) press in at some little avenue or other; and though much could not thereat get in, yet a little was sufficient to counterbalance the pressure of so small a cylinder of quicksilver, as then remained in the tube.

Boyle subsequently used the length of such a column of mercury or its equivalent as a measure of the completeness of the vacuum he succeeded in producing in any experiment. We do the same today, but express our results in millimeters of mercury or in fractions of a millimeter of mercury. A well-constructed pump of Boyle's type today will hardly lower the pressure below a quarter of an inch of mercury. Pumps of a different type are required to produce the high vacua used in the modern laboratory and in the manufacture of electric light bulbs and radio tubes.

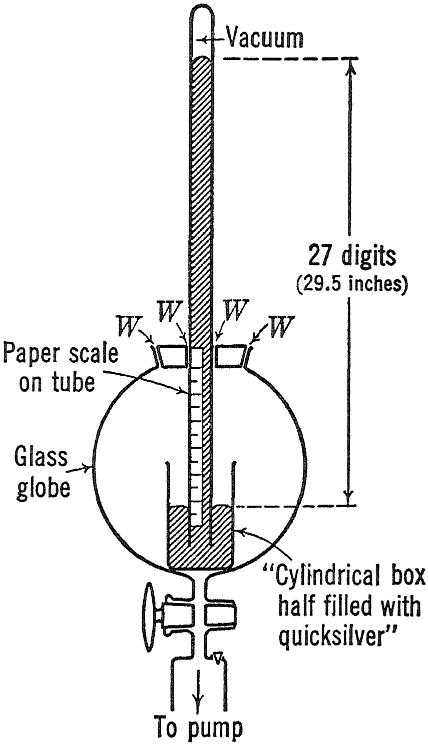

FIG. 6. Diagram of Boyle's apparatus for the experiment of removing the air above the reservoir of a barometer; *W* indicates "intervals" filled with "diachylon." The pump was that shown in Fig. 4.

> Now (to satisfy ourselves farther, that the falling of the quicksilver in the tube to a determinate height, proceedeth from the æquilibrium, wherein it is at that height with the external air, the one gravitating, the other pressing with equal force upon the subjacent mercury) we returned the key [Fig. 4] and let in some new air; upon which the mercury immediately began to ascend (or rather to be impelled upwards) in the tube, and continued ascending, till, having returned the key, it immediately rested at the height which it had then attained: and so, by

turning and returning the key, we did several times at pleasure impel it upwards, and check its ascent. And lastly, having given a free egress at the stop-cock to as much of the external air as would come in, the quicksilver was impelled up almost to its first height: I say almost, because it stopt near a quarter of an inch beneath the paper-mark formerly mentioned; which we ascribed to this, that there was (as is usual in this experiment) some little particles of air engaged among those of the quicksilver; which particles, upon the descent of the quicksilver, did manifestly rise up in bubbles towards the top of the tube, and by their pressure, as well as by lessening the cylinder by as much room as they formerly took up in it, hindered the quicksilver from regaining its first height.

This experiment was a few days after repeated, in the presence of those excellent and deservedly famous Mathematic Professors, Dr. *Wallis*, Dr. *Ward*, and Mr. *Wren*,[5] who were pleased to honour it with their presence; and whom I name, both as justly counting it an honour to be known to them, and as being glad of such judicious and illustrious witnesses of our experiment; and it was by their guess, that the top of the quicksilver in the tube was defined to be brought within an inch of the surface of that in the vessel.

And here, for the illustration of the foregoing experiment, it will not be amiss to mention some other particulars relating to it.

First then, when we endeavoured to make the experiment with the tube closed at one end with diachylon instead of an hermetical seal, we perceived, that upon the drawing of some of the air out of the receiver, the mercury did indeed begin to fall, but continued afterwards to subside, though we did not continue pumping. When it appeared, that though the diachylon, that stopt the end of the tube, were so thick and strong, that the external air could not press it in, (as experience taught us that it would have done, if there had been but little of it;) yet the subtler parts of it were able (though slowly) to insinuate themselves through the very body of the plaister, which it seems was not of so close a texture, as that which we mentioned ourselves to have successfully made use of, in the experiment *de vacuo* some years ago. So that now we begin to suspect, that perhaps one reason, why we cannot perfectly pump out the air, may be, that when the vessel is almost empty, some of the subtler parts of the external air may, by the pressure of the atmosphere, be strained through the very body of the diachylon into the receiver. But this is only conjecture.

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[5] These men were all at Oxford in the period 1655–1660 when the embryonic Royal Society was forming. Wren is the famous architect who rebuilt London after the great fire; Wallis and Ward were distinguished mathematicians. Wallis served the Parliamentary Armies in the Civil War by deciphering Royalist dispatches (a fact of which little was probably said after the Restoration in 1660); Wren was "intruded" into All Souls College by a parliamentary committee during the Cromwellian period.

Here we see Boyle recording his experimental troubles. A tube sealed at the upper end with wax (diachylon) was often not leakproof. The conjecture that air might be a mixture of materials of differing degrees of "subtlety" is the basis of the experiments described in Sec. 4 of this Case History, and we see here how this thought could well have arisen from the experimental problem of obtaining airtight seals.

> Another circumstance of our experiment was this, that if (when the quicksilver in the tube was fallen low) too much ingress were, at the hole of the stop-cock, suddenly permitted to the external air; it would rush in with that violence, and bear so forcibly upon the surface of the subjacent quicksilver, that it would impel it up into the tube rudely enough to endanger the breaking of the glass.
>
> We formerly mentioned, that the quicksilver did not, in its descent, fall as much at a time, after the two or three first exsuctions of the air, as at the beginning. For, having marked its several stages upon the tube, we found, that at the first suck it descended an inch and ⅜, and at the second an inch and ⅜; and when the vessel was almost emptied, it could scarce at one exsuction be drawn down above the breadth of a barley-corn. And indeed we found it very difficult to measure, in what proportion these decrements of the mercurial cylinder did proceed; partly, because (as we have already intimated) the quicksilver was soon drawn below the top of the receiver; and partly because, upon its descent at each exsuction, it would immediately reascend a little upwards; either by reason of the leaking of the vessel at some imperceptible hole or other, or by reason of the motion of restitution in the air, which, being somewhat compressed by the fall as well as weight of the quicksilver, would repel it a little upwards, and make it vibrate a little up and down, before they could reduce each other to such an æquilibrium as both might rest in.
>
> But though we could not hitherto make observations accurate enough, concerning the measures of the quicksilver's descent, to reduce them into any hypothesis, yet would we not discourage any from attempting it; since, if it could be reduced to a certainty, it is probable, that the discovery would not be unuseful.
>
> And, to illustrate this matter a little more, we will add, that we made a shift to try the experiment in one of our above mentioned [in a section of Boyle's book not reproduced herein] small receivers, not containing a quart; but (agreeably to what we formerly observed) we found it as difficult to bring this to be quite empty as to evacuate the greater; the least external air that could get in (and we could not possibly keep it all perfectly out) sufficing, in so small a vessel, to display a considerable pressure upon the surface of the mercury, and thereby hinder that in the tube from falling to a level with it. But this is remarkable, that having two or three times tried the experiment in a small vessel upon the very first cylinder of air that was drawn out of the receiver, the mercury fell in the tube 18 inches and a half, and another trial 19 inches and a half. . . .

The ratio of the volume of the receiver — i.e., the vessel being evacuated — to the volume of the cylinder of the pump determines the effects of each stroke of the piston. With Boyle's large receiver, probably this ratio was something like 20 to 1. Each stroke of the piston would thus reduce the pressure by about 1/21 which for the first stroke would mean a fall in mercury level of about 1½ inch; with a small receiver whose volume was less than that of the pump cylinder the pressure would be reduced by more than one half (by 18 or 19 inches, Boyle records).

The next few paragraphs of the book, which are omitted here, discuss Boyle's futile attempts to reason in numerical terms about the phenomena he had observed. He was unable to reduce his qualitative observations to a quantitative basis; he was unable to use the new conceptual scheme for he did not see at that time that if two vessels of equal volume, one full of air at atmospheric pressure, the other essentially empty, are connected, the pressure becomes the same in both vessels, namely, half of what it originally was in the first vessel.

> For farther confirmation of what hath been delivered, we likewise tried the experiment in a tube of less than two foot long: and, when there was so much air drawn out of the vessel, that the remaining air was not able to counterbalance the mercurial cylinder, the quicksilver in the tube subsided so visibly, that (the experiment being tried in the little vessel lately mentioned) at the first suck it fell above a span, and was afterwards drawn lower and lower for a little while; and the external air being let in upon it, impelled it up again almost to the top of the tube: so little matters it, how heavy or light the cylinder of quicksilver to subside is, provided its gravity overpower the pressure of as much external air as bears upon the surface of that mercury into which it is to fall.

In other words, it is unnecessary to start with a barometer in this experiment, for a short inverted tube filled with mercury will suffice. This is the equivalent of the lower portion of the Torricellian tube; it is far more convenient than the long tube, and the simplest vacuum gauges used today in chemical and physical laboratories are constructed in this way.

> Lastly, we also observed, that if (when the mercury in the tube had been drawn down, and by an ingress permitted to the external air, impelled up again to its former height) there were some more air thrust up by the help of the pump into the receiver, the quicksilver in the tube would ascend much above the wonted height of 27 digits, and immediately upon the letting out of that air would fall again to the height it rested at before. [Here Boyle pumps air *into* the receiver and shows that the increased pressure causes the height of the mercury to increase beyond the barometric height.]

> Your Lordship will here perhaps expect, that as those, who have treated of the Torricellian experiment, have for the most part maintained the affirmative, or the negative of that famous question, whether or no that noble experiment infer a vacuum? so I should on this occasion interpose my opinion touching that controversy; or at least declare, whether or no, in our engine, the exsuction of the air do prove the place deserted by the air sucked out to be truly empty, that is, devoid of all corporeal substance. But besides that I have neither the leisure, nor the ability, to enter into a solemn debate of so nice a question; your Lordship may, if you think it worth the trouble, in the Dialogues not long since referred to, find the difficulties on both sides represented, which then made me yield but a very wavering assent to either of the parties contending about the question: nor dare I yet take upon me to determine so difficult a controversy.
>
> For on the one side it appears, that notwithstanding the exsuction of the air, our receiver may not be destitute of all bodies, since any thing placed in it, may be seen there; which would not be, if it were not pervious to those beams of light, which rebounding from the seen object to our eyes, affect us with the sense of it: and that either these beams are corporeal emanations from some lucid body, or else at least the light they convey doth result from the brisk motion of some subtle matter, I could, if I mistake not, sufficiently manifest out of the Dialogues above-mentioned, if I thought your Lordship could seriously imagine that light could be conveyed without, at least, having (if I may so speak) a body for its vehicle.

In the eighteenth and nineteenth centuries, as in the seventeenth, it would have been taken for granted that light was either a beam of particles that would pass through glass or else a motion in a medium that pervaded glass. The latter view seemed to be established by experiment early in the nineteenth century and the medium was given the name "luminiferous ether" or "ether" (not to be confused with the anaesthetic with the same name). The same medium could be invoked to explain the action of magnetism (see Boyle's next two paragraphs). This medium was imagined to be far too subtle, to use Boyle's phrase, to be subject to mechanical rarefaction or compression as is air. As the study of radiant energy proceeded, the conceptual scheme that postulated ether as a medium became inadequate because it failed to account for certain phenomena. The answer to the question raised by Boyle's contemporaries, if a vacuum is really empty how can you see through it, cannot be given today in terms of any one simple conceptual scheme. Modern views simply challenge the assumption that seemed so obvious to Boyle and many later scientists, namely, that light must for its conveyance require "a body for its vehicle."

> By the sixteenth experiment, it also appears that the closeness of our receiver hinders it not from admitting the effluvia of the load-stone;[6] which makes it very probable that it also freely admits the magnetical steams of the earth; concerning which, we have in another treatise endeavoured to manifest that numbers of them do always permeate our air.
>
> But on the other side it may be said, that as for the subtle matter which makes the objects enclosed in our evacuated receiver, visible, and the magnetical effluvia of the earth that may be presumed to pass through it, though we should grant our vessel not to be quite devoid of them, yet we cannot so reasonably affirm it to be replenished with them, as we may suppose, that if they were gathered together into one place without intervals between them, they would fill but a small part of the whole receiver. As in the thirteenth experiment, a piece of match was inconsiderable for its bulk, whilst its parts lay close together, that afterwards (when the fire had scattered them into smoke) seemed to replenish all the vessel. For (as elsewhere our experiments have demonstrated) both light and the effluvia of the load-stone may be readily admitted into a glass, hermetically sealed, though before their admission, as full of air as hollow bodies here below are wont to be; so that upon the exsuction of the air, the large space deserted by it, may remain empty, notwithstanding the pretence of those subtle corpuscles, by which lucid and magnetical bodies produce their effects.

In short, "those subtle corpuscles, by which lucid and magnetical bodies produce their effects" are quite independent of the particles that compose the air. This may be considered a preview of the doctrine of the ether as it was expounded by all scientists 75 years ago. The relevance of the experiment with the match is not obvious. The thirteenth experiment consisted in allowing the smoke from a "slow match" — a slow-burning material used for ignition of cannon — to fill an evacuated receiver, which it did, of course, rapidly. This phenomenon inspired Boyle perhaps unduly; he saw in it a visualization of the way "subtle material" such as air will expand at once and fill a space; he likewise recognized that a very minute amount of match was consumed in producing enough smoke to fill a large receiver. Therefore, he argues that the still more subtle corpuscles that convey light need be of but little bulk if solidified all together.

The controversy between the Vacuists and the Plenists, referred to in the next paragraph, goes back at least to Aristotle. In the form referred

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[6] What we would now call the field of a magnet. In short, a magnet — a piece of the naturally occurring magnetized iron ore is called a loadstone — will exert a force on iron placed in a vacuum. This had been demonstrated by the Florentine experiments and also by von Guericke before Boyle's experiments. The phrase "magnetical steams of the earth" in the same sentence refers to the earth's magnetic field, about which Boyle speculated in another book.

to by Boyle, it continued until the close of the century. The plenists confused the "subtle material the vehicle of light" with air. To them the explanation of why water will not run out of an inverted bottle with a narrow neck (unless air is shaken in or another opening made) was as follows: if the water comes out, the surrounding medium must be displaced, and it can be displaced only if there is somewhere for it to go. If a second opening is provided in the bottle, the displaced medium can enter; therefore, the water runs out.

According to the Plenists the world was full, by definition; a vacuum was unthinkable; these were the postulates of their position. A further premise of their position, but one not recognized, was that the medium was essentially incompressible; otherwise the water might run out of an inverted bottle by compressing rather than displacing the surrounding medium. It may be left to the reader to see how the position of the Plenists became untenable in the light of the Torricellian experiment unless some additional and arbitrary assumptions were introduced.

> And as for the allegations above-mentioned, they seemed to prove but that the receiver devoid of air, may be replenished with some etherial matter, as some modern Naturalists write of, but not that it really is so. And indeed to me it yet seems, that as to those spaces which the Vacuists would have to be empty, because they are manifestly devoid of air and all grosser bodies; the Plenists (if I may so call them) do not prove that such spaces are replenished with such a subtle matter as they speak of, by any sensible effects, or operations of it (of which divers new trials purposely made, have not yet shewn me any) but only conclude that there must be such a body, because there cannot be a void. And the reason why there cannot be a void, being by them taken, not from any experiments, or phænomena of nature, that clearly and particularly prove their hypothesis, but from their notion of a body, whose nature, according to them, consisting only in extension (which indeed seems the property most essential to, because inseparable from a body) to say a space devoid of body, is, to speak in the schoolmen's phrase, a contradiction *in adjecto*. This reason, I say, being thus desumed, seems to make the controversy about a vacuum rather a metaphysical, than a physiological question;[7] which therefore we shall here no longer debate, finding it very difficult either to satisfy Naturalists with this Cartesian notion of a body, or to manifest wherein it is erroneous, and substitute a better in its stead.
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> But though we are unwilling to examine any farther the inferences wont to be made from the Torricellian experiment, yet we think it not

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[7] This curious use of the word "physiological" is now obsolete; in the seventeenth century the word "physiology" was sometimes used as equivalent to natural science.

impertinent to present your Lordship with a couple of advertisements concerning it.

First then, if in trying the experiment here or elsewhere, you make use of the English measures that mathematicians and tradesmen are here wont to employ, you will, unless you be forewarned of it, be apt to suspect that those that have written of the experiment have been mistaken. For whereas men are wont generally to talk of the quicksilver's remaining suspended at the height of between six or seven and twenty inches; we commonly observed, when divers years since we first were solicitous about this experiment, that the quicksilver in the tube rested at about 29 inches and a half above the surface of the restagnant quicksilver in the vessel, which did at first both amaze and perplex us, because though we held it not improbable that the difference of the grosser English air, and that of Italy and France, might keep the quicksilver from falling quite as low in this colder, as in those warmer climates; yet we could not believe that that difference in the air should alone be able to make so great an one in the heights of the mercurial cylinders; and accordingly upon enquiry we found, that though the various density of the air be not to be overlooked in this experiment, yet the main reason why we found the cylinder of mercury to consist of so many inches, was this, that our English inches are somewhat inferior in length to the digits made use of in foreign parts, by the writers of the experiment.[8]

The next thing I desire your Lordship to take notice of, is, that the height of the mercurial cylinder is not wont to be found altogether so great as really it might prove, by reason of the negligence or incogitancy of most that make the experiment. For oftentimes upon the opening of the inverted tube into the vesselled mercury, you may observe a bubble of air to ascend from the bottom of the tube through the subsiding quicksilver to the top; and almost always you may, if you look narrowly, take notice of a multitude of small bubbles all along the inside of the tube betwixt the quicksilver and the glass; (not now to mention the particles of air that lie concealed in the very body of the mercury:) many of which, upon the quicksilver's forsaking the upper part of the tube, do break into that deserted space where they find little or no resistance to their expanding of themselves. [It is difficulties such as this that are the basis of one's skepticism about the accuracy of Perier's reports (see p. 8).] Whether this be the reason, that upon the application of warm bodies to the emptied part of the tube,[9] the subjacent mercury would be depressed somewhat lower, we shall not determine; though it

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[8] Difficulties of this sort have led to an international agreement on standards of measurement. The accuracy required in modern experiments has meant that providing standards has become a rather elaborate matter.

[9] We are now quite certain that this is the reason. To the extent that there is air in the space above the mercury in the Torricellian tube, warming and cooling this space will affect the height of the column since air expands and contracts with changes in temperature, a fact well known by 1660.

seem very probable, especially since we found, that, upon the application of linen cloths dipped in water, to the same part of the tube, the quicksilver would somewhat ascend; as if the cold had condensed the imprisoned air (that pressed upon it) into a lesser room. But that the deserted space is not wont to be totally devoid of air, we were induced to think by several circumstances: for when an eminent mathematician, and excellent experimenter, had taken great pains and spent much time in accurately filling up a tube of mercury, we found that yet there remained store of inconspicuous bubbles, by inverting the tube, letting the quicksilver fall to its wonted height; and by applying (by degrees) a red-hot iron to the outside of the tube, over against the upper part of the mercurial cylinder, (for hereby the little unheeded bubbles, being mightily expanded, ascended in such numbers, and so fast to the deserted space, that the upper part of the quicksilver seemed, to our wonder, to boil.) We farther observed, that in the trials of the Torricellian experiment, we have seen made by others, and (one excepted) all our own, we never found that, upon the inclining of the tube, the quicksilver would fully reach to the very top of the sealed end: which argued, that there was some air retreated thither that kept the mercury out of the unreplenished space. [This is the forerunner of many such methods of checking on the performance of an apparatus. If Perier had reported that he had made this test in each instance, one would be more inclined to take seriously the reported accuracy of his results. But despite Perier's statement that he "carefully rid the tube of air," one remains skeptical of his ability to repeat the Torricellian experiment with an accuracy of a twelfth of an inch.]

If your Lordship should now demand what are the best expedients to hinder the intrusion of the air in this experiment; we must answer, that of those which are easily intelligible without ocular demonstration; we can at present suggest, upon our own trials, no better than these. First, at the open end of the tube the glass must not only be made as even at the edges as you can, but it is very convenient (especially if the tube be large) that the bottom be every way bent inwards, that so the orifice not much exceeding a quarter of an inch in diameter, may be the more easily and exactly stopped by the experimenter's finger; between which and the quicksilver, that there may be no air intercepted (as very often it happens that there is) it is requisite that the tube be filled as full as possibly it can be, that the finger which is to stop it, pressing upon the accumulated and protuberant mercury, may rather throw down some, than not find enough exactly to keep out the air. It is also an useful and compendious way not to fill the tube at first quite of mercury, but to leave near the top about a quarter of an inch empty; for if you then stop the open end with your finger, and invert the tube, that quarter of an inch of air will ascend in a great bubble to the top, and in its passage thither, will gather up all the little bubbles, and unite them with itself into one great one; so that if by reinverting the tube, you let that bubble return to the open end of it, you will have a much closer mercurial cylin-

> der than before, and need but to add a very little quicksilver more to fill up the tube exactly. And lastly, as for those lesser and inconspicuous parcels of air which cannot this way be gleaned up, you may endeavour, before you invert the tube, to free the quicksilver from them by shaking the tube, and gently knocking on the outside of it, after every little parcel of quicksilver which you pour in; and afterwards, by forcing the small latitant bubbles of air to disclose themselves and break, by imploying a hot iron in such manner as we lately mentioned. I remember that by carefully filling the tube, though yet it were not quite free from air, we have made the mercurial cylinder reach to 30 inches and above an eighth, and this in a very short tube: which we therefore mention, because we have found, by experience, that in short tubes a little air is more prejudicial to the experiment than in long ones, where the air having more room to expand itself, doth less potently press upon the subjacent mercury.

Note the type of extremely helpful suggestions given by Boyle for the benefit of others who wished likewise to experiment; before the publication of this book in 1660 few if any instances are on record of a similar concern with the difficulties of other experimenters except in so far as the recipes of the alchemists can be considered in this category.

3. BOYLE'S EXPERIMENTS ON AIR AS A MEDIUM FOR TRANSMITTING SOUND

Boyle's published record of two experiments on air as a medium for transmitting sound is given in this section. The first is Experiment 27 in his book of 1660; the second is Experiment 41 of his second book on pneumatics, published in 1669.

Boyle's description of his twenty-seventh experiment in his account of 1660 follows.

> That the air is the medium, whereby sounds are conveyed to the ear, hath been for many ages, and is yet the common doctrine of the schools. But this received opinion hath been of late opposed by some philosophers upon the account of an experiment made by the industrious *Kircher*, and other learned men; who have (as they assure us) observed, that if a bell, with a steel clapper, be so fastened to the inside of a tube, that upon the making the experiment *de vacuo* [see footnote 1] with that tube, the bell remained suspended in the deserted space at the upper end of the tube: and if also a vigorous load-stone be applied on the outside of the tube to the bell, it will attract the clapper, which, upon the removal of the load-stone falling back, will strike against the opposite side of the bell, and thereby produce a very audible sound; whence divers have concluded, that it is not the air, but some more subtle body, that is the medium of sounds. But because we conceived, that, to invalidate such a consequence from this ingenious experiment, (though the most luciferous that could well be made without some such engine as ours) some things

might be speciously enough alledged; we thought fit to make a trial or two, in order to the discovery of what the air doth in conveying of sounds, reserving divers other experiments triable in our engine concerning sounds, till we can obtain more leisure to prosecute them. Conceiving it then the best way to make our trial with such a noise, as might not be loud enough to make it difficult to discern slighter variations in it, but rather might be, both lasting (that we might take notice by what degrees it decreased) and so small, that it could not grow much weaker without becoming imperceptible; we took a watch, whose case we opened, that the contained air might have free egress into that of the receiver. And this watch was suspended in the cavity of the vessel only by a pack-thread, as the unlikeliest thing to convey a sound to the top of the receiver; and then closing up the vessel with melted plaister, we listened near the sides of it, and plainly enough heard the noise made by the balance. [Boyle clearly recognized the importance of controlling the conditions in an experiment. The method of supporting the source of the noise at first sight appears irrelevant. On further reflection, however, it is clear that the sound might be transmitted through this support. If so, a thread seemed less likely to convey sound than a metal or wooden support. To make sure that a watch so suspended by a thread in air could still be heard, Boyle proceeded to determine whether he could hear the watch *before* he pumped out the air.] Those also of us, that watched for that circumstance, observed, that the noise seemed to come directly in a streight line from the watch unto the ear. And it was observable to this purpose, that we found a manifest disparity of noise, by holding our ears near the sides of the receiver, and near the cover of it: which difference seemed to proceed from that of the texture of the glass, from the structure of the cover (and the cement) through which the sound was propagated from the watch to the ear. But let us prosecute our experiment [that is, let us start pumping the air out of the receiver in which the watch is suspended by a thread]. The pump after this being employed, it seemed, that from time to time the sound grew fainter and fainter; so that when the receiver was emptied as much as it used to be for the foregoing experiments, neither we, nor some strangers, that chanced to be then in the room, could, by applying our ears to the very sides, hear any noise from within; though we could easily perceive, that by the moving of the hand, which marked the second minutes, and by that of the balance, that the watch neither stood still, nor remarkably varied from its wonted motion. And to satisfy ourselves farther, that it was indeed the absence of the air about the watch, that hindered us from hearing it, we let in the external air at the stop-cock; and then though we turned the key and stopt the valve, yet we could plainly hear the noise made by the balance, though we held our ears sometimes at two foot distance from the outside of the receiver; and this experiment being reiterated into another place, succeeded after the like manner. Which seems to prove, that whether or no the air be the only, it is at least the principal medium of sounds. [A very cautious interpretation of the experimental findings. Boyle recognizes

> that there might be two or more media by which sound was transmitted, but if so the second medium did not play the principal part in the usual case. His search for a second more "subtle medium" is recorded in Sec. 4.] And by the way it is very well worth noting, that in a vessel so well closed as our receiver, so weak a pulse as that the balance of a watch, should propagate a motion to the air in a physically streight line, notwithstanding the interposition of so close a body as glass, especially glass of such thickness as that of our receiver; since by this it seems the air imprisoned in the glass must, by the motion of the balance, be made to beat against the concave part of the receiver, strongly enough to make its convex part beat upon the contiguous air, and so propagate the motion to the listner's ears. [Boyle here reverts to a discussion of the fact that before the air was pumped out, one could hear the watch imprisoned in the receiver.] I know this cannot but seem strange to those, who, with an eminent modern philosopher, will not allow, that a sound, made in the cavity of a room, or other place so closed, that there is no intercourse betwixt the external and internal air, can be heard by those without, unless the sounding body do immediately strike against some part of the inclosing body. But not having now time to handle controversies, we shall only annex, that after the foregoing experiment, we took a bell of about two inches in diameter at the bottom, which was supported in the midst of the cavity of the receiver by a bent stick, which by reason of its spring pressed with its two ends against the opposite parts of the inside of the vessel: in which, when it was closed up, we observed, that the bell seemed to sound more dead than it did when just before it sounded in the open air. And yet, when afterwards we had (as formerly) emptied the receiver, we could not discern any considerable change (for some said they observed a small one) in the loudness of the sound. Whereby it seemed, that though the air be the principal medium of sound, yet either a more subtle matter may be also a medium of it, or else an ambient body, that contains but very few particles of air, in comparison of those it is easily capable of, is sufficient for that purpose. And this, among other things, invited us to consider, whether in the above-mentioned experiment made with the bell and the load-stone, there might not in the deserted part of the tube remain air enough to produce a sound; since the tubes for the experiment *de vacuo* (not to mention the usual thinness of the glass) being seldom made greater than is requisite, a little air might bear a not inconsiderable proportion to the deserted space: and that also, in the experiment *de vacuo*, as it is wont to be made, there is generally some little air, that gets in from without, or at least store of bubbles, that arise from the body of the quicksilver, or other liquor itself, observations heedfully made have frequently informed us; and it may also appear, by what hath been formerly delivered concerning the Torricellian experiment.

Experimentation with a Torricellian vacuum was certainly difficult. We now know that the two major sources of error in the study of the propagation of sound in a vacuum are (i) the presence of air in the evacuated space, (ii) the transmission of sound by the solid support of the source of the sound.

We now turn to the record of some experiments performed some six or seven years later with the aid of the second and improved model of Boyle's pneumatic engine. Boyle's original drawing of this arrangement is reproduced in Fig. 7. Here he shows a still more convenient method

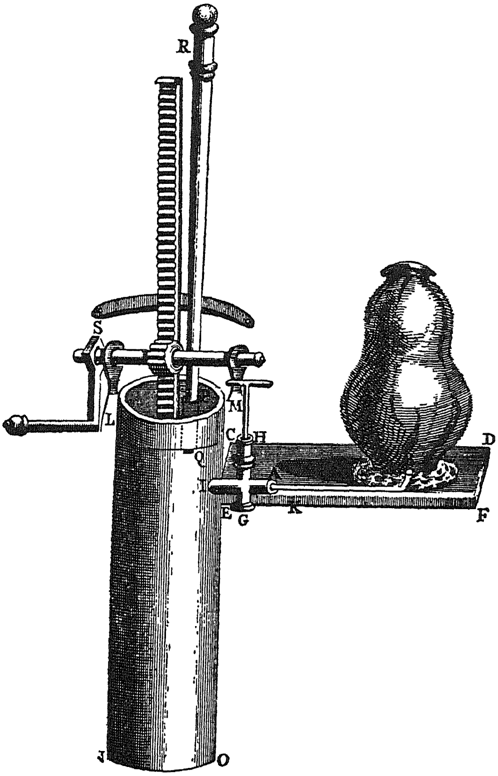

Fig. 7. Boyle's second air pump. This illustration is partly diagrammatic: the iron plate *CDEF* onto which the glass receiver is sealed is imagined to be cut away so as to show the tube *AB* connecting the receiver with the pump through the valve *HG*; the structure of the pump is not indicated, but was essentially the same as in the first model.

of performing experiments *in vacuo*. For in this case the apparatus to be studied rests on an iron plate under a bell jar, which is then sealed by wax to the plate and the air evacuated through a hole in the bottom of the plate connected by a tube to the pump. This is still the usual arrangement in lecture-table demonstrations of experiments in a vacuum.

EXPERIMENT 41 [of the book entitled *A Continuation of New Experiments Physico-Mechanical Touching the Spring and Weight of the Air, and their Effects*, published in 1669].

About the propagation of sounds in the exhausted receiver.

To make some further observation than is mentioned in the published experiments, about the production and conveying of sounds in a glass whence the air is drawn out, we employed a contrivance, of which, because we make use of it in divers other experiments, it will be requisite to give your lordship here some short description.

We caused to be made at the turner's a cylinder of box, or the like close and firm wood, and of a length suitable to that of the receiver it was to be employed in. Out of the lower basis of this cylinder (which might be about an inch and a half in diameter) there came a smaller cylinder or axle-tree, not a quarter so thick as the other, and less than an inch long; this was turned very true, that it might move to and fro; or, as the tradesmen call it, ride very smoothly in a little ferrule or ring of brass, that was by the same turner made for it in the midst of the fixed trencher (as we call a piece of solid wood, shaped like a mill-stone) being four or five inches, more or less (according to the wideness of the receiver) in breadth, and between one and two in thickness; and in a large and round groove or gutter, purposely made in the lower part of this trencher, I caused as much lead as would fill it up to be placed and fastened, that it might keep the trencher from being easily moved out of its place or posture, and in the upper part of this trencher it was intended that holes should be made at such places as should be thought fit, to place bodies at several distances as occasion should require. The upper basis of the cylinder had also coming out of the midst of it another axle-tree, but wider than the former, that, into a cavity made in it, it might receive the lower end of the turning-key divers times already mentioned, to which it was to be fastened by a slender peg of brass thrust through two correspondent holes, the one made in the key, and the other in the newly-mentioned socket (if I may so call it) of the axle-tree. Besides all which, there were divers horizontal perforations bored here and there in the pillar itself, to which this axis belonged, which pillar we shall, to avoid ambiguity, call the vertical cylinder. The general use of this contrivance (whose other parts need not to be mentioned before the experiments where they are employed) is, that the end of the turning-key being put into the socket, and the lower axis of the vertical cylinder into the trencher, by the motion of the key a body fastened at one of the holes to the cylinder may be approached to, or removed from, or made to rub or strike against another body fastened in a convenient posture to the upper part of the trencher. [The apparatus here described was depicted by Boyle as shown in Fig. 8.]

To come now to our trial about sounds, we caused a hand-bell (whose handle and clapper were taken away) to be fastened to a strong wire, that, one end of the wire being made fast in the trencher, the other end,

> which was purposely bent downwards, took hold of the bell. In another hole made in the circumference of the same trencher was wedged in (with a wooden peg) a steel-spring, to whose upper part was tied a gad of iron or steel, less than an inch long, but of a pretty thickness. The length of this spring was such, as to make the upper part of the hammer (if I may so call the piece of iron) of the same height with the bell, and the distance of the spring from the bell was such, that when it was forced back the other way, it might at its return make the hammer strike briskly upon the outside of the bell.

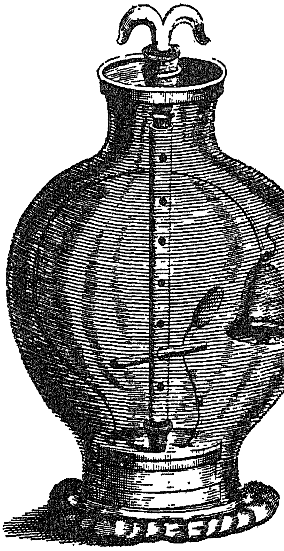

FIG. 8. Wood engraving from Boyle's book, showing the "cylinder or axle tree" connected to a "turning key" which enabled Boyle to strike a bell in a vacuum.

Boyle used a brass cover on some of his bell jars, thus enabling him to have a "key," fitted through a carefully constructed opening, which could be turned without admitting air. The difficulties of having this key turn in an airtight bearing are very great. There must have been a considerable amount of leakage in the apparatus. In the third paragraph below, Boyle describes an experimental precaution against leakage of air around the key. If he had at this time developed instruments for measuring the air pressure *inside* an evacuated vessel (as he later did), he could have carried out all these experiments with more assurance. He would then have made his observations at the same low pressure, say that corresponding to 1 inch-of-mercury.

The trencher being thus furnished and placed in a capped receiver (as you know, for brevity sake, we use to call one that is fitted with one or other of the brass covers, often mentioned already) the air was diligently pumped out; and then, by the help of the turning-key, the vertical cylinder was made to go round, by which means as often as either of a couple of stiff wires or small pegs that were fastened at right angles into holes, made not far from the bottom of the cylinder, passed (under the bell, and) by the lately mentioned spring, they forcibly did in their passage bend it from the bell, by which means, as soon as the wire was gone by, and the spring ceased to be pressed, it would fly back with violence enough to make the hammer give a smart stroke upon the bell: and by this means we could both continue the experiment at discretion, and make the percussions more equally strong, than it would otherwise have been easy to do.

The event of our trial was, that, when the receiver was well emptied, it sometimes seemed doubtful, especially to some of the by-standers, whether any sound were produced or no; but to me, for the most part, it seemed, that after much attention I heard a sound, that I could but just hear; and yet, which is odd, methought it had somewhat of the nature of shrilness in it, but seemed (which is not strange) to come from a good way off. Whether the often turning of the cylindrical key kept the receiver from being so stanch as else it would have been, upon which score some little air might insinuate itself, I shall not positively determine; but to discover what interest the presence or the absence of the air might have in the loudness or lowness of the sound, I caused the air to be let into the receiver, not all at once, but at several times, with competent intervals between them; by which expedient it was easy to observe, that the vertical cylinder being still made to go round, when a little air was let in, the stroke of the hammer upon the bell (that before could now and then not be heard, and for the most part be but very scarcely heard) began to be easily heard; and when a little more air was let in, the sound grew more and more audible, and so increased, until the receiver was again replenished with air; though even then (that we omit not that phænomenon) the sound was observed to be much less loud than when the receiver was not interposed between the bell and the ear.

And whereas in the already published physico-mechanical experiments [Experiment 27, p. 30], I acquainted your lordship with what I observed about the sound of an ordinary watch in the exhausted receiver, I shall now add, that that experiment was repeated not long since, with the addition of suspending in the receiver a watch with a good alarum, which was purposely so set, that it might, before it should begin to ring, give us time to cement on the receiver very carefully, exhaust it very diligently, and settle ourselves in a silent and attentive posture. And to make this experiment in some respect more accurate than the others we made of sounds, we secured ourselves against any leaking at the top, by imploying a receiver that was made all of one piece of glass (and consequently had no cover cemented on to it) being furnished only within (when it was first blown) with a glass-knob or button, to which a string might be tied. And because it might be suspected, that if the watch were suspended by its own silver chain, the tremulous motion of its sounding bell might be propagated by that metalline chain [the same question that arose in Experiment 27] to the upper part of the glass, to obviate this as well as we could, we hung the watch, not by its chain, but a very slender thread, whose upper end was fastened to the newly mentioned glass-button.

These things being done, and the air being carefully pumped out, we silently expected the time, when the alarum should begin to ring, which it was easy to know by the help of our other watches; but not hearing any noise so soon as we expected, it would perhaps have been doubted whether the watch continued going, if for prevention we had not ordered the matter so, that we could discern it did not stand still: wherefore I desired an ingenious gentleman to hold his ear just over the button at which the watch was suspended, and to hold it also very near to the receiver; upon which he told us, that he could perceive, and but just perceive something of sound that seemed to come from far; though neither we that listened very attentively near other parts of the receiver, nor he, if his ears were no more advantaged in point of position than ours, were satisfied that we heard the watch at all. Wherefore ordering some air to be let in, we did, by the help of attention, begin to hear the alarum, whose sound was odd enough, and, by returning the stop-cock to keep any more air from getting in, we kept the sound thus low for a pretty while, after which a little more air, that was permitted to enter, made it become more audible; and when the air was yet more freely admitted, the by-standers could plainly hear the noise of the yet continuing alarum at a considerable distance from the receiver. [By using a thread for a support, and eliminating the turning key (and thus the leakage), Boyle has finally succeeded in reducing the sound to a point where it cannot be heard. When air is allowed to enter the receiver, the sound is readily audible. The evidence that air is the medium for transmitting sound is now quite convincing.]

From what has hitherto been related, we may learn what is to be thought of what is delivered by the learned *Mersennus*,[10] in that book of his Harmonicks, where he makes this to be the first proposition. *Sonus à campanis, vel altis corporibus non solum producitur in illo vacuo (quicquid tandem illud sit) quod sit in tubis hydrargyro plenis, posteaque depletis, sed etiam idem acumen, quod in aere libero vel clauso penitus observatur & auditur.*[11] For the proof of which assertion, not long after,

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[10] Father Mersenne, the indefatigable reporter of experimental philosophy through whom Pascal first learned of Torricelli's experiment. Boyle seems to be referring to his report of the Florentine work on the propagation of sound in a vacuum carried out with a Torricellian vacuum.

[11] A free translation of the Latin passage is as follows: Not only is the sound of even the shrillest bells produced in the vacuum (whatever that may finally turn

he speaks thus: *porro variis tubis, quorum extremis lagenæ vitreæ adglutinantur, observari campanas in illo vacuo appensas propriisque malleis percussas idem penitus acumen retinere, quod in aere libero habent: atque soni magnitudinem ei sono, qui sit in aere quem tubus clausus includit, nihil cedere.*[12] But though our experiments sufficiently manifest, that the presence or absence of the common air is of no small importance as to the conveying of sounds, and that the interposition of glass may sensibly weaken them; yet so diligent and faithful a writer as *Mersennus* deserves to be favourably treated; and therefore I shall represent on his behalf, that what he says may well enough have been true, as far as could be gathered from the trials he made. For, first, it is no easy matter, especially for those that have not peculiar and very close cements, to keep the air quite out for any considerable time in vessels consisting of divers pieces, such as he appears to have made use of; and next, the bigness of the bell in reference to the capacity of the exhausted glass, and the thickness of the glass, and the manner whereby the bell was fastened to the inside of the glass, and the hammer or clapper was made to strike, may much vary the effect of the trial, for reasons easy to be gathered out of the past discourse, and therefore not needful to be here insisted on. And upon this account we chose to make our experiment with sounds that should not be strong or loud, and to produce them after such a manner, as that as little shaking as could be might be given by the sounding body to the glass it was included in.

4. BOYLE'S ATTEMPT TO DISCOVER A MEDIUM MORE SUBTLE THAN AIR

We have already noted Boyle's concern with the possibility that in addition to the air which he could pump out of his receivers, there might be present in the atmosphere more subtle material that would pass through holes too small to allow the passage of air. Such a medium, which had been postulated by Descartes and to some degree confused with air by subsequent proponents of the Plenist doctrine, might conceivably be still present in an evacuated receiver and still subject to movement by mechanical means. To test this possibility, Boyle contrived a series of ingenious experiments some of which are described in the following account of Experiments 38, 39, and 40 of his book of 1669. All these experiments yielded negative results.

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out to be) which he makes by filling tubes with mercury and then pouring them off [i.e., by performing the Torricellian experiment], but also the pitch is observed to be the same as that heard in free but entirely enclosed air.

[12] "Further, bells hung in the vacuum, produced in inverted glass flagons to whose mouths tubes have been glued, are observed when struck with their own hammers to maintain the same pitch that they would have in the open air. Also it is noted that the loudness of the tone is no less than that produced by the bells when the tubes contain air."

EXPERIMENT 38 [from Boyle's *Continuation* of 1669]

About an attempt to examine the motions and sensibility of the Cartesian Materia subtilis, *or the Æther, with a pair of bellows made of a bladder, in the exhausted receiver.*

I will not now discuss the controversy betwixt some of the modern atomists and the Cartesians; the former of whom think, that betwixt the earth and the stars, and betwixt these themselves, there are vast tracts of space that are empty, save where the beams of light do pass through them; and the latter of whom tell us, that the intervals betwixt the stars and planets, among which the earth may perhaps be reckoned, are perfectly filled, but by a matter far subtler than our air, which some call celestial, and others aether. I shall not, I say, engage in this controversy; but thus much seems evident, that if there be such a celestial matter, it must make up far the greatest part of the universe known to us. For the interstellar part of the world, if I may so stile it, bears so very great a proportion to the globes, and their atmospheres too, if other stars have any, as well as the earth, that it is almost incomparably greater in respect of them, than all our atmosphere is in respect of the clouds, not to make the comparison between the sea and the fishes that swim in it.

Wherefore I thought it might very well deserve a heedful inquiry, whether we can by sensible experiments (for I hear what has been attempted by speculative arguments) discover any thing about the existence, or the qualifications of this so vast aether; and I hoped our curiosity might be somewhat assisted by our engine, if I could manage in it such a pair of bellows as I designed: for I proposed to myself to fasten a convenient weight to the upper basis, and clog the lower with another great enough to keep it horizontal and immoveable; that when by the help of the turning-key frequently above mentioned, the upper basis should be raised to its full height, the cavity of the bellows might be brought to its full dimensions: this done, I intended to exhaust the receiver, and consequently the thus opened bellows, with more than ordinary diligence, that so both the receiver and they might be carefully freed from air: after which I purposed to let go the upper base of the bellows, that, being hastily depressed by the incumbent weight, it might speedily enough fall down to the lower basis, and by so much, and so quickly lessening the cavity, might expel thence the matter (if any were) before contained in it, and that (if it could by this way be done) at the hole of a slender pipe fastened either near the bottom of the bellows, or in the upper basis; against, or over the orifice, of which pipe there was to be placed at a convenient distance, either a feather, or (if that should prove too light) the sail of a little windmill made of cards, or some other light body, and fit to be put into motion by the impulse of any matter that should be forced out of the pipe.

By this means it seemed not improbable that some such discovery might be made, as would not be altogether useless in our inquiry. For if, notwithstanding the absence of the air, it should appear by the effects, that a stream of other matter capable to set visible bodies a moving, should issue out at the pipe of the compressed bellows, it would also appear that there may be a much subtler body than common air,[13] and as yet unobserved by the vacuists, or (their adversaries) the schools, that may even copiously be found in places deserted by the air; and that it is not safe to conclude from the absence of the air in our receivers, and in the upper part of those tubes where the Torricellian experiment is made, that there is no other body left but an absolute vacuity, or (as the atomists call it) a *vacuum coacervatum*. But if, on the other side, there should appear no motion at all to be produced, so much as in the feather, it seemed that the vacuists might plausibly argue, that either the cavity of the bellows was absolutely empty, or else that it would be very difficult to prove by any sensible experiment that it was full; and if, by any other way of probation, it be demonstrable that it was replenished with aether, we, that have not yet declared for any party, may by our experiment be taught to have no confident expectations of easily making it sensible by mechanical experiments; and may also be informed, that it is really so subtle and yielding a matter that does not either easily impel such light bodies as even feathers, or sensibly resist, as does the air itself, the motions of other bodies through it, and is able, without resistance, to make its passage through the pores of wood and leather, and also of closer bodies, which we find not that the air doth in its natural or wonted state penetrate.

To illustrate this last clause, I shall add, that to make the trial more accurate, I waved the use of other bellows (especially not having such as I desired) and caused a pair of small bellows to be made with a bladder, as a body, which some of our former experiments have evinced to be of so close a texture, that air will rather break it than pass through it; and that the bladder might no where lose its entireness by seams, we glued on the two bases, the one to the bottom and the other to the opposite part of it, so that the neck came out at a hole purposely made for it in the upper basis; and into the neck it was easy to insert what pipe we thought fit, binding the neck very close to it on the outside. We had likewise thoughts to have another pair of tight bellows made with a very light clack [the valve that allows air to be drawn into the bellows] in the lower basis, that by hastily drawing up the other basis, when the receiver and bellows were very carefully exhausted, we might see by the rest, as the lifting up of the clack, whether the subtle matter that was expelled by the upper basis in its ascent would, according to the modern doctrine of the circle made by moving bodies, be impelled up or not. [The phrase "modern doctrine" refers to certain ideas of Descartes which in the middle of the seventeenth century were modern!]

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[13] More subtle because it would not have been removed by his pump, yet not so subtle as to fail to be moved in a stream by a quick compression of a bellows; this is a very limited definition of a subtle fluid (see p. 10).

We also thought of placing the little pipe of the bladder-bellows (if I may so call them) beneath the surface of water exquisitely freed from air, that we might see, whether upon the depression of the bellows by the incumbent weight, when the receiver was carefully exhausted, there would be any thing expelled at the pipe that would produce bubbles in the liquor wherein its orifice was immersed.

To bring now our conjectures to some trial, we put into a capped receiver the bladder accommodated as before is mentioned; and though we could have wished it had been somewhat larger, because it contained but between half a pint and a pint, yet in regard it was fine and limber, and otherwise fit for our turn, we resolved to try how it would do; and to depress the upper basis of these little bellows the more easily and uniformly, we covered the round piece of pasteboard that made the upper basis with a pewter-plate (with a hole in it for the neck of the bladder) which nevertheless, upon trial, proved not ponderous enough, whereby we were obliged to assist it by laying on it a weight of lead. And to secure the above-mentioned feather (which had a slender and flexible stem, and was left broad at one end, and fastened by cement at the other, so as to stand with its broad end at a convenient distance just over the orifice of the pipe) from being blown aside to either hand, we made it to move in a perpendicular slit in a piece of pasteboard that was fastened to one part of the upper basis, as that which the feather was glued to was to another part. [Figure 9 is a reproduction of Boyle's pictures of this apparatus, the details of the arrangement of the feather being shown separately. Turning the key raised the top of the bellows; the lead weight caused it to fall when desired.] These things being thus provided, the pump was set a-work; and as the ambient air was from time to time withdrawn, so the air in the bladder expanded itself so strongly, as to lift up the metalline weight, and yet in part to sally out at the little glass-pipe of our bellows, as appeared by its blowing up the feather and keeping it suspended till the spring of the air in the bladder was too far weakened to continue to do as it had done. In the meantime we did now and then, by the help of a string fastened to the turning-key and the upper basis of the bellows, let down that basis a little, to observe how upon its sinking the blast against the feather would decrease as the receiver was further and further exhausted: and when we judged it to be sufficiently freed from air, we then let down the weight, but could not perceive that by shutting of the bellows, the feather was at all blown up, as it had been wont to be, though the upper basis were more than usually depressed: and yet it seems somewhat odd, that when, for curiosity, in order to a further trial, the weight was drawn up again, as the upper basis was raised from the lower, the sides of the bladder were sensibly (though not very much) pressed, or drawn inwards. The bellows being thus opened, we let down the upper basis again, but could not perceive that any blast was produced; for though the feather that lay just over and near the orifice of the little glass pipe had some motion, yet this seemed plainly to be but a shaking and almost vibrating motion (to the right and left hand) which it was put into by the upper basis, which the string kept from a smooth and uniform descent, but not to proceed from any blast issuing out of the cavity of the bladder: and for further satisfaction we caused some air to be let into the receiver, because there was a possibility, that unawares to us the slender pipe might by some accident be choaked; but though upon the return of the air into the receiver, the bases of the bellows were pressed closer together, yet it seemed, that, according to our expectation, some little air got through the pipe into the cavity of the bladder: for when we began to withdraw again the air we had let into the receiver, the bladder began to swell again, and upon our letting down the weight, to blow up and keep up the feather, as had been done before the receiver had been so well exhausted. What conjecture the opening and shutting of our little bellows, more than once or twice, without producing any blast sensible by the raising of the feather, gave some of the by-standers, may be easily guessed by the preamble of this experiment; but whilst I was endeavouring to prosecute it for my own farther information, a mischance that befel the instrument kept me from giving myself the desired satisfaction.

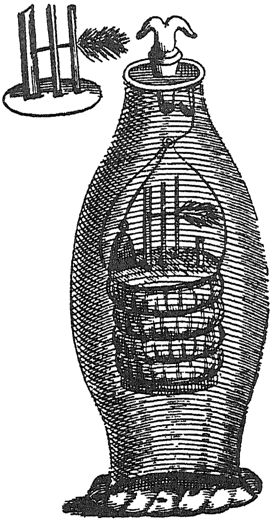

FIG. 9. Boyle's picture of the "bladder-bellows" and feather that he used in trying to find a medium more subtle than air.

EXPERIMENT 39

About a further attempt to prosecute the inquiry proposed in the foregoing Experiment.

Considering with myself, that by the help of some contrivances not difficult, a syringe might be made to serve, as far as our present occasion required, instead of a pair of bellows; I thought it would not be improper to try a differing, and, in some regards, a better way to prosecute an attempt which seemed to me to deserve our curiosity.

I caused then to be made for the formerly mentioned syringe [mentioned in an earlier experiment], instead of its straight pipe, a crooked one, whose shorter leg was parallel to the longer; and this pipe was for greater closeness, after it was screwed on carefully, fastened with cement to the barrel; and because the brass-pipe could scarce be made small enough, we caused a short and very slender pipe of glass to be put into the orifice of the shorter leg, and diligently fastened to it with close cement: then we caused the sucker (by the help of oil, water, and moving it up and down) to be made to go as smoothly as might be, without lessening the stanchness of the syringe. After this there was fastened to the handle of the rammer a weight, made in the form of a ring or hoop, which, by reason of its figure, might be suspended from the newly mentioned handle of the rammer, and hang loose on the outside of the cylinder, and which, both by its figure and its weight, might evenly and swiftly enough depress the sucker, when that being drawn up the weight should be let go. This syringe, thus furnished, was fastened to a broad and heavy pedestal, to keep it in its vertical posture, and to hinder it from tottering, notwithstanding the weight that clogged it. And besides all these things, there was taken a feather which was about two inches long, and of which there was left at the end a piece about the breadth of a man's thumb-nail (the rest on either side of the slender stalk, if I may so call it, being stript off) to cover the hole of the slender glass-pipe of the syringe; for which purpose the other extreme of it was so fastened with cement to the lower part of the syringe (or to its pedestal) that the broad end of the feather was placed (as the other feather was in the foregoing experiment) just over the little orifice of the glass, at such a convenient distance, that when the sucker was a little (though but very little) drawn up and let go again, the weight would depress it fast enough to blow up the broad part of the feather, as high as was permitted by the resistance of the stalk (and that was a good way) the spring of which would presently restore the whole feather to its former position. [Figure 10 shows the syringe with the feather, and Fig. 11, the arrangement by which a syringe could be operated in an evacuated receiver, though in this figure the syringe is used to raise liquid from a small vessel.]

All these things being done, and the handle of the rammer being tied to the turning-key of a capped receiver, the syringe and its pedes-

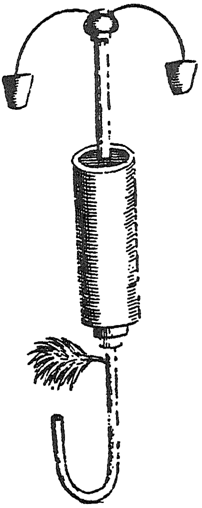

Fig. 10. Boyle's syringe with a feather, used in his further search for a more subtle medium.

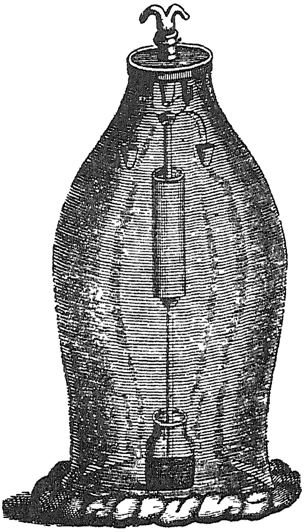

Fig. 11. The syringe of Fig. 10 mounted in a receiver and arranged to raise a liquid from a small vessel.

tal were inclosed in a capacious receiver (for none but such an one could contain them, and give scope for the rammer's motions) and the pump being set on work, we did, after some quantity of air was drawn out, raise the sucker a little by the help of the turning-key, and then turning the same key the contrary way, we suffered the weight to depress the sucker, that we might see at what rate the feather would be blown up; and finding that it was impelled forcibly enough, we caused the pumping to be so continued that a pretty many pauses were made, during each of which we raised and depressed the sucker as before, and had the opportunity to observe, that as the receiver was more and more exhausted of the air, so the feather was less and less briskly driven up, till at length, when the receiver was well emptied, the usual elevations and depressions of the sucker would not blow it up at all that I could perceive, though they were far more frequently repeated than ever before; nor was I content to look heedfully myself, but I made one, whom I had often employed about pneumatical experiments, to watch attentively, whilst I drew up and let down the sucker; but he affirmed that he could not discern the least beginning of ascension in the feather. And indeed to both of us it seemed that the little and inconsiderable motion that was sometimes (not always) to be discerned in the feather, proceeded not from anything that issued out of the pipe, but from some little shake, which it was difficult not to give the syringe and pedestal, by the raising and depressing of the sucker.

And that which made our phænomenon the more considerable was, that the weight that carried down the sucker being still the same, and the motions of the turning-key being easy to be made equal at several times, there seemed no reason to suspect that contingencies did much (if at all) favor the success; but there happened a thing which did manifestly enough disfavor it. For I remember, that before the syringe was put into the receiver, when we were trying how the weight would depress it, and it was thought, that though the weight were conveniently shaped, yet it was a little of the least, I would not alter it, but foretold, that when the air in the cavity of the syringe (that now resisted the quickness of its descent, because so much air could not easily and nimbly get out at so small a pipe) should be exhausted with the other air of the receiver, the elevated sucker would fall down more easily, which he that was employed to manage the syringe whilst I watched the feather, affirmed himself afterwards to observe very evidently: so that when the receiver was exhausted, if there had been in the cavity of the syringe a matter as fit as air to make a wind of, the blast ought to have been greater, because the celerity that the sucker was depressed with was so.

After we had long enough tried in vain to raise the feather, I ordered some air to be let into the receiver; and though when the admitted air was but very little, the motions of the sucker had scarce, if at all, any sensible operation upon the feather, yet when the quantity of air began to be somewhat considerable, the feather began to be a little moved upwards, and so by letting in air not all at once, but more and more from time to time, and by moving the sucker up and down in the intervals of those times of admission, we had the opportunity to observe, that as the receiver had more air in it, the feather would be more briskly blown up. [This experiment was devised to test Boyle's supposition that air at low pressure, a somewhat more subtle fluid than air at atmospheric pressure, would manifest its presence by raising the feather at least a little; the result bore out Boyle's expectation.]

But not content with a single trial of an experiment of this consequence, we caused the receiver to be again exhausted, and prosecuted the trial with the like success as before, only this one circumstance that we added, for confirmation, may be fit to be here taken notice of. Having, after the receiver was exhausted, drawn up and let fall the sucker divers times ineffectually, though hitherto we had not usually raised it any higher at a time, than we could by one turn of the hand, both because we could not so conveniently raise it higher by the hand alone, and because we thought it unnecessary, since that height sufficed to make the air briskly toss up the feather; yet *ex abundanti* we now took an instrument that was pretty long, and fit so to take hold on the turning-key, that we could easily raise the sucker between two and three inches, by our estimate, at a time, and nimbly depress it again; and for all this, which would much have increased the blast, if there had been a matter fit for it in the cavity of the syringe, we could not sensibly blow up the feather till we had let a little air into the receiver.

> To be able to make an estimate of the quantity of air pumped out, or let in, when the feather was strongly or faintly, or not at all raised by the fall of the sucker, we took off the receiver, and conveyed a gage into it, but though for a while we made some use of our gage, yet a mischance befalling it before the operation was quite ended, I shall forbear to add anything concerning that trial, and proceed to say something of another attempt, wherein, though I foresaw and met with such difficulties, as kept me from doing altogether what I desired, yet the success being almost as good as could be expected, I shall venture to acquaint your lordship with the trial, which was this.

At this point Boyle describes an experiment in which the exit tube from his syringe was so arranged that any effluent would bubble through water. He found that in his exhausted receiver a syringe worked up and down gave no evidence that any bubbles could be forced through the liquid. He then continues as follows.

> I had indeed thoughts of prosecuting the inquiry by dropping from the top of the exhausted receiver light bodies conveniently shaped, to be turned around or otherwise put out of their simplest motion of descent, if they met with any resistance in their fall; and by making such bodies move horizontally and otherwise in the receiver, as would probably discover whether they were assisted by the medium. And other contrivances and ways I had in my thoughts, whereby to prosecute our enquiry; but wanting time for other experiments, I could not spare so much as was necessary to exhaust large receivers so diligently as such nice trials would exact; and therefore I resolved to desist till I had more leisure than I then had, or have since been master of.
>
> In the interim, thus much we seem to have already discovered by our past trials, that if when our vessels are very diligently freed from air, they are full of æther, that æther is such a body as will not be made sensibly to move a light feather by such an impulse as would make the air manifestly move it, not only whilst it is no thinner than common air, but when it is very highly rarefied (which, if I mistake not, it was in our experiment so much, as to be brought to take up above an hundred times more room than before). . . .

EXPERIMENT 40

About the falling, in the exhausted receiver, of a light body, fitted to have its motion visibly varied by a small resistance of the air.

> Partly to try, whether in the space deserted by the air, drawn out of our receivers, there would be any thing more fit to resist the motion of other light bodies through it, than in the former experiment we found it to impel them into motion; and partly for another purpose to be mentioned by and by, we made the following trials.

We took a receiver, which, though less tall than we would have had, was the longest we could procure; and that we might be able, not so properly to let down as to let fall a body in it, we so fastened a small pair of tobacco-tongs to the inside of the receiver's brass-cover, that by moving the turning-key we might, by a string tied to one part of them, open the tongs, which else their own spring would keep shut. This being done, the next thing was to provide a body which would not fall down like a stone, or another dead weight through the air, but would, in the manner of its descent, shew, that its motion was somewhat resisted by the air; wherefore, that we might have a body that would be turned about horizontally, as it were, in its fall, we thought fit to join crosswise four broad and light feathers (each about an inch long) at their quills with a little cement, into which we also stuck perpendicularly a small label of paper, about an 8th of an inch in breadth, and somewhat more in height, by which the tongs might take hold of our light instrument without touching the cement, which else might stick to them. [Figure 12 is a reproduction of Boyle's drawing of this apparatus.]

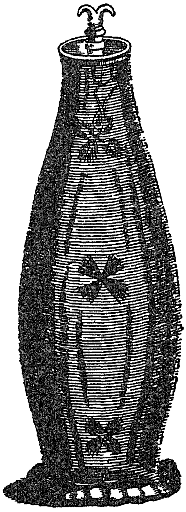

Fig. 12. Boyle's arrangement for allowing a feather cross to fall in an evacuated receiver.

By the help of this small piece of paper the little instrument, of which it made a part, was so taken hold of by the tongs, that it hung as horizontal as such a thing could well be placed; and then the receiver being cemented on to the engine, the pump was diligently plied, till it appeared by a gage [here Boyle begins to use a gage, and to good purpose; he had previously met misfortune with this device (p. 46)] which had been conveyed in. that the receiver had been carefully exhausted; lastly, our eyes being attentively fixed upon the connected feathers, the tongs were by the help of the turning-key opened, and the little instrument let fall, which, though in the air it had made some turns in its descent from the same height which it now fell from, yet now it descended like a dead weight, without being perceived by any of us to make so much as one turn, or a part of it: notwithstanding which I did, for greater security, cause the receiver to be taken off and put on again, after the feathers were taken hold of by the tongs; whence being let fall in the receiver unexhausted, they made some turns in their descent, as they also did being a second time let fall after the same manner.

But when after this, the feathers being placed as before, we repeated the experiment by carefully pumping out the air, neither I nor any of the by-standers could perceive any thing of turning in the descent of the feathers; and yet for further security we let them fall twice more in the unexhausted receiver, and found them to turn in falling as before; whereas when we did a third time let them fall in the well exhausted receiver, they fell after the same manner as they had done formerly, when the air, that would by its resistance have turned them around, was removed out of their way.

N.B. 1. Though, as I intimated above, the glass wherein this experiment was made, were nothing near so tall as I would have had it, yet it was taller than any of our ordinary receivers, it being in height about 22 inches.

2. One that had more leisure and conveniency might have made a more commodious instrument than that we made use of; for being accidentally visited by that sagacious mathematician Dr. *Wren*, and speaking to him of this matter, he was pleased with great dexterity as well as readiness to make me a little instrument of paper, on which, when it was let fall, the resistance of the air had so manifest an operation, that I should have made use of it in our experiment, had it not been casually lost when the ingenious maker was gone out of these parts.

3. Though I have but briefly related our having so ordered the matter that we could conveniently let fall a body in the receiver when very well exhausted; yet, to contrive and put in practice what was necessary to perform this, was not so very easy, and it would be difficult to describe it circumstantially without very many words; for which reason I forbear an account that would prove too tedious to us both. . . .

ANNOTATIONS

1. But here I must be so sincere as to inform your lordship, that this fortieth experiment seemed not to prove so much as did the foregoing made with the syringe; for being suspicious, that, to make the feathered body above mentioned turn in its fall, there would need a resistance not altogether inconsiderable, I caused the experiment to be repeated, when the receiver was, by our estimate, little or nothing

> more than half exhausted, and yet the remaining air was too far rarefied to make the falling body manifestly turn.

The Annotation of the experiment just described shows Boyle in his tedious vein. By his own admission the experiment with the falling feathers is of little value, certainly of less value than the preceding experiments designed for essentially the same purpose. "Then why not omit the long description and merely summarize the result?" an impatient modern reader may be inclined to exclaim. The essence of reporting experimental results is to record in detail only those experiments that because of their outcome seem to have real significance (the results may be positive or negative). While admiring Boyle's candor and his determination to report all the details, which set the standard for subsequent investigations, one must admit that unless a greater degree of selection had been made by later experimenters the literature of science would have become impossibly burdened with irrelevant details of inconclusive inquiries. Many generations of experimentalists have gradually evolved an unwritten code that governs the way in which experiments are now reported. The essence of this code is accurate and complete recording of those experiments that the experimenter himself believes to be significant; inconclusive and incomplete experiments need not be reported or indeed even mentioned. But in the seventeenth century the danger was that too little would be reported rather than too much.

5. THE DISCOVERY OF BOYLE'S LAW

As has been noted, the first edition of Robert Boyle's book on *New Experiments Physico-Mechanical Touching the Spring of the Air* was published in 1660. Not long after, two books appeared in which the authors vigorously attacked both Boyle's experiments and his interpretations. One was by the famous writer on political philosophy, Thomas Hobbes (1588–1679), the other by an obscure supporter of the Aristotelian position (as interpreted by scholars of the Middle Ages) by the name of Franciscus Linus (1595–1675). Hobbes's position was that of a Plenist (see p. 26) and his arguments were based in part on a misunderstanding of Boyle's views and in part on the premise that a subtle matter existed which filled all the space. The experiments recorded in the preceding section deal with Boyle's attempts to obtain evidence for the existence of the "subtle matter" postulated by the Plenists. Linus's objections were directed against the whole conceptual scheme developed by Torricelli and Pascal, to which Boyle had made few additions. Probably similar objections had been expressed more than once before in the decade or more in which the news of Torricelli's experiment had spread and the new ideas were being discussed.

Linus put forward the hypothesis that the space above the mercury column in a Torricellian tube contained an invisible membrane or cord which he called a *funiculus.* The nature of this membrane was such that the maximum height to which it could draw up a column of mercury was about 29½ inches. In support of this fantastic notion Linus cited the well-known fact that if the upper end of the Torricellian tube is closed with a finger one seems to feel the flesh being pulled in. This way of performing the Torricellian experiment with a tube open at both ends Linus described as follows (as quoted by Boyle):

> If you take a tube open at both ends of a good length, suppose forty inches long, and fill it with mercury, and place your finger on the top as before, taking away your lower finger, you will find the mercury to descend even to its wonted station [i.e., to a height of approximately 29½ inches], and your finger on the top to be strongly drawn within the tube, and to stick close unto it. Whence again it is evidently concluded that the mercury placed in its own station is not there upheld by the external air, but suspended by a certain internal cord [Linus's alleged *funiculus*], whose upper end being fastened to the finger, draws and fastens it after this manner into the tube.

Boyle replied to this and similar arguments that the pressure of the outside air forced the flesh of one's finger into the top of a barometric tube; there was no need to assume that an invisible funiculus was pulling the finger down. But Boyle was always anxious to answer arguments by experiments. So he devised a new experiment, the results of which could not be explained by the aid of his adversary's hypothesis of a funiculus. In the course of this experiment Boyle noted the numerical relation between pressure and volume that we now call Boyle's Law. The discovery of an important physical law was in this instance rather in the nature of a by-product of Boyle's desire to bring overwhelming evidence to bear against a rival conceptual scheme. Controversy has often been of great importance in stimulating new advances in experimental science.

Boyle's Description of his Discovery of the Relation Between Pressure and Volume. Boyle published the results of the new experiment, as well as lengthy arguments against both Hobbes and Linus, as an Appendix to the second edition of his book. This appeared in 1662. In Part II of this Appendix, entitled "Wherein the Adversaries Funicular Hypothesis is Examined," Boyle refers to Linus and his funiculus hypothesis in these words:

> The other thing, that I would have considered touching our adversary's hypothesis is, that it is needless. For whereas he denies not, that the

> air has some weight and spring, but affirms, that it is very insufficient to perform such great matters as the counterpoising of a mercurial cylinder of 29 inches, as we teach that it may; we shall now endeavour to manifest by experiments purposely made [note this phrase], that the spring of the air is capable of doing far more than it is necessary for us to ascribe to it, to salve [14] the phænomena of the Torricellian experiment.

Boyle at this point proceeds to describe how he prepared a J tube of glass with the short leg sealed off and the long leg open (Fig. 13). He kept pouring mercury into the open end until the difference in levels of the mercury in the two legs was 29 inches. This meant to him, as it does to us, that the total pressure on the enclosed air in the short leg (see Fig. 13) was about twice the usual atmospheric pressure, and Boyle noted "not without delight and satisfaction" that the volume of the compressed air was reduced about half. But before proceeding to discuss the numerical relation between pressure and volume that he obtained in these experiments, we may be permitted to skip to the conclusions that he drew from these experiments in regard to the crucial point, namely, the existence or nonexistence of Linus's funiculus.

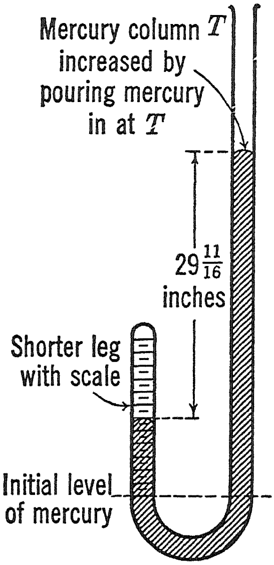

Fig. 13. Boyle's J tube, with a scale on the shorter leg reading 24 as compared to the initial reading of 48 (see Table 1, Column *A*).

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[14] The word "solve" has been changed to "salve" (a form of "save") in agreement with the first edition (1660) of Boyle's book.

When the volume of the compressed air in the short arm was reduced to one fourth of the original volume, Boyle noted that the difference in levels of the mercury was a little over 88 inches. When to this is added the pressure of the air in terms of inches of mercury, we can readily see, as Boyle did, that the total pressure was 88 + 29 = 117 inches-of-mercury as compared with 29 and a fraction, the original pressure. This is within an inch of being equal to four times the original pressure (116 inches-of-mercury). Boyle then concludes:

> It is evident, that as common air, when reduced to half its wonted extent, obtained near about twice as forcible a spring as it had before; so this thus comprest air being further thrust into half this narrow room, obtained thereby a spring about as strong again as that it last had, and consequently four times as strong as that of the common air. And there is no cause to doubt, that if we had been here furnished with a greater quantity of quicksilver and a very strong tube, we might, by a further compression of the included air, have made it counterbalance the pressure of a far taller and heavier cylinder of mercury. For no man perhaps yet knows, how near to an infinite compression the air may be capable of, if the compressing force be competently increased. [We now know that at room temperature some gases are converted to liquids if sufficiently compressed, others like those composing the atmosphere are not; for all gases, however, there is a temperature below which sufficient compression will cause liquefaction.] So that here our adversary [Linus] may plainly see, that the spring of the air, which he makes so light of, may not only be able to resist the weight of 29 inches, but in some cases of above a hundred inches [that is, including the atmospheric pressure] of quicksilver, and that without the assistance of his Funiculus, which in our present case has nothing to do. And to let you see, that we did not (as a little above) inconsiderately mention the weight of the incumbent atmospherical cylinder as a part of the weight resisted by the imprisoned air, we will here annex, that we took care, when the mercurial cylinder in the longer leg of the pipe was about an hundred inches high, to cause one to suck at the open orifice [*T*, Fig. 13]; whereupon (as we expected) the mercury in the tube did notably ascend. Which considerable phænomenon cannot be ascribed to our examiner's Funiculus, since by his own confession that cannot pull up the mercury, if the mercurial cylinder be above 29 or 30 inches of mercury.

Here then is the point of the experiment. Linus, to explain the height of the mercury column in the Torricellian experiment, had to postulate a maximum pull of the funiculus corresponding to only 29 inches of mercury. Yet by combining the force of expansion of the compressed air in the short arm of his apparatus with the partial evacuation of the air above the long arm (by means of sucking with his mouth) Boyle is able to pull up a column of mercury whose length is several times

29 inches. If a funiculus is involved in this (as Linus postulated), how can it pull up such a long column, Boyle asks. His answer follows.

> And therefore we shall render this reason of it, that the pressure of the incumbent air being in part taken off by its expanding itself into the sucker's dilated chest; the imprisoned air was thereby enabled to dilate itself manifestly, and repel the mercury, that compress it, till there was an equality of force betwixt the strong spring of that comprest air on the one part, and the tall mercurial cylinder, together with the contiguous dilated air, on the other part.

Numerical Relation of Pressure and Volume. Boyle's method of measuring volume was crude; it consisted of measuring the distance between the top of the sealed off shorter leg and the mercury level in the same leg. Clearly this measurement of a distance is a true measure of the volume only if the tube is of uniform diameter, which would be true only approximately. A paper scale divided into inches and fractions was pasted on the outside of the shorter leg and a similar but longer scale on the outside of the longer leg. The position of the two mercury levels could then be noted and the difference in pressure recorded. The results were given by Boyle in a table which is reproduced in Table 1.

Table 1. Compression of air (Boyle's original data).

A	*B*	*C*	*D*	*E*
48	00	Added to 29 1/8 makes	29 2/16	29 2/16
46	01 7/16		30 9/16	30 6/16
44	02 13/16		31 15/16	31 12/16
42	04 6/16		33 8/16	33 1/7
40	06 3/16		35 5/16	35
38	07 14/16		37	36 15/19
36	10 2/16		39 5/16	38 7/8
34	12 8/16		41 10/16	41 2/17
32	15 1/16		44 3/16	43 11/16
30	17 15/16		47 1/16	46 3/5
28	21 3/16		50 5/16	50
26	25 3/16		54 5/16	53 10/13
24	29 11/16		58 13/16	58 2/8
23	32 3/16		61 5/16	60 18/23
22	34 15/16		64 1/16	63 6/11
21	37 15/16		67 1/16	66 4/7
20	41 9/16		70 11/16	70
19	45		74 2/16	73 11/19
18	48 12/16		77 14/16	77 2/3
17	53 11/16		82 12/16	82 4/17
16	58 2/16		87 14/16	87 3/8
15	63 15/16		93 1/16	93 1/5
14	71 5/16		100 7/16	99 6/7
13	78 11/16		107 13/16	107 7/13
12	88 7/16		117 9/16	116 4/8

A. The number of equal spaces in the shorter leg, that contained the same parcel of air diversely extended.

B. The height of the mercurial cylinder in the longer leg, that compressed the air into those dimensions.

C. The height of the mercurial cylinder that counterbalanced the pressure of the atmosphere.

D. The aggregate of the two last columns *B* and *C*, exhibiting the pressure sustained by the included air.

E. What that pressure should be according to the hypothesis, that supposes the pressures and expansions to be in reciprocal proportion.

As to the origin of the hypothesis that pressure and volume are reciprocally related, Boyle has this to say:

> I shall readily acknowledge, that I had not reduced the trials I had made about measuring the expansion of the air to any certain hypothesis, when that ingenious gentleman Mr. *Richard Townley* was pleased to inform me, that having by the perusal of my physico-mechanical experiments been satisfied that the spring of the air was the cause of it, he endeavoured (and I wish in such attempts other ingenious men would follow his example) to supply what I had omitted concerning the reducing to a precise estimate, how much air dilated of itself loses of its elastical force, according to the measures of its dilatation. [Boyle in his book had tried without success to reduce to numerical terms the effectiveness of his engine in terms of the ratio of the volumes of the cylinder and the receiver. One of his readers seems to have grasped the point that probably pressure and volume were inversely proportional to each other.] He added, that he had begun to set down what occurred to him to this purpose in a short discourse, whereof he afterwards did me the favour to shew me the beginning, which gives me a just curiosity to see it perfected. But, because I neither know, nor (by reason of the great distance betwixt our places of residence) have at present the opportunity to inquire, whether he will think fit to annex his discourse to our appendix, or to publish it by itself, or at all; and because he hath not yet, for aught I know, met with fit glasses to make an any-thing-accurate table of the decrement of the force of the dilated air; our present design invites us to present the reader with that which follows, wherein I had the assistance of the same person, that I took notice of in the former chapter, as having written something about rarefaction [this appears to refer to Hooke]: whom I the rather make mention of on this occasion, because when he first heard me speak of Mr. *Townley's* suppositions about the proportion, wherein air loses of its spring by dilatation, he told me he had the year before (and not long after the publication of my pneumatical treatise) made observations to the same purpose, which he acknowledged to agree well enough with Mr. *Townley's* theory: and so did (as their author was pleased to tell me) some trials made about the same time by that noble virtuoso and eminent mathematician the Lord *Brouncker*, from whose further enquiries into this matter, if his occasions will allow him to make them, the curious may well hope for something very accurate.

It is interesting that at least three of Boyle's contemporaries suggested the relation that we now know as Boyle's law as a result of reading about Boyle's difficulties in calculating the effectiveness of his engine. Boyle obviously became so interested in the numerical relation between pressure and volume that his initial objective, namely, to raise a column of mercury more than 29 inches by suction, is rather lost sight of. Certainly in the presentation of all this material, his adversary's point of view is brought in rather casually, though he does finally conclude with the statement,

> I suppose we have already said enough to shew what was intended: namely, that to salve the phænomena there is not of our adversary's hypothesis [i.e., the funiculus] any need: the evincing of which will appear to be of no small moment in our present controversy to him that considers, that the two main things, that induced the learned examiner to reject our hypothesis, are, that nature abhors a vacuum; and that though the air have some weight and spring, yet, these are insufficient to make out the known phænomena; for which we must therefore have recourse to his Funiculus. Now as we have formerly seen, that he has not so satisfactorily disproved as resolutely rejected a vacuum, so we have now manifested, that the spring of the air may suffice to perform greater things than what our explication of the Torricellian experiments and those of our engine obliges us to ascribe to it. Wherefore since besides the several difficulties, that incumber the hypothesis we oppose, and especially its being scarce, if at all, intelligible, we can add that it is unnecessary; we dare expect, that such readers as are not biassed by their reverence for *Aristotle*, or the Peripatetick schools, will hardly reject an hypothesis, which, besides that it is very intelligible, is now proved to be sufficient, only to imbrace a doctrine, that supposes such a rarefaction and condensation, as many famous Naturalists rejected for its not being comprehensible, even when they knew of no other way (that was probable) of salving the phænomena wont to be explicated by it.

In this same chapter Boyle describes some experiments on what he calls the "debilitated force of expanded air." This amounts to another way of measuring the relation between volume and pressure. In this case the original sample of air is not compressed but expanded by diminishing the pressure. This Boyle accomplished very simply by enclosing a sample of air in a long thin tube closed at the upper end and immersed for several feet in a long tube of mercury. When the inner tube is *raised,* the contained air is allowed to expand, a suitable scale serving to measure the change in volume (assuming uniform bore) and the diminished pressure. (This experiment can be conveniently performed today by using an inverted glass burette for the inner tube and a tall glass cylinder to contain the mercury.)

Boyle makes no explicit statement about the effect of temperature on the accuracy of his results. He was quite aware, however, of the fact that air expands on heating and contracts on cooling. He was curious to see whether the air compressed to a quarter of its volume behaved in this respect like air under atmospheric pressure. He therefore warmed the short leg of his bent tube with a candle and cooled it with water, noting in qualitative terms the changes of volume that occurred.

They were not large. This fact must have assured Boyle that the minor fluctuations in the room temperature during the experiment in which he varied the height of the column of mercury would not affect the significance of his results. We now know that the pressure of a given volume of gas increases by about $1/530$ of its value at room temperature for every (Fahrenheit) degree increase in temperature. Therefore, an increase of as much as five degrees during Boyle's experiment would have introduced an error of only about $5/530$ or a little less than $1/100$, which is about the difference between the observed and calculated pressures (Columns *D* and *E*, Table 1) in the extreme case.

Today, no one would think of measuring the relation between pressure and volume of a gas with any pretense to accuracy unless the temperature were controlled. Careful experiments have shown that even at constant temperature Boyle's law,

$$\text{Pressure} \times \text{Volume} = \text{constant},$$

or

$$\frac{P_1}{P_2} = \frac{V_2}{V_1},$$

is only approximately true for gases at atmospheric pressure. The deviations from Boyle's law (the change in the product of volume and pressure as pressure increases) are greater the greater is the pressure for a given gas; the gases that are not far from the point of condensation deviate widely from Boyle's law.

An interesting comparison can be made between Boyle's law and the relation between pressure in a liquid and depth below the surface. The first is based on experimental findings and is only approximate; the second *appears* to be a consequence of definitions and was presented in the sixteenth century as a deduction from self-evident propositions in a manner reminiscent of geometry. The hydrostatic principle here involved may be expressed by a "law" in the form P (pressure in the liquid) $= D$ (depth) $+ A$ (atmospheric pressure), if appropriate units are taken. On analysis, it becomes evident that this is true only if the change of density of the liquid with pressure can be neglected (it can be for all practical purposes for considerable depths of water). Constant temperature throughout the liquid must be assumed (just as Boyle's law is true only for constant temperature). The deviations from Boyle's law decrease with decreasing pressure, and for very attenuated gases the observed relations between pressure and volume follow Boyle's law closely. To the extent that the hydrostatic law defines an ideal liquid, it may be comparable with Boyle's law as a definition of an ideal gas.

Boyle's formulation of the relation between two variables, volume and pressure of a gas, is typical of a vast amount of scientific information that began to be accumulated about the middle of the seventeenth century. In the case at hand, this information was obtained incidentally to a controversy about the Torricellian conceptual scheme as extended by Boyle. As scientific experimentation continued, however, the aim of the investigator was often more directly to obtain quantitative data about the relation between two variables, one of which was said to be a function of the other. The realization of what were the significant variables was usually closely connected with the development of new concepts or conceptual schemes (theories). But the experimental difficulties of controlling or measuring the other variables were often considerable. The recognition of the variable factors in a changing situation and the development of methods of measuring these factors often constitute a major advance in science.

The concept that air was compressible did not originate with Boyle. Torricelli, in his letter of June 28, 1644 describing his first experiments, in explaining what he means by the pressure of the atmosphere uses the analogy of a cylinder of wool (easily compressible by hand), and there had been earlier discussions of the compressibility of air. On the other hand, Pascal, in his treatise written in 1648 (published in 1663), makes little reference to the vast difference in compressibility between water and air. He makes use of the analogy between hydrostatic pressure and air pressure but treats air for the most part as though it were water of very low density. One can say that Boyle extended Torricelli's conceptual scheme by emphasizing the "spring of the air." He was led to do so because the operation of von Guericke's pump depends on the fact that air expands and contracts with changing pressure almost instantaneously and to a very large extent; one can "feel" the spring of the air when one operates an air pump!

Boyle noted in his first book that there were at least two ways of imagining the composition of air to account for its great compressibility. One was to think of the particles as each being compressible like a spring or a bit of wool. One can conceive of the air, wrote Boyle, as "a heap of little bodies, lying one upon another, as may be resembled to a fleece of wool." The other way was to think of the particles as whirled around in the subtle fluid postulated by Descartes as filling all space. According to this latter view, Boyle said, "it imports very little, whether the particles of the air have the structure requisite to springs, or be of any other form (how irregular soever) since their elastical power is not made to depend upon their shape or structure, but upon the vehement agitation."

Boyle declares he is not willing "to declare peremptorily for either of them [i.e., the ideas] against the other." He goes on to say, "I shall decline meddling with a subject, which is much more hard to be explicated than necessary to be so by him, whose business it is not, in this letter, to assign the adequate cause of the spring of the air, but only to manifest, that the air hath a spring, and to relate some of its effects."

Boyle was an adherent of what is sometimes called the corpuscular philosophy — a point of view that derives from one branch of ancient Greek thought. One could speculate and argue whether matter could be divided and subdivided indefinitely or whether there were ultimate particles, often called atoms. Either of the "explanations" put forward by Boyle for the "spring of the air" was in harmony with the atomistic idea of the structure of matter. Though reserving the right in his first account of the subject to experiment later to test the alternative concepts, he seems to have done so only indirectly by searching for Descartes' subtle fluid. When speculation about the nature of gases became important for the advance of chemistry at the end of the eighteenth century, the picture of a gas then in favor was that of contiguous but easily compressible particles filling the space. This atomic picture was still a speculative idea, however, hardly a working hypothesis, until Dalton used it to relate the constant ratio by weights of elements in compounds. The distinction between a general speculative idea, a working hypothesis on a grand scale, and a new conceptual scheme is well illustrated by comparing the history, in the seventeenth century, of the notion of matter being composed of atoms with that of the idea of a sea of air surrounding the earth. The first remained a speculative idea throughout the period; the second soon emerged as a new conceptual scheme which by 1700 was almost universally accepted. It was not until Dalton in 1805 put forward his "atomic theory" (certainly at first only a working hypothesis on a grand scale) that from the general speculative idea one could draw deductions that could be tested by experiment (Case 4 of this series).

At what point in history the conceptual scheme about air and air pressure became a "fact" and whether or not the atomic nature of matter is now a "fact" can be left for the reader to debate. If one adopts a cautious attitude about science, one will reserve the use of the word "fact" to designate reproducible observations (at least when one is attempting to speak carefully about science). The word "theory" is commonly used to mean either a working hypothesis or a well-accepted conceptual scheme. Because of the resulting ambiguities, we prefer to use the phrases "working hypothesis on a grand scale" or "broad working hypothesis" for a new idea in its initial phases. As soon as the deductions from such a hypothesis have been confirmed by experimental test and the hypothesis is accepted by several scientists, it is convenient to speak of it as a conceptual scheme. In a cautious mood one retains the phrase no matter how certain one may feel about the postulates. The reader need hardly be reminded that in 1950 the ideas about the structure of the nucleus of the atom are in a state where working hypotheses on a grand scale are in the process of becoming conceptual schemes (or if one must use the word, new theories!).

6. NOTES ON THE DEVELOPMENT OF SCIENCE IN THE MIDDLE OF THE SEVENTEENTH CENTURY

The Two Traditions. As was pointed out in the Foreword, the development of experimental science in the seventeenth century was the consequence of the combination of deductive reasoning with the cut-and-try type of experimentation. Two great figures of this period who contributed to the study of pneumatics symbolize the two traditions whose combination produced modern science. Blaise Pascal was primarily a mathematician, Robert Boyle primarily an experimentalist. A study of their writings illustrates the two streams of thought and action that were found in the seventeenth century. In Pascal's treatise on hydrostatics and his work on pneumatics it is hard to tell whether or not most of the so-called experiments were ever performed. They may well have been intended rather as pedagogic devices — as demonstrations that the reader performs in his imagination in order better to understand the principles expounded. The argument is by deductive reasoning from a few postulates; here and there a check by actual experiment, as the case of the Puy-de-Dôme observations, may be of great significance. Yet it will be recalled that one may question whether Pascal's collaborator, Perier, was an accurate reporter; it seems probable that, convinced of the general effect he was looking for, namely, the change of barometric reading with height, he could not resist the temptation to give results with such an accuracy as to carry conviction to those steeped in the tradition of mathematical reasoning (see pp. 8 and 28).

Boyle in one of his discussions of hydrostatics (1666) gently pokes fun at Pascal for having written of experiments that appeared impossible of execution. Pascal, said Boyle, does not state that he actually tried the experiments; "he might possibly have set them down as things that *must* happen, upon a just confidence that he was not mistaken in his ratiocinations." He further chides Pascal for not giving sufficient details that anyone can repeat his experiments (if he ever really did them). Boyle was on solid ground here, for, as we have seen, he was if anything overconscientious in recording all possible information that might be of assistance to another investigator. As an example of some of the things Pascal described that strained one's credulity, Boyle refers to an experiment in which a man sits 20 feet under water and places against his thigh a tube that extends above the surface of the water. But, writes Boyle, Pascal "neither teaches us how a man shall be enabled to continue under water, nor how, in a great cistern full of water 20 feet deep, the experimenter shall be able to discern the alterations. . ."

One can trace through the history of physics and chemistry the two traditions represented by Pascal and Boyle, though sometimes both appear to be almost equally represented in the work of a single man, as in the cases of Galileo, Newton, and perhaps Lavoisier. In the twentieth century one thinks of the names of Einstein and Lord Rutherford, one a mathematician, the other an experimentalist, each representing by his revolutionary work the best in the two approaches that together made modern science.

Science and the Practical Arts. The study of pneumatics may have started as the result of an interest by a professor in the practical art of pumping water. Galileo,[15] in his *Dialogues Concerning Two New Sciences*, published in 1638, places in the scientific record for the first time what must have been a well-known fact to those who built and operated pumps, namely, that water will not rise in a lift pump above about 34 feet. One of the characters in the dialogues says, "I once saw a cistern which had been provided with a pump under the mistaken impression that the water might thus be drawn with less effort or in greater quantity than by means of the ordinary bucket. . . This pump worked perfectly so long as the water in the cistern stood above a certain level; but below this level the pump failed to work. When I first noticed this phenomenon I thought the machine was out of order; but the workman whom I called in to repair it told me the defect was not in the pump but in the water, which had fallen too low to be raised through such a height; *and he added that it was not possible, either by a pump or by any other machine working on the principle of attraction, to lift water a hair's breadth above eighteen cubits.*"

The words that we have italicized convey important historical information. It seems quite clear that Galileo's interest in a scientific problem had arisen from the observation of a practical art, namely, pumping water; furthermore, it seems evident that the knowledge about the limitations of a lift pump was common among the workmen. Indeed, illustrations from books of the sixteenth century show tandem pumps (one above the other) lifting water from mines. It is interesting that while Galileo himself made little or no contribution to the solu-

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[15] Galileo Galilei (1564–1642), regarded by many as the real founder of modern science; certainly the greatest single figure in physical science after Archimedes and before Newton; a professor at the universities of Pisa and Padua and later resident at the court of the Grand Duke of Florence.

tion of the scientific problem of relating the limitation of a water pump to other phenomena, his pupil Torricelli did.

Although pneumatics in origin was thus closely related to a practical art (and pumps with their various parts — valves, cylinders, plungers — recur throughout the story), the advance in science did not change the art of pumping water — at least not in the seventeenth century. There is no evidence, indeed, that any of Boyle's work had immediate consequences of practical value. Even in scientific work his devices for collecting gases *in vacuo* and transferring them under pressure to an evacuated vessel were scarcely employed by chemists until the twentieth century. An alternative procedure — the use of the pneumatic trough — which was invented somewhat later than Boyle's time, was found to be preferable. A study of the work of the "pneumatic chemists" of the late eighteenth century (Case 2 of this series) shows how little was the influence of the techniques for handling gases worked out by Boyle and Papin.

The failure of the scientific world to use vacuum pumps in the eighteenth century is readily explained by anyone who has had experience with evacuated systems. Boyle's pumps were expensive and difficult to operate, and before glass blowing and metal working had reached a high state of development, it was almost impossible to insure against leaks. It was only in the second half of the nineteenth century that distillations at pressures of an inch of mercury came into common practice. The development of the incandescent light which originally required a high vacuum (pressure of 10^{-3} mm-of-mercury or less) stimulated the improvement of vacuum pumps for industrial purposes. New types of pumps together with chemical procedures now make it possible to evacuate large vessels to a pressure as low as 10^{-5} mm-of-mercury; indeed, pressures as low as 10^{-10} mm-of-mercury have been reported.

Denis Papin (1647–1712) was Boyle's collaborator in his later work in pneumatics. He was the inventor of the pressure cooker (originally called Papin's digester) which has only in the middle of the twentieth century come into its own as a device useful to the housewife. This invention was closely related to Boyle's studies of the behavior of materials not only *in vacuo* but in compressed air. John Evelyn, in his famous diary under date of April 15, 1682, records with appreciation that the members of the Royal Society partook of a supper cooked in a digester. He remarks, "This philosophical supper caused much mirth amongst us and exceedingly pleased all the company." The fact that Papin later made several designs for steam engines serves to connect Boyle's work with the practical developments of the eighteenth century.

Newcomen's atmospheric engine (1712) can be thought of as a practical outcome of the work of the investigators of pneumatics in the seventeenth century. But the connection is far from direct. By the end of the seventeenth century, the Torricellian scheme was accepted as a matter of course. So, too, was the concept of air as an elastic fluid, and the connection between water and steam was beginning to be understood. Therefore, while no *direct* applications of the new discoveries in pneumatics to the practical arts can be traced in the seventeenth century, it is clear that all scientists and inventors who were concerned with gases or vapors were from Boyle's time on thinking in terms of the new concepts and Torricelli's conceptual scheme. In the seventeenth and eighteenth centuries, advances in science and progress in the practical arts by continued empirical experimentation were two parallel activities. The scientists and inventors were in communication and shared the same ideas, but it was not until the nineteenth century that the concepts of science and the accumulated scientific information became of major importance to the practical men of industry and commerce. And only in the twentieth century have the two activities — science and the practical arts — become intimately associated in almost every industrial activity.

Science and Society. The casual way in which Robert Boyle refers to the work of other investigators is worthy of special notice. So incomplete are his references that we cannot tell today how much of his work in pneumatics was original. This disorganized state of scientific communications is typical of the first half of the seventeenth century. When the new experimental philosophy was beginning to attract attention, news of scientific discoveries usually circulated by means of letters between learned men. The publication of scientific books was sporadic and often greatly delayed. The need for some regular method of recording short notices about scientific experiments led to the establishment of scientific journals in the second half of the century. The formation of scientific societies was of great significance in this connection since they sponsored scientific journals which, in the case of the *Transactions* of the Royal Society (London) and the *Mémoires* of the French Academy (Paris), have continued almost without interruption to the present day. For those students who are interested in either the political ferment in England of the seventeenth century or the connection between the development of literature and philosophic thought, a study of the founding of the Royal Society will be rewarding. The books listed below in the first section are recommended as a basis for a consideration of the interaction of science and society in this period.

SUGGESTED READING

1. *A Bibliography of the Honourable Robert Boyle,* by J. F. Fulton (Oxford University Press, Oxford, 1932).

2. Science and Society

The Life and Works of the Honourable Robert Boyle, by Louis Trenchard More (Oxford University Press, New York, 1944). The first 113 pages are recommended; with the author's evaluation of Robert Boyle's work in chemistry the editor of this Case cannot agree.

Scientists and Amateurs: A History of the Royal Society, by Dorothy Stimson (H. Schuman, New York, 1948).

The Role of Scientific Societies in the Seventeenth Century, by Martha Ornstein (University of Chicago Press, Chicago, ed. 3, 1938).

The Seventeenth Century Background, by Basil Willey (Columbia University Press, New York, 1942), is to be especially recommended for students interested in literature as collateral reading. The first three chapters present an interesting view of the impact of Bacon's ideas and Galileo's work.

3. Supplementary Reading to the Case History

The Physical Treatises of Pascal. The Equilibrium of Liquids and the Weight of the Mass of the Air [by Blaise Pascal], translated by I. H. B. and A. G. H. Spiers, with introduction and notes by Frederick Barry (Columbia University Press, New York, 1937).

This little volume, containing all of Pascal's "brief but brilliantly ingenious labors in natural science, together with the remarkably well-executed investigations of Perier which completed them, was put together by Perier and published at Paris in 1663, a year after Pascal's death." Since the text translated includes a summary of Boyle's early work on pneumatics, and since this Columbia edition furthermore contains translations of relevant passages from the writings of Stevin, Galileo, and Torricelli, the volume is a useful one indeed. Information about the influence of Hero of Alexandria's *Pneumatica* is given in an article by Marie Boas in *Isis,* vol. 40 (1949), p. 38.

The Science of Mechanics, by Ernst Mach (first German edition, 1883; last major revisions, 1911; English translation by T. J. McCormack, Open Court Publishing Co., Chicago, 1893; current (1942) edition considerably rearranged). For hydrostatics and pneumatics, see especially chap. i, secs. vi and vii and chap. iii, sec. x.

This historical and critical survey of mechanics has become a landmark in the development of the logical analysis of science. Although it contains a wealth of useful facts and penetrating critiques, some caution is needed in using it today. The historical research available to Mach was both limited and biased in such a way that he inevitably tended to overemphasize the contributions of certain individuals.

CASE 2

The Overthrow of the Phlogiston Theory

The Chemical Revolution of 1775-1789

EDITED BY

JAMES BRYANT CONANT

CASE 2

The Overthrow of the Phlogiston Theory

INTRODUCTION

The overthrow of the phlogiston theory involved the development of a superior conceptual scheme. There can be no doubt that the author of the new ideas was the French chemist Lavoisier, often referred to as the "father of modern chemistry." The chemical revolution did not occur overnight, however, and Lavoisier did not accomplish his results singlehanded. By studying the evolution of a new conceptual scheme we can see the difficulties with which pioneers in science almost always have to contend, and the false steps that usually accompany even the most successful forward marches. We likewise see how, by the end of the eighteenth century, science had become an organized activity with its own methods of making public new results. As compared with the first half of the seventeenth century, the interchange between leading investigators was prompt and effective. As compared with our own time, or even with the middle of the nineteenth century, however, the publication of results was sporadic and incomplete. For example, although the English experimenters Priestley and Cavendish could read of Lavoisier's work soon after it was completed (and vice versa), the fact that the Swedish chemist Scheele had prepared pure oxygen gas and studied its properties remained unknown to what was then the "scientific world" for several years. Scheele's experiments were completed before 1773. His characterization of a new gas which he called "fire air" was quite unambiguous. The manuscript of his book on *Air and Fire* describing these discoveries and interpreting them was not delivered to the printer before 1775 and not published until 1777. This delay prevented his discovery of oxygen, which antedated Priestley's, from being the effective discovery that influenced the work of other men.

The chemical revolution may be conveniently thought of as occurring in the following stages:

(1) Lavoisier's experiments with sulfur and phosphorus in 1772 in which he noted a "prodigious quantity of air was fixed."
(2) The effective discovery of oxygen, the unraveling of its relation to the calcination of metals in air, and its role in the respiration of animals, 1774–1778.
(3) The determination of the composition of water, 1782–1783.
(4) The extension and precise formulation of the new conceptual scheme in terms of a new chemical nomenclature in Lavoisier's *Traité Élémentaire de Chimie,* 1789.

In this Case we shall center our attention on the second of these stages. In many ways this is the most interesting part of the entire story, for one can trace here the stumbling way in which two great scientists — Joseph Priestley (1733–1804) the English nonconformist clergyman, and Antoine Lavoisier (1743–1794) of Paris — proceeded through the jungle of new experimental facts. One can see how the publications of the two men influenced the course of scientific history. In the case of Lavoisier we can follow his line of reasoning and see his errors particularly clearly because of the way in which his most important single paper was given to the world. On the threshold of success, he is diverted by a faulty interpretation of an experiment and recovers his sense of direction only after some months of labor and with the assistance of the English chemist. We are here permitted to follow the course of a revolutionary scientific discovery in much the same fashion as a slow-motion picture of a critical moment enables us to understand what happened in a football game.

The chemical transformations involved in this case are few, and in the light of modern chemistry they are relatively simple. It will assist the student of this example of "science in the making" to master first a few chemical facts as they are expressed in terms of the conceptual scheme that has been the gospel of chemists since Lavoisier's final triumph.

Air is primarily a mixture of two gases, oxygen and nitrogen. Combustion and respiration involve chemical reactions between carbon compounds and oxygen; the products of these reactions are water and carbon dioxide, except in the case of charcoal, when carbon dioxide alone is formed. When a metal is heated in air, it forms an oxide by combining with the oxygen; the product was known to the early chemists as a "calx" and the process as "calcination." When many oxides of metals are heated with charcoal, the oxygen combines with the charcoal forming carbon dioxide ("fixed air" to the chemists of the eighteenth century) and the metal. Mercury oxide, a red powder, also known as red precipitate or *mercurius calcinatus per se,* has the unusual property of being converted into the metal mercury and oxygen when heated quite hot *without charcoal.* Therefore, one can start with mercury metal and obtain the oxide by heating the metal in air, and then by heating the oxide still hotter, regenerate the mercury. If one arranges to collect the gas evolved in this last process, one will have oxygen gas at one's disposal. The three reactions with which Lavoisier and Priestley were concerned were:

Calcination

$$\underset{\substack{\text{mercury}\\\text{metal}}}{2\text{Hg}} \quad \underset{\text{plus}}{+} \quad \underset{\substack{\text{oxygen}\\\text{gas}}}{\text{O}_2} \quad \xrightarrow[\text{yields}]{\text{heated}} \quad \underset{\substack{\text{oxide of}\\\text{mercury}\\\text{(red powder)}}}{2\text{HgO}}$$

Decomposition of oxide

$$\underset{\substack{\text{oxide of}\\\text{mercury}}}{2\text{HgO}} \quad \xrightarrow[\text{yields}]{\substack{\text{heated}\\\text{very hot}}} \quad \underset{\substack{\text{mercury}\\\text{metal}}}{2\text{Hg}} \quad \underset{\text{plus}}{+} \quad \underset{\substack{\text{oxygen}\\\text{gas}}}{\text{O}_2}$$

Reduction with addition of charcoal (also called reduction with phlogiston!)

$$\underset{\substack{\text{oxide of}\\\text{mercury}}}{2\text{HgO}} \quad \underset{\text{plus}}{+} \quad \underset{\substack{\text{charcoal}\\\text{(carbon)}}}{\text{C}} \quad \xrightarrow[\text{yields}]{\text{heated}} \quad \underset{\substack{\text{mercury}\\\text{metal}}}{2\text{Hg}} \quad \underset{\text{plus}}{+} \quad \underset{\substack{\text{carbon}\\\text{dioxide}\\\text{or ``fixed}\\\text{air''}}}{\text{CO}_2}$$

The Phlogiston Theory. A few words about the phlogiston theory are necessary by way of introduction. Joseph Priestley never gave up his belief in the theory. In his last book, published in 1796, he wrote, "There have been few, if any, revolutions in science so great, so sudden, and so general, as the prevalence of what is now usually termed the *new system of chemistry*, or that of the *Anti*phlogistons, over the doctrine of Stahl, which was at one time thought to have been the greatest discovery that had ever been made in the science. I remember hearing Mr. Peter Woulfe,[1] whose knowledge of chemistry will not be questioned, say, that there had hardly been any thing that deserved to be called a *discovery* subsequent to it. Though there had been some who occasionally expressed doubts of the existence of such a principle as that of

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[1] Chemist and mineralogist, born 1727, died 1803, resident of London and Paris, member of the Royal Society from 1767.

phlogiston, nothing had been advanced that could have laid the foundation *of another system* before the labors of Mr. Lavoisier and his friends, from whom this new system is often called that of the *French*."

The significance of this quotation lies in the admission by Priestley, the die-hard upholder of the phlogiston theory, that Lavoisier and his friends had brought about a chemical revolution. Although still raising doubts about the new views and retaining the vocabulary of the phlogiston theory, Priestley in this last publication seems to be admitting that he is fighting a rear-guard action. His statement as to the former high position held by Stahl's doctrine of phlogiston is confirmed by the writings of many eighteenth-century scientists. The phlogiston theory was a broad conceptual scheme into which could be fitted most of the chemical phenomena of the mid-eighteenth century. The lineage of this theory can be traced back to the alchemists. (It should be noted that a metal, according to this theory, is more complex than is the corresponding oxide.) In particular, it accounted for one of the simplest chemical processes then employed for practical ends, namely, the preparation of metals from their ores. The transformation of an earthy substance into a metal in the smelting process appeared to be much the same whether the metal was iron, or tin, or copper. What could be more plausible than to assume that in each instance the ore, when heated with charcoal, took up a "metallizing principle" which conferred upon the earth the properties of a metal? If one called this hypothetical substance phlogiston, an "explanation" for metallurgy was at hand:

$$\begin{array}{ccccc} \text{Metallic ore} & + & \text{Phlogiston} & \longrightarrow & \text{Metal} \\ \text{(an oxide)} & & \text{from} & & \\ & & \text{charcoal} & & \end{array}$$

The fact that charcoal would burn by itself when heated indicated to the founders of the phlogiston theory that the phlogiston escaped in the process and became combined with the air. In general, substances that burned in air were said to be rich in phlogiston; the fact that combustion soon ceased in an enclosed space was taken as clear-cut evidence that air had the capacity to absorb only a definite amount of phlogiston. When air had become completely phlogisticated it would no longer serve to support combustion of any material, nor would a metal heated in it yield a calx; nor could phlogisticated air support life, for the role of air in respiration was to remove the phlogiston from the body. Everything fitted together very well.

The phlogiston theory was almost universally accepted at the time of the American Revolution and was the basis of the chemistry then taught to college students as part of their instruction in natural philosophy. The lecture notes of Professor Samuel Williams, the Hollis Professor of Mathematics and Natural Philosophy, 1780–1788, at Harvard illustrate the convincing way in which the phlogiston theory could be presented to a class. Presenting the subject of Pneumatics, Professor Williams listed six different airs, and about common or atmospherical air had this to say:

"Among the various kinds of permanently elastic Fluids we may begin with *Common or Atmospherical Air.* Atmospherical Air is that which we breathe, with which we are constantly surrounded, and which is common to every country and place. And with regard to this kind of Air several observations may be made. Thus: Common or atmospherical Air may combine, or be charged with many substances. — Thus water is held in solution by Air, and Rain, Snow, and Hail appear to be precipitations from it. . . . But what is worthy of a particular observation, common or atmospherical Air is generally charged with a large quantity of *Fire* or *Phlogiston.* The Chemists sometimes speak of Fire and Phlogiston as being the same thing, or signifying the same element. But we are not absolutely certain that this is the case. By Phlogiston we mean no more than *the principle* of Inflammability; or that by which bodies become combustible or capable of burning. — And that there is such a principle or element as Phlogiston, and that common Air may be charged with large quantities of it may be easily represented.

"*Example:* Take some combustible substance and let it be inflamed or set on fire: In this state inclose it in a vessel containing a small quantity of atmospherical air. *Effect.* The combustion will continue but a small time and then cease. Part of the combustible substance is reduced to ashes and the other part remains entire. And the Air appears to be changed and altered . . . Here then we have a representation of what the chemists call Phlogiston and of the Air's being loaded with it. In the confined air the combustible matter continues burning until the air becomes loaded with something that prevents any further combustion. And being confined by the closeness of the vessel whatever the matter be with which the air is loaded it is confined within the vessel and cannot escape. . . .

"It seems therefore from this Experiment that Phlogiston must be a real Substance, and that the Air is loaded or saturated with it. For what can the enclosing the combustible matter in the Phial do but to prevent the escape or dispersion of some real substance? And is it not evident that so long as the air can receive this substance from the combustible matter so long the body will continue burning; and that as soon as the Air is saturated and can receive no more of the Phlogiston, the combustion must cease for no more Phlogiston can escape or be thrown out from the burning body. And therefore when fresh air is admitted to receive Phlogiston, the combustion will again take place.—And hence are derived the phrases of *phlogisticated* and *dephlogisticated* air. By phlogisticated air is intended air which is charged or loaded with Phlogiston, and by dephlogisticated air is meant Air which is free from Phlogiston; or which does not contain this principle or element of inflammability."

Qualitatively, the phlogiston theory was a satisfactory framework to accommodate the chemical phenomena known in the 1770's. Even some quantitative changes could be accounted for as explained by Professor Williams later in the same lecture:

"We generally estimate the purity of the air by its fitness for the purposes of combustion, respiration, and animal life. And the more free it is from Phlogiston, the principle of inflammability, or any noxious effluvia or mixture, the more fit it is found for this purpose . . . *Experiment.* Take a receiver which holds one gallon and put a lighted candle into it, and let the air be confined.—*Effect:* The candle will burn dimmer and dimmer until the light goes out. Observe the time, and this will be found to be in about one minute after it was put in.—*Remarks:* It appears from this experiment that about one gallon of common air is requisite to support so small a fire or flame as that of this candle for the space of one minute. In this time the quantity of air is diminished by about 1/15 or 1/16 of its bulk."

The diminution in bulk of the air, Professor Williams explains, is a consequence of the phlogistication of the air. For he says, "The greatest diminution of air by Phlogiston is about one-fourth of its first quantity and air which is diminished to its utmost by any one process cannot be any further diminished by another."

Lavoisier's Broad Working Hypothesis. The increase in weight of metals on calcination was, however, a quantitative observation that presented great difficulties to those who thought in terms of phlogiston. After the discovery of the compound nature of water, an explanation was contrived, but it had only a short life, for the phlogiston theory was then going to pieces rapidly.

Lavoisier's new system of chemistry seems to have started with his pondering on the very large increase in weight when phosphorus was burned in air. In a sealed note deposited with the Secretary of the French Academy on November 1, 1772, Lavoisier wrote:

"About eight days ago I discovered that sulfur in burning, far from losing weight, on the contrary, gains it; it is the same with phosphorus; this increase of weight arises from a prodigious quantity of air that is fixed during combustion and combines with the vapors.

"This discovery, which I have established by experiments, that I regard as decisive, has led me to think that what is observed in the combustion of sulfur and phosphorus may well take place in the case of all substances that gain in weight by combustion and calcination; and I am persuaded that the increase in weight of metallic calxes is due to the same cause."

We seem to see here the flash of genius that puts forward a bold working hypothesis on a grand scale without much evidence to support it. Yet there is no doubt, as Lavoisier always claimed, that the essential idea in his theory was contained in this note; *something* was taken up from the atmosphere in combustion and calcination. This was exactly opposite, be it noted, to the phlogiston doctrine. But what was the something? Lavoisier experimented with gases in a search for the answer without much success until the winter of 1774–1775. His book recounting his experiments (largely a repetition of the work of Joseph Black[2] and Priestley), published in 1774, gives the details of his experiment with phosphorus. (He never reported further on his experiments with sulfur, which were in part, at least, erroneous.) He convincingly demonstrates that the white solid produced when phosphorus burns in air confined over mercury weighs about twice as much as the phosphorus that produced it. But as to the nature of the "prodigious quantity of air" that is fixed in the process he remains uncertain. It was the experiments with red oxide of mercury that first put him on the right track. Perhaps it is not too much to say that the unique properties of this oxide made possible a relatively rapid advance in the chemistry of combustion. For no other oxide among all those known even today has the properties of (*a*) decomposing into the metal and oxygen when heated alone below "red heat"; (*b*) being readily prepared free from carbonate; (*c*) being formed when the metal is heated in air at atmospheric pressure.

For a successful investigation a chemist should have pure chemical compounds; mixtures of compounds are very baffling. Furthermore, he must study, if possible, relatively simple reactions that yield only a few products. If by changing the conditions the reaction can be reversed (i.e., be made to run in the other direction) so much the better, for he can then proceed by synthesis and analysis. For example, in the

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[2] Joseph Black (1728–1799), Professor of Anatomy and Chemistry at Glasgow, later Professor of Chemistry at Edinburgh. His work on latent and specific heats (see Case 3 of this series) was of first importance in the development of eighteenth-century physics. His investigation of the process of preparing lime from limestone was a model for later chemical investigations; from him Lavoisier learned the significance of the quantitative study of a simple chemical reaction (limestone → lime + carbon dioxide) that could be reversed.

case of the red oxide of mercury, he can start with mercury and oxygen and prepare the oxide, or conversely, he can start with the red oxide and prepare mercury and oxygen.

1. THE OPENING PHASE OF THE CHEMICAL REVOLUTION

We now come to the crucial events in the chemical revolution (the overthrow of the phlogiston theory), namely, the effective discovery of oxygen. The following chronology of events may prove a useful guide.

February 1774. The French chemist, Bayen, calls attention to the fact that red oxide of mercury yields mercury when heated alone (no charcoal needed as with other calxes). He erroneously identifies the gas evolved as "fixed air" (carbon dioxide)!

August 1774. Priestley prepares oxygen by heating red oxide of mercury, but mistakes the new gas for "laughing gas."

October 1774. Priestley tells Lavoisier of his experiment.

March 1775. Priestley makes the effective discovery of oxygen.

Easter 1775. Lavoisier communicates his memoir "On the Nature of the Principle which Combines with Metals during Calcination and Increases their Weight" to the French Academy.

November 1775. Priestley corrects, in print, Lavoisier's faulty interpretation of the experiment.

May 1777. Lavoisier communicates to the French Academy his memoir on respiration of animals; his ideas about oxygen are now clear.

August 1778. Lavoisier publishes his revised "Easter Memoir."

In order to read intelligently the papers by Lavoisier and Priestley dealing with the discovery of oxygen, a few facts about the oxides of nitrogen must be at hand. These facts are related to Priestley's "nitrous air test" for the purity of common air. Priestley had some years before prepared an oxide of nitrogen that plays an important part in this story; it is nitric oxide (NO), called by Priestley and his contemporaries "nitrous air." Priestley knew that this colorless gas, which is insoluble in water, when mixed with air produced a red gas ("red fumes") that was soluble in water. He found that air in which a candle had been burned until the flame went out would not produce soluble red fumes with "nitrous air." The reason for this, we now know, is that the reaction is between the "nitrous air" and the oxygen:

$2NO$	$+$	O_2	$\longrightarrow$	$2NO_2$
"nitrous air"	plus	oxygen	yields at once	"red fumes" that dissolve in water

Since the product of this almost instantaneous reaction is soluble in water, it is evident that if the two gases are mixed over water there will be a diminution in volume. Indeed, if only the two pure gases were at hand and the volumes were chosen correctly, there would be no residual gas left after the reaction; the diminution would be complete. Since air is only about one-fifth oxygen, there will always be a large amount of residual gas when "nitrous air" and common air are mixed; the nitrogen does not react and is only very slightly soluble in water.

Priestley conceived the idea of using this reaction to test the "goodness" of common air. He found by repeated trials that with ordinary air (the best he knew) the maximum contraction occurred when one volume of "nitrous air" was mixed with two volumes of common air over water. Under these conditions the residue, measured a few minutes later, was only about 1.8 volumes. That is, the diminution in volume was as great as the whole volume of added "nitrous air" and about 20 percent more! With air that was thoroughly "bad" the final volume would be equal to the volume of the "nitrous air" plus the common air (three volumes). Intermediate values represented to Priestley intermediate grades of "goodness." This test was well known among chemical investigators since Priestley had published his results in 1772. It was therefore natural that not only Priestley himself but Lavoisier should apply the "nitrous air test" to any new "air" that would support combustion.

Both Priestley and Lavoisier were at first misled by the application of this test to pure oxygen. Priestley corrected his own error, but Lavoisier interpreted the results correctly only after Priestley had publicly shown where the trouble lay. From the preceding paragraphs it will be evident to the reader that "nitrous air" and pure oxygen react, and when the reaction is carried out over water a large contraction in volume occurs. If Priestley's standard procedure for testing the goodness of air is followed, one volume of "nitrous air" will be added to two volumes of oxygen. Under these conditions all the "nitrous air" is used up but a large amount of oxygen is left over. The actual diminution in volume will be deceptively similar to that found when common air is at hand, but the residual gas instead of being nitrogen is oxygen. There is a small but significant quantitative difference. With common air the resulting gas — the residue — occupies only 1.8 volumes if 2.0 volumes are initially employed; with pure oxygen the final volume is nearer 1.6 volumes. The fact that these numbers are as close as they are is more or less an accident since Priestley chose his standard operating procedure purely empirically (by trial and error); with larger amounts of "nitrous air," the difference between common air and oxygen would be more apparent, as will be evident in a moment. At all events, both Priestley and Lavoisier overlooked the clue offered to them by the somewhat larger diminution in volume of the new gas when subjected to Priestley's test for its "goodness."

The striking contrast between the behavior of common air and oxygen when treated with "nitrous air" over water lies in the properties of the residual gas. (This can be strikingly shown as a lecture-table demonstration, using graduated cylinders as containers in a pneumatic trough.) In the first case, nitrogen mixed with a little "nitrous air" is left; in the other, oxygen. Therefore, the residue in the one instance will support neither combustion nor animal life, nor will it react further with "nitrous air." In the other, the residue has all the properties of the original sample. Any one of the simple tests will at once make this striking difference apparent; a lighted candle, a live mouse, or the addition of "nitrous air" will convince anyone that the two samples of residual gas were totally different. But it never occurred to Lavoisier to try any of these experiments; nor did it occur to Priestley either. Only by the "accident" he describes (see Sec. 4) did Priestley come to examine what was left over when "nitrous air" had diminished his new air from red oxide of mercury! The fact that both investigators took the wrong turn in the road at a critical point in a study of the first importance illustrates how much more complicated is the advance of science than "collecting the facts, classifying the facts, formulating laws, and elaborating from the laws adequate theories."

In comparing the work of Priestley and Lavoisier it is well to bear in mind the differences in their scientific experience up to the year 1774. Priestley was then 41 years old and had started his study of "airs" (gases) some seven years before with an investigation of the fixed air generated in a brewery near his house in Leeds (where he was then the minister of a "dissenting" chapel). In the meantime, he had become the leading pneumatic chemist of the day, having improved the equipment for handling gases and discovered a number of new gases. Lavoisier, on the other hand, was not only ten years younger but a newcomer to the field of experimental chemistry who had only within the past two years repeated many of the early experiments on gases in order to learn the necessary techniques. Yet both the experienced older man and the brash young, inexperienced experimenter made essentially the same mistake and almost at the same moment. In both instances unconscious assumptions invalidated their chains of reasoning.

A few words are now in order about the two versions of Lavoisier's first communication of his experiments on oxygen. Lavoisier read his paper "On the Nature of the Principle which Combines with Metals during Calcination and Increases their Weight" for the first time to the French Academy of Science on Easter, 1775. (It is sometimes referred to as the Easter Memoir of 1775.) It was immediately published, presumably in the form in which he read it, in the May 1775 number of the *Journal de Physique* (page 429). (This magazine was edited by Rozier and carried the full title *Observations sur La Physique, sur L'Histoire Naturelle et sur Les Arts et Métiers.*) The official publication of the Academy of Sciences, the *Mémoires de l'Académie des Sciences*, was at that time months or years late in appearing; this fact gave the authors ample opportunity to revise their communications before their final and authoritative printing. Lavoisier's Easter Memoir of 1775 was again read to the Academy on August 8, 1778 and reëdited at that time, incorporating a few very important changes. A comparison between the text in Rozier's *Journal* of May 1775 and the official paper published after 1778 affords the rare opportunity previously mentioned of viewing a great discovery in the making.

In the spring of 1775 Lavoisier just missed seeing the full significance of the experiments with the red precipitate of mercury (oxide of mercury). He appears to have thought that he had common air at hand rather than a new gas; it was the experiment with Priestley's method of testing the "goodness" of an air by the use of "nitrous air" that was primarily responsible for his erroneous conclusion. For the sixth point in the first version of his paper (May 1775) states that the gas evolved from red oxide of mercury "was diminished like common air by an addition of a third of nitrous air." Priestley, on reading this sometime in the summer of 1775, hastened to record in a book of his, printed a few months later, that this was wrong (see Sec. 3). We cannot be certain that these words of his rival put Lavoisier back on the right track, but we find from Lavoisier's laboratory notebooks that in the following February (1776) he had prepared an "air" from a sample of red oxide of mercury and found it to be considerably "better" than common air *by the test with "nitrous air."* In May 1777, Lavoisier read to the Academy a paper on the respiration of animals in which he makes clear that air is a mixture of two gases, one "highly respirable," the other unable to support combustion or respiration. By 1778 there was no doubt in anyone's mind that a new gas, *not* common air, was produced on heating red oxide of mercury. Therefore, point 6 is completely altered in the final version of the Easter Memoir, and of course so is the final conclusion.

It is interesting to note how relatively few corrections and changes were required to make the original version of Lavoisier's paper correspond with the final and complete interpretation of his results. The similarity of the two versions is evidence that Lavoisier was very close to his final goal. Yet the first version is almost self-contradictory, for the gas from the red oxide is "common air" yet also "purer than common air." For the moment Lavoisier wanted to have it both ways! Though Lavoisier at first went wrong on an important point and was set right by Priestley, it was only Lavoisier, we must remember, who saw the real significance of the discovery of oxygen. He built the new facts into his own conceptual scheme and gave an enduring explanation of combustion. To Priestley goes the honor of being the effective discoverer of oxygen, but to the end of his life it was still "dephlogisticated air" to him.

In the following translation the new words and sentences *added* to the May 1775 version (Rozier's *Journal*) by Lavoisier are enclosed in braces and printed in italics. The material deleted from this first version in the preparation of the second and final form of the communication is printed in boldface type. If the changes are extensive the two versions are printed in parallel columns, the first version being on the left. The footnotes and the explanatory material enclosed in brackets were written by the translator, the editor of this Case, to assist the reader.

2. ENGLISH TRANSLATION OF THE TWO VERSIONS OF THE EASTER MEMOIR OF LAVOISIER

This memoir was read before the French Academy of Sciences at its Easter meeting in 1775, and again on August 8, 1778 (*Mémoires de l'Académie des Sciences,* 1775, p. 520). It carried the following footnote: "The first experiments relative to this Memoir were made more than a year ago; those on 'precipitate of mercury *per se*' were first attempted with a burning glass in the month of November, 1774, and continued with all precautions and necessary care in the laboratory of Montigny, conjointly with M. Trudaine on February 28 and March 1 and 2 of this year; finally they were once more repeated on the 31st of last March in the presence of M. The Duke de la Rochefoucault, and MM. Trudaine, de Montigny, Macquer and Cadet."

Memoir On The Nature Of The Principle Which Combines With Metals During Calcination and Increases Their Weight

Are there different kinds of air? Does it suffice that a body should be in a state of permanent elasticity in order to be considered a kind of air? Are the different airs that nature offers us, or that we succeed in making, exceptional substances or modifications of atmospheric air? Such are the principal questions embraced in the plan I have formed and the problems which I propose to develop {*in succession*} before the Academy. But since the time devoted to our public meetings does not allow me to treat any one of these questions in full, I will confine myself today to one particular case, and will limit myself to showing that the principle which unites with metals during calcination, which increases their weight, and which is a constituent of the calx is

neither one of the constituent parts of the air, nor a particular acid distributed in the atmosphere, that it is the air itself entire without alteration, without decomposition even to the point that if one sets it free after it has been so combined it comes out more pure, more respirable, if this expression may be permitted, than the air of the atmosphere and is more suitable to support ignition and combustion.

{*nothing else than the healthiest and purest part of air; so that if air, after entering into combination with a metal, is set free again, it emerges in an eminently respirable condition, more suited than atmospheric air to support ignition and combustion.*}

The majority of metallic calces are only reduced, that is to say, only return to the metallic condition, by immediate contact with a carbonaceous material, or with some substance containing what is called phlogiston. The charcoal that one uses is entirely destroyed during the operation when the amount is in suitable proportion, whence it follows that the air set free from metallic reductions with charcoal is not simple; it is in some way the result of the combination of the elastic fluid set free from the metal and that set free from the charcoal; thus, though this fluid is obtained in the state of fixed air, one is not justified in concluding that it existed in this state in the metallic calx before its combination with the carbon.

These reflections have made me feel how essential it is, in order to unravel the mystery of the reduction of metallic calces, that all my experiments be performed on calces which can be reduced without any addition [that is, without the addition of charcoal]. The calces of iron have this property: in fact, all those, whether natural or artificial, which we have placed in the focus of a burning glass either that of M. the Regent or of M. de Trudaine, in each case were totally reduced without addition.

In consequence, I tried with the aid of a burning glass to reduce several kinds of iron calces under large glass bell-jars turned upside down in mercury, and by this method I succeeded in setting free a large quantity of **elastic fluid** {*air*}; but, as at the same time this **elastic fluid** {*air*} mixed with the common air contained in the bell, this circumstance cast great uncertainty on my results; none of the experiments to which I submitted this air was completely conclusive, and it was impossible to be sure whether the phenomena obtained depended on the common air, on that released from the iron calces, or on the combination of the two together. These experiments not having fulfilled my object, I omit the details here; they will find their natural place in other memoirs. [Those who have studied Case 1 of this series will be interested in comparing this method of reporting with that used by Boyle concerning his experiments with the subtle fluid.]

> Since these difficulties proceeded from the very nature of iron, from the refractory quality of its calces, and from the difficulty of reducing them without addition, I considered them as insurmountable, and henceforth decided to address myself to another kind of calx more easily treated and which, like iron calces, possessed the property of being reduced without addition. *Mercurius calcinatus per se*, which is nothing else than a calx of mercury, as several authors have already maintained and as the reader of this Memoir will be even convinced, *mercurius calcinatus per se*, I repeat, seemed to me completely suitable for what I had in view; no one today is unaware that this substance can be reduced without addition at a very moderate degree of heat. Although I have repeated many times the experiments I am going to report, I have not thought it necessary to give particular details of any of them here, for fear of occupying too much space, and I have therefore combined into one account the observations made during several repetitions of the same experiment.

Throughout this memoir Lavoisier is referring to only one compound of mercury, namely the red oxide; he refers to it as *precipitated mercury per se,* to indicate that it was obtained by heating mercury by itself. We have translated it as *mercurius calcinatus per se,* the Latin phrase used by Priestley to describe the same material.

> In order to be sure that *mercurius calcinatus per se* was a true metallic calx, whether it would give the same results and the same kind of air on reduction, I tried at first to reduce it by the ordinary method, that is to say, to use the accepted expression, by the addition of phlogiston. I mixed one ounce of this calx with 48 grains[3] of powdered charcoal, and introduced the whole into a little glass retort of at most two cubic inches capacity, which I placed in a reverberatory furnace of proportionate size. The neck of this retort was about a foot long, and three to four lines in diameter [a line is one-twelfth of an inch]; it had been bent in different places by means of an enameler's lamp, and its tip was such that it could be fixed under a bell-jar of sufficient size, filled with water, {*and turned upside down in a trough of water. The apparatus now before the eyes of the Academy suffices to give an idea of the operation.*} This apparatus, simple as it is, is the more exact that there is no soldering or luting or any passage through which air might leak in or escape.
>
> As soon as a flame was applied to the retort and the heat had begun to take effect, the ordinary air contained in the retort expanded, and a small quantity passed into the bell-jar; but in view of the small size of the part of the retort that remained empty, this air could not introduce

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[3] The system of weights employed was: 1 pound (Paris standard) = 16 ounces; 1 ounce = 8 gros; 1 gros = 72 grains; or 1 pound (Paris) = 9216 grains. The English avoirdupois pound of 16 ounces (still commonly used) is somewhat lighter, and is divided into 7000 grains.

a sensible error, and at the most it could scarcely amount to a cubic inch. When the retort began to get hotter, air was very rapidly disengaged and rose through the water into the bell-jar; the operation did not last more than three-quarters of an hour, the flame being used sparingly during this interval. When all the calx of mercury had been reduced and the air ceased rising, I marked the height at which the water stood in the bell-jar and found that the quantity of air set free amounted to 64 cubic inches, without allowing for the volume necessarily absorbed in passing through the water.

I submitted this air to a large number of tests, which I will not describe in detail, and found (1) that it was susceptible to combination with water on shaking and gave to it all the properties of acidulated, gaseous, or aerated waters such as those of Seltz, Pougues, Bussang, Pyrmont, etc.; (2) that animals placed in it died in a few seconds; (3) that candles and all burning bodies were instantly extinguished in it; (4) that it precipitated lime water; (5) that it combined very easily with either the fixed or the volatile alkalis, removing their causticity and giving them the property of crystallizing. [Fixed alkalis are materials like slaked lime or caustic soda that absorb carbon dioxide to form carbonates which, unlike the alkalis, are not caustic amorphous solids but noncaustic crystalline solids; volatile alkali is ammonia.] All these are precisely the qualities of the kind of air known as fixed air,

or mephitic air such as is obtained from all metallic calces by the addition of charcoal such as is set free from fermenting matters. It was thus unquestionable that *mercurius calcinatus per se* should be included in the category of metallic calces.

{*obtained by the reduction of minium* [an oxide of lead] *by powdered charcoal,*} such as is set free {*from calcareous earths and effervescent alkalis by their combination with acids, or*} from fermenting {*vegetable*} matters, {*etc.*}. It was thus unquestionable that *mercurius calcinatus per se* {*gave the same products as other metallic calces on reduction with addition of phlogiston and that it*} should {*consequently*} be included in the {*general*} category of metallic calces.

Lavoisier up to this point has added nothing new. Bayen, another French chemist, had recently reported similar results; Lavoisier's work represented a careful rechecking. How important such independent verification may be is evident from what follows. For Bayen had reported that the gas evolved when the mercury calx was heated by itself was also fixed air! How he could come to such an erroneous conclusion no one knows, but he was obviously not a skillful experimenter with gases.

It remained only to examine this calx alone, to reduce it without addition, to see if some air {*elastic fluid*} would be set free, and if so, to determine **what state it was in** {*its nature*}. To accomplish this I put into a retort of the same size as before (two cubic inches) one ounce of *mercurius calcinatus per se*, alone; I arranged the apparatus in the same way as for the preceding experiment, so that all the circumstances were exactly the same; the reduction was a little more difficult than with the addition of charcoal; it required more heat and there was no perceptible effect till the retort began to get slightly red-hot; then air was set free little by little, and passed into the bell-jar, and the same degree of heat being maintained for 2½ hours, all the *mercurius calcinatus per se* was reduced.

The operation completed, 7 gros, 18 grains of {*liquid*} mercury were found, partly in the neck of the retort and partly in a glass vessel which I had placed at the tip of the retort under the water; the amount of air in the bell-jar was found to be 78 cubic inches; from which it follows, that supposing all the loss of weight is attributed to the air, each cubic inch must weigh a little less than two-thirds of a grain, which does not differ much from the weight of ordinary air.

Having established these first results, I hastened to submit the 78 cubic inches of air I had obtained to all the tests suitable for determining its nature, and I found, much to my surprise:

(1) that it was not susceptible to combination with water upon shaking;	(1) that it was not susceptible to combination with water upon shaking;
(2) that it did not precipitate lime water;	(2) that it did not precipitate lime water {*but only made it turbid to an almost imperceptible degree*};
(3) that it did not combine with fixed or volatile alkalis;	(3) that it did not combine with fixed or volatile alkalis;
(4) that it did not at all diminish their caustic qualities;	(4) that it did not at all diminish their caustic qualities;

[these first four tests were designed to show whether the gas was in whole or part "fixed air" as Bayen had reported; obviously it was not;]

(5) that it could be used again for the calcination of metals;	(5) that it could be used again for the calcination of metals;
(6) that it was diminished like common air by an addition of a third of nitrous air; [4]	

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[4] "Addition of a third of nitrous air" means that one volume of "nitrous air" to two volumes of air to be tested was used — the mixture being, of course, allowed to stand over water.

finally, that it had none of the properties of fixed air: far from causing animals to perish, it seemed on the contrary more suited to support their respiration; not only were candles and burning objects not extinguished in it, but the flame increased in a very remarkable manner and gave much more light than in common air.

All these circumstances convinced me fully that this air **was not only common air but that it was more respirable, more combustible,** and consequently that it was more pure than even the air in which we live.

(6) finally, that it had none of the properties of fixed air: far from causing animals to perish, it seemed on the contrary more suited to support their respiration; not only were candles and burning objects not extinguished in it, but the flame increased in a very remarkable manner and gave much more light than in common air; {*charcoal burned in it with a radiance almost like that of phosphorus, and all combustible bodies in general were consumed with astonishing speed.*} All these circumstances convinced me fully that this air, {*far from being fixed air, was in a state more respirable and more combustible,*} and consequently that it was more pure than even the air in which we live.

It seems proved accordingly that the principle which combines with metals during calcination and which augments their weight is nothing else than the purest part of the very air which surrounds us, which we breathe, and which in this operation passes from a condition of elasticity to that of solidity; if then it is obtained in the form of fixed air in all the metallic reductions in which charcoal is used, this effect is due to **the charcoal itself** {*the combination of the latter with the pure part of the air*}, and it is very likely that all metallic calces, like that of mercury, would give **only common air** {*only eminently respirable air*} if they could all be reduced without addition like *mercurius calcinatus per se.*

The nitre referred to in the next paragraph is potassium nitrate, a compound of the metal potassium, oxygen, and nitrogen; from it chemists early learned to prepare nitric acid and hence other nitrates. Mixed with charcoal and sulfur it yields black gunpowder. This paragraph, which deals with the explosion of powder, may be omitted.

Everything that has been said of the air from metallic calces may naturally be applied to that obtained from nitre by detonation; we know from a number of experiments already published, the majority of which I have repeated, that most of this air is in the form of fixed air, that it is fatal to any animal breathing it, that it has the property of **precipitating lime water and of** combining with lime and alkalis, of softening them and making them crystallize; but since the detonation of nitre only takes place after the addition of charcoal or of some body which contains

phlogiston, it is very probable {*it cannot be doubted*} that in this circumstance also **common air** {*eminently respirable air*} is converted into fixed air;

from which it follows that the air combined with nitre which produces the terrible explosions of gunpowder is **common** atmospheric air deprived of its elasticity. **From the fact that common air changes to fixed air when combined with charcoal it would seem natural to conclude that fixed air is nothing but a combination of common air and phlogiston. This is Mr. Priestley's opinion and it must be admitted that it is not without probability; however, when one looks into the facts in detail, contradictions arise so frequently I feel it necessary to ask natural philosophers and chemists still to suspend judgment; I hope to be soon in a position to communicate the reasons for my doubts.**

from which it follows that the air combined with nitre which produces the terrible explosions of gunpowder is {*the respirable part of*} atmospheric air deprived of its elasticity {*and which is one of the constituent principles of nitric acid. Since charcoal disappears completely in the revivification of mercuric calx and since only mercury and fixed air are produced by this operation, one is forced to conclude that the principle to which has hitherto been given the name of fixed air, is the result of the combination of the eminently respirable portion of the air with charcoal; and this is what I propose to develop in a more satisfactory manner in subsequent memoirs which I shall devote to this object.*}

A diagram of the apparatus used by Lavoisier in reducing red oxide of mercury with and without the addition of charcoal is shown in Fig. 1. The use of a reverberatory furnace (that is, one in which the heat is reflected down on the retort as well as coming from the flame below) enabled Lavoisier to heat the retort to a dull red heat. This temperature is required for the decomposition of the oxide if no charcoal is employed. Lavoisier does not state in this paper how he removed samples of the gas for the various tests, but in some of his later equipment the gas was removed through a small orifice near the top of the bell jar to smaller vessels by a suitable suction device. The methods of collecting gases over water or mercury and transferring them from one vessel to another had been greatly improved by Joseph Priestley a short time before.

The paragraph on page 82 in which Lavoisier records the weight of mercury recovered from the decomposition of the oxide and the amount of gas evolved is of great significance. Here Lavoisier is invoking a principle that underlay his whole work. One biographer of the French chemist, recalling that Lavoisier was a man of business affairs first and a chemist second, has spoken of Lavoisier's "principle of the balance sheet." Lavoisier had early in his career used the balance, and in repeating Joseph Black's work had undoubtedly been impressed by the Scotch chemist's success in accounting for the weights of the starting materials and of the products in a chemical reaction. In the paragraph mentioned we see Lavoisier in his first major chemical contribution comparing the weight of the initial oxide (1 ounce) with the mercury produced (7 gros 18 grains) and deducing that the only other product (the gas) must account for the difference in weight (1 ounce = 8 gros and 1 gros = 72 grains; therefore the difference would be 7 gros 72 grains minus 7 gros 18 grains = 54 grains). He concludes that the 78 cubic inches of the air evolved must weigh 54 grains or about 54/78 grain per cubic inch (54/78 is a little more than 2/3, which is 52/78).

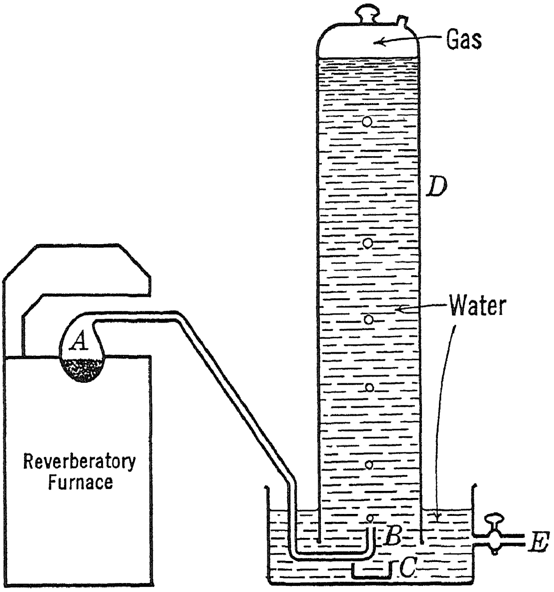

FIG. 1. Diagram of apparatus used by Lavoisier in collecting the gas evolved when red oxide of mercury is heated.

The weight of 1 cubic inch of air at the usual temperature and pressure of a laboratory had been given as 0.46 (or 36/78) grain by Lavoisier in a book published a few years earlier. Therefore, his statement that the estimated weight of 2/3 grain per cubic inch "does not differ much from the weight of ordinary air" is an optimistic statement by an investigator looking for an agreement between two numbers. Lavoisier was aware, of course, that this estimate of the density of the air was extremely rough, for his method of insuring the collection of all the mercury was far from sufficient for the purposes. (Note that the weight of the air evolved was a small difference between two relatively large numbers; such a situation is always unfavorable for accurate measurements. The failure to collect 3 percent, or 16 grains, of the mercury would have increased the estimated weight of the total gas by that amount, or by 16/78 grain per cubic inch, which is about the discrepancy observed.) Lavoisier does not record the pressure or temperature, though he does so in all his later experiments, where his calculations can be made with a higher degree of accuracy. The significance of the paragraph lies, therefore, not in the result, which is far too approximate to be useful, but in Lavoisier's mode of reasoning. Within the limits of experimental error he is trying to apply the *principle of the balance sheet.*

In his textbook of 1789 Lavoisier wrote: "We must lay it down as an incontestable axiom, that in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment . . . Upon this principle, the whole art of performing chemical experiments depends." Whether or not Lavoisier came to this principle because as a member of the firm that collected taxes he was used to balancing his books in terms of money, the principle was the foundation of his work. In the nineteenth century the exactness of this principle was tested by very careful experimentation, using balances far more sensitive than those available in Lavoisier's time. In every case it was found that the weight of the factors was equal to that of the products within the small experimental error of the measurements. The principle was thus considered a generalization of experimental fact, rather than an axiom; it became known as the Law of Conservation of Mass (or Matter). We now have good reason to believe on both theoretical and experimental grounds that in the form in which it was expressed by Lavoisier and by the scientists of the nineteenth century it is only an approximation. Whenever energy is released or absorbed in a chemical change (and that is in practically every instance) a very very small change in mass occurs; the change is too small to be detected even with the most accurate measurements of the weights involved in even the most energetic chemical reaction. Those changes, however, that take place when the nuclei of atoms are altered liberate amounts of energy of another order of magnitude from those connected with chemical reactions; in this case the change of mass is significant and is directly related to the energy evolved. It is common nowadays to speak of the combination in the twentieth century of the two principles of conservation of mass and of conservation of energy into one — the principle of conservation of mass and energy.

This doctrine is accepted as a guiding principle by physicists and chemists today.

Those who have some knowledge of quantitative chemistry will interpret the equations given on page 69 for the reduction of mercury oxide with and without charcoal as stating that the volumes of oxygen and of carbon dioxide produced from 1 ounce of oxide should be the same (at the same temperature and pressure). Actually Lavoisier obtained 64 cubic inches of carbon dioxide and 78 of oxygen; the difference is due to the solubility of carbon dioxide in water. Indeed, if the gas had been allowed to stand over the water for any length of time or had been shaken with it, almost all of it would have gone into solution. In later experiments Lavoisier collected carbon dioxide over mercury. In this memoir we see him struggling with the difficulties of carrying out chemical experiments in such a way as to make quantitative observations meaningful. This is the beginning of the long and arduous road that had to be traveled before chemistry could become a quantitative science.

Lavoisier's reasoning in 1775 and 1778 is worth examining with some care. His broad working hypothesis of 1772 was that "something" was taken up from the air when a metal was calcined. At first he thought that this "something" might be fixed air and had experimented in vain to prove this. In other words, his broad working hypothesis, when made specific by substituting the words "fixed air" for "something," yielded deductions that were *not* confirmed by experimental test. Now, thanks perhaps to the unconscious tip that Priestley had conveyed to him in conversation in the fall of 1774, he had a calx which on heating yielded a gas that behaved like common air. Substituting common air for the "something" in his broad working hypothesis yielded a deduction that appeared to be confirmed by the experiment. But note carefully that deductions from broad working hypotheses are never directly confirmed or negated. A specific experiment must always be related to the deductions by one or more limited working hypotheses. This is where the difficulties arise and in this case we can see exactly how they arose in 1775. Of the six tests recorded by Lavoisier in his first version of the Easter Memoir, the first four gave convincing evidence that the gas was not fixed air. (In each test a limited working hypothesis was implicit, an "if . . . then" type of reasoning was employed.) The fifth and sixth tests, together with the experiments with the candle and with animals, seemed to provide conclusive evidence that the gas was common air. On the supposition that the gas was common air, Lavoisier could say, "If I perform the following manipulations, then the result will be such and such." (This last is a limited working hypothesis that is confirmed or negated by test.) In other words, there is the haunting question whether another substance could also behave in this same manner; of these tests the nitrous air test appeared to be the most specific and must have appealed to Lavoisier because it was at least roughly quantitative. But the similarity in behavior of the new gas and common air in this test was, we have seen, only apparent. The assumption that there would be no further diminution in volume if more nitrous air were added was implicit in the report of Easter 1774, for that was the case with common air. Priestley, as we shall see in the next section, corrected the assumption as a result of an accident; Lavoisier corrected it after having learned of Priestley's use of the nitrous air test to show that the gas was *not* common air.

As far as the significance of the nitrous air test was concerned, both Priestley and Lavoisier agreed by the spring of 1776. They would now say that an air is common air if it is diminished by a third of nitrous air, *provided* it is not further diminished on adding more nitrous air. They would both agree that a new air was present when the calx of mercury was heated. But as to the broad working hypothesis of Lavoisier, they disagreed completely. Priestley stuck to the conceptual scheme in which phlogiston was the determining factor in calx formation. Lavoisier saw his broad working hypothesis now made specific by substituting the words "a constituent of the atmosphere which supports combustion" for his "something." His working hypothesis on a grand scale was about to attain the status of a new conceptual scheme.

3. PRIESTLEY'S COMMENTS ON LAVOISIER'S EASTER MEMOIR

Priestley's comments on Lavoisier's paper were printed in Section XVI of Volume II of his *Experiments and Observations on Different Kinds of Air* the dedication of which is dated November 1, 1775. The title of this section, one of the last in the book, is "An Account of some Misrepresentations of the Author's Sentiments, and of some Differences of Opinion with respect to the Subject of Air." The relevant passages (from pages 320–323) follow[5] (the words included in brackets have been added to enable the reader to follow the discussion in modern terms); the opening words refer to a discussion of Lavoisier's remark about Priestley's opinion as to the relation of fixed air to phlogiston, which is not relevant to the discussion of the experiments.

> Having mentioned the paper of Mr. Lavoisier's, published in Mr. Rosier's Journal, I would observe, that it appears by it, that, after I left Paris, where I procured the *mercurius calcinatus* [red oxide of mercury] above mentioned, and had spoken of the experiments that I had made, and that I intended to make with it, he began his experiments upon the

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[5] All extracts from Priestley's book used in this Case are taken from the second edition (1776).

> same substance, and presently found what I have called *dephlogisticated air* [oxygen], but without investigating the nature of it, and indeed, without being fully apprised of the degree of its purity. For he had only tried it with one-third of nitrous air, and observed that a candle burned in it with more vigour than in common air; and though he says it *seems to be* more fit for respiration than common air, he does not say that he had made any trial how long an animal could live in it.

Priestley felt he had been unfairly treated by Lavoisier because the French chemist made no mention in his paper of the facts communicated to him in the fall of 1774 by Priestley. Historians have been discussing ever since how essential this verbal communication was in fact. The incident, quite apart from the entertaining way in which Priestley rebukes Lavoisier, is of interest as illustrating the state of scientific communication toward the end of the eighteenth century. As in the seventeenth century, investigators did not feel under any special obligation to refer to the work of others. Lavoisier makes no mention of Bayen's paper published a year before; possibly he assumed that everybody had read it. Since the middle of the nineteenth century, practice has changed in this respect. Investigators are today very scrupulous in referring to published work and even verbal communications.

> He therefore inferred, as I have said that I myself had once done, that this substance had, during the process of calcination, imbibed atmospherical air, not in part, but in whole. But then he extends his conclusion, and, as it appears to me, without any evidence, to all the metallic calces; saying that, very probably, they would all of them yield only common air, if, like *mercurius calcinatus*, they could be reduced without addition. For he considers the fixed air [carbon dioxide], which is yielded by most of them, to come from the charcoal, made use of to revivify the calx. Whereas it will be seen, in the course of my experiments, that several of those calces yield fixed air by *heat only*, without any addition of charcoal [that is, without addition of charcoal before being heated. Priestley was in error here; Lavoisier was right. Those calces from which Priestley obtained fixed air (carbon dioxide) were impure; they contained carbonates which are decomposed on heating yielding carbon dioxide].
>
> He adds, that since common air is changed into fixed air when it is combined with charcoal, it would seem natural to conclude, that fixed air is only a combination of common air and phlogiston (an opinion which, as has been seen before, he ascribes to me) and it is not, he says, without probability; but adds, that it is so often contradicted by facts, that he desires philosophers and chymists to suspend their judgments; hoping that it will soon be in his power to explain the motives of his doubts. I, for one, am waiting with some impatience for this explanation. [But when it came, Priestley rejected it!]
>
> Mr. Lavoisier also concludes, from his observations, that the air pro-

duced by the detonation of nitre and the firing of gunpowder is common air. When he sees this volume of mine, he will, I doubt not, be convinced of the imperfection of his theory, and of this mistake, which he has been led into by means of it. [The detonation of nitre is not relevant to the case at hand.]

Mr. Lavoisier as well as Sig. Landriani, Sig. F. Fontana, and indeed all other writers except myself, seems to consider common air (divested of the effluvia that float in it, and various substances that are dissolved in it, but which are in reality foreign to it) as a simple *elementary body*; whereas I have, for a long time, considered it as a *compound*; and this notion has been of great service to me in my inquiries.

As a concurrence of unforeseen and undesigned circumstances has favoured me in this inquiry, a like happy concurrence may favour Mr. Lavoisier in another; and as, in this case, truth has been the means of leading him into error, error may, in its turn, lead him into truth. It will have been seen, in the course of my writings, that both these circumstances have frequently happened to myself; and indeed examples of both of them will be found in my first section concerning this very subject of dephlogisticated air.

It is pleasant when we can be equally amused with our own mistakes, and those of others. I have voluntarily given others many opportunities of amusing themselves with mine, when it was entirely in my power to have concealed them. But I was determined to shew how little *mystery* there really is in the business of experimental philosophy, and with how little *sagacity*, or even *design*, discoveries (which some persons are pleased to consider as great and wonderful things) have been made.

4. THE STEPS LEADING TO PRIESTLEY'S DISCOVERY OF OXYGEN

Having read Priestley's comments written in the summer of 1775 on Lavoisier's Easter Memoir of the same year, we are ready to examine the record of how Priestley himself at first erroneously interpreted his experiments with oxygen. In the summer of 1774 he first started studying the gas evolved when red oxide of mercury is heated, as he relates in the account reproduced here.

A few words of explanation are required to make clear to the reader who has little or no knowledge of chemistry how Priestley made his first error, which was a completely erroneous identification of the new gas. He tested the "new air" (which was in reality oxygen) with a lighted candle and found that the candle was not extinguished but burned brightly. Now a few years before, Priestley had prepared an oxide of nitrogen that has the unusual property of supporting combustion. He did not know, of course, that it was an oxide of nitrogen, but he called it "phlogisticated nitrous air" for he had prepared it by letting "nitrous air" (nitric oxide) stand with metallic iron or certain other substances which decompose the nitric oxide, taking away some of the oxygen and yielding the other oxide, which supports combustion. Although in Priestley's terminology it was "phlogisticated," he apparently gave no explanation of why phlogistication made the nitrous air inflammable. The chemical reaction is as follows:

			slowly			
$2NO$	+	Fe	→	N_2O	+	FeO
"nitrous air," colorless, insoluble gas; will not support combustion	plus	metallic iron	yields	"phlogisticated nitrous air" (modern name: nitrous oxide) somewhat soluble in water; supports combustion; commonly called "laughing gas"	plus	iron oxide

The product we now call nitrous oxide; this modern name is confusing in this narrative, since in Priestley's day our modern nitric oxide was called "nitrous air." Fortunately, nitrous oxide plays only a minor role and will hereafter be designated as "laughing gas," for it is often so called from the fact that today it is used for anesthesia, particularly by dentists, and the patient sometimes becomes quite merry before the anesthesia is complete! Priestley's sample of this gas was a mixture of the original nitric oxide and "laughing gas." When the mixture was agitated with water, the oxide that supports combustion was dissolved. The significance of this fact will be evident in what follows.

Priestley's account of his experiments leading to the identification of oxygen as a new gas are described in Section III of Volume II of his *Experiments*. After some rather amusing general remarks about experimental difficulties, he recounts the experiments performed in 1774 and the totally erroneous conclusions he drew from them. (It was at this time that he confused oxygen with "phlogisticated nitrous air," that is, "nitrous air exposed to iron.") On March 1, 1775 Priestley decided to apply his "nitrous air test" to the "air" obtained from the red oxide. The results of this experiment showed that the new "air" was at least very much like common air. It is a remarkable coincidence that Lavoisier almost simultaneously and quite independently was performing the same experiment; he decided on the basis of the result that he had at hand a purified common air, as is evident from the first version of his memoir. But Priestley, more or less by accident, went further. He found that the residual gas, or air, left after the reaction with nitrous air and the subsequent diminution in volume would still allow a candle to burn brightly. This accidental discovery was followed up by experiments with a mouse which, he found, would live in this residual gas. Priestley then began to suspect that the air under investigation not only was *at least as good as common air* but might be *better*. This he proved by showing that even after a mouse had lived in it for some time, the nitrous air diminished its volume more than common air.

"Being now fully satisfied of the superior goodness of this kind of air," he found by careful trials with increasing amounts of nitrous air that he could get an increasing diminution in volume until more than four half measures (for one measure of the gas being tested) were used. This proved that a substance quite different from common air was at hand. The effective discovery of oxygen by Priestley had occurred.

Priestley's own account now follows (pages 29–49 of Volume II). The material in brackets is added to assist the reader.

General Observations on the Role of Chance Discoveries

> The contents of this section will furnish a very striking illustration of the truth of a remark, which I have more than once made in my philosophical writings, and which can hardly be too often repeated, as it tends greatly to encourage philosophical investigations; viz. that more is owing to what we call *chance*, that is, philosophically speaking, to the observation of *events arising from unknown causes*, than to any proper *design*, or pre-conceived *theory* in this business. This does not appear in the works of those who write *synthetically* upon these subjects; but would, I doubt not, appear very strikingly in those who are the most celebrated for their philosophical acumen, did they write *analytically* and ingenuously.
>
> For my own part, I will frankly acknowledge, that, at the commencement of the experiments recited in this section, I was so far from having formed any hypothesis that led to the discoveries I made in pursuing them, that they would have appeared very improbable to me had I been told of them; and when the decisive facts did at length obtrude themselves upon my notice, it was very slowly, and with great hesitation, that I yielded to the evidence of my senses. And yet, when I re-consider the matter, and compare my last discoveries relating to the constitution of the atmosphere with the first, I see the closest and the easiest connexion in the world between them, so as to wonder that I should not have been led immediately from the one to the other. That this was not the case, I attribute to the force of prejudice, which, unknown to ourselves, biasses not only our *judgments*, properly so called, but even the perceptions of our senses: for we may take a maxim so strongly for granted, that the plainest evidence of sense will not intirely change, and often hardly modify our persuasions; and the more ingenious a man is, the more

> effectually he is entangled in his errors; his ingenuity only helping him to deceive himself, by evading the force of truth.

These observations of Priestley's have been the basis for some criticism of his scientific judgment by historians of science. As in some of the comments on the accidental nature of his experiments later in this same account, Priestley is here frank almost to the point of naïveté. Yet anyone conversant with the way chemical discoveries are made even today will hardly take exception to his remarks.

Priestley's Views on the Nature of the Atmosphere

In the following passage, Priestley refers to "agitation in water" as a method of purifying a gas. In this process, for which he had invented an apparatus, two things happened of which he was ignorant and both of which made the gas more fit for respiration. One was the dissolving in the water of the carbon dioxide in the gas; the other was the addition to the gas of some oxygen, which came from the dissolved air present in ordinary samples of water. Priestley is quite correct in what he says about the "process of vegetation"; green plants not only use up carbon dioxide but evolve oxygen.

> There are, I believe, very few maxims in philosophy that have laid firmer hold upon the mind, than that air, meaning atmospherical air (free from various foreign matters, which were always supposed to be dissolved, and intermixed with it) is a *simple elementary substance*, indestructible, and unalterable, at least as much so as water is supposed to be. In the course of my inquiries, I was, however, soon satisfied that atmospherical air is not an unalterable thing; for that the phlogiston with which it becomes loaded from bodies burning in it, and animals breathing it, and various other chemical processes, so far alters and depraves it, as to render it altogether unfit for inflammation, respiration, and other purposes to which it is subservient; and I had discovered that agitation in water, the process of vegetation, and probably other natural processes, by taking out the superfluous phlogiston, restore it to its original purity. But I own I had no idea of the possibility of going any farther in this way, and thereby procuring air purer than the best common air. I might, indeed, have naturally imagined that such would be air that should contain less phlogiston than the air of the atmosphere; but I had no idea that such a composition was possible. [Here as throughout his life Priestley is using the concept of phlogiston to explain combustion and calcination.]

Priestley's First Experiments with Red Oxide of Mercury

Publication of these results in Priestley's *Experiments*, as given below, followed the communication of three letters announcing the essential facts to the Royal Society; they are dated March 15, April 1, and May 29, 1775, and were printed in volume 65 of the *Philosophical Transactions of the Royal Society* for that year, which seems to have appeared more promptly than the corresponding record of the French Academy.

> At the time of my former publication, I was not possessed of a *burning lens* of any considerable force; and for want of one, I could not possibly make many of the experiments that I had projected, and which, in theory, appeared very promising. I had, indeed, a *mirror* of force sufficient for my purpose. But the nature of this instrument is such, that it cannot be applied, with effect, except upon substances that are capable of being suspended, or resting on a very slender support. It cannot be directed at all upon any substance in the form of *powder*, nor hardly upon any thing that requires to be put into a vessel of quicksilver [liquid metallic mercury]; which appears to me to be the most accurate method of extracting air from a great variety of substances, as was explained in the Introduction to this volume. But having afterwards procured a lens of twelve inches diameter, and twenty inches focal distance, I proceeded with great alacrity to examine, by the help of it, what kind of air a great variety of substances, natural and factitious, would yield, putting them into the vessels . . . which I filled with quicksilver, and kept inverted in a bason of the same. Mr. Warltire, a good chymist, and lecturer in natural philosophy, happening to be at that time in Calne, I explained my views to him, and was furnished by him with many substances, which I could not otherwise have procured.

Priestley's statements about the mirror are at first sight somewhat perplexing. The point is not important, however. Apparently Priestley had a concave mirror enabling him to bring a beam of sunlight to a focus and thus concentrate the radiant energy. However, the material placed at the focus of a concave mirror is *between* the source of light and the reflecting surface. It must be small if it is not to cut off a large portion of the beam of light. With a lens there is, of course, no such difficulty (see Fig. 2).

> With this apparatus, after a variety of other experiments, an account of which will be found in its proper place, 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. [The gas evolved, which was oxygen, displaced the mercury.] 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. [This showed that the gas was not carbon dioxide which he suspected would be formed.] But what surprized me more than I can well express, was, that a candle burned in this air with a remarkably vigorous flame, very much like that enlarged flame with which a candle burns in nitrous air, exposed to iron or liver of sulphur [calcium sulfide which, like iron,

transforms nitric oxide into laughing gas (see p. 91); that is, Priestley thought he was dealing with what we now call laughing gas]; but as I had got nothing like this remarkable appearance from any kind of air besides this particular modification of nitrous air [laughing gas], and I knew no nitrous acid was used in the preparation of *mercurius calcinatus*, I was utterly at a loss how to account for it. ["Nitrous air" requires a nitrate for its preparation and this in turn requires nitric acid or its equivalent. This acid was called nitrous acid in Priestley's day.]

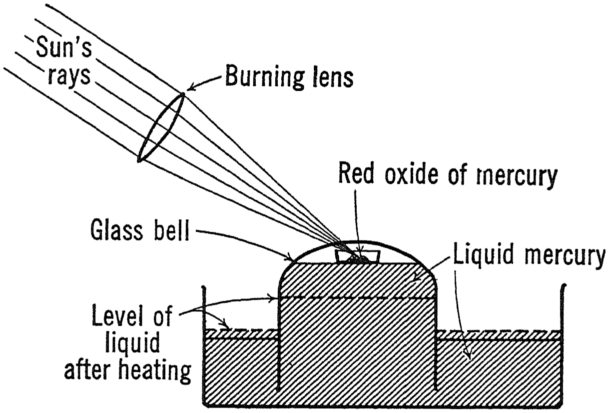

Fig. 2. Priestley's method of heating red oxide of mercury with a burning lens.

In this case, also, though I did not give sufficient attention to the circumstance at that time, the flame of the candle, besides being larger, burned with more splendor and heat than in that species of nitrous air [i.e., laughing gas]; and a piece of red-hot wood sparkled in it, exactly like paper dipped in a solution of nitre [potassium nitrate used in the manufacture of gunpowder], and it consumed very fast; an experiment which I had never thought of trying with nitrous air. [Priestley probably means here nitrous air modified by exposure to iron.]

At the same time that I made the above-mentioned experiment, I extracted a quantity of air, with the very same property, from the common *red precipitate*, which being produced by a solution of mercury in spirit of nitre [nitric acid], made me conclude that this peculiar property, being similar to that of the modification of nitrous air above mentioned, depended upon something being communicated to it by the nitrous acid [nitric acid]; and since the *mercurius calcinatus* is produced by exposing mercury to a certain degree of heat, where common air has access to it, I likewise concluded that this substance had collected something of *nitre*, in that state of heat, from the atmosphere [a not unlikely supposition but erroneous, for it is in fact the oxygen of the nitric acid that is left united with the mercury when the red oxide is prepared from the nitrate].

This, however, appearing to me much more extraordinary than it ought to have done, I entertained some suspicion that the mercurius

> calcinatus, on which I had made my experiments, being bought at a common apothecary's, might, in fact, be nothing more than red precipitate; though, had I been any thing of a practical chymist, I could not have entertained any such suspicion. However, mentioning this suspicion to Mr. Warltire, he furnished me with some that he had kept for a specimen of the preparation, and which, he told me, he could warrant to be genuine. This being treated in the same manner as the former, only by a longer continuance of heat, I extracted much more air from it than from the other.

This is an example of careful chemical experimentation. More than one chemist has gone astray by the wrong identification of his materials. Red oxide prepared via mercury nitrate, that is, by dissolving mercury in nitric acid, evaporating, and heating the residue might be different from the red powder produced by heating mercury in air.

> This experiment might have satisfied any moderate skeptic: but, however, being at Paris in the October following, and knowing that there were several very eminent chymists in that place, I did not omit the opportunity, by means of my friend Mr. Magellan, to get an ounce of mercurius calcinatus prepared by Mr. Cadet, of the genuineness of which there could not possibly be any suspicion; and at the same time, 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; and who, I dare say, cannot fail to recollect the circumstance.

By an interesting coincidence Lavoisier obtained his sample of red oxide of mercury from the same Parisian apothecary. The two samples may well have come from the same bottle. Priestley's conversation with Lavoisier has been the subject of much debate among historians of science. Since at this time he was inclined to think the gas in question was laughing gas, he could not have told Lavoisier of the discovery of a new gas. Yet the fact that the gas was *not* carbon dioxide ("fixed air") and that it did support combustion was an important fact to one who, like Lavoisier, was intent on solving the problem of combustion and calcination. The French chemist Bayen in February of the same year had published the erroneous statement that the red powder on heating alone gave fixed air. Bayen's work may have provided the stimulus for Lavoisier's examination of the behavior of red oxide of mercury on heating, but it is far more likely that it was Priestley's remarks to him. These were made in October; according to Lavoisier's own statement, he started his experiments in November.

> At the same time, I had no suspicion that the air which I had got from the mercurius calcinatus was even wholesome, so far was I from

knowing what it was that I had really found; taking it for granted, that it was nothing more than such kind of air as I had brought nitrous air to be by the processes above mentioned; and in this air I have observed that a candle would burn sometimes quite naturally, and sometimes with a beautiful enlarged flame, and yet remain perfectly noxious.

At the same time that I had got the air above mentioned from mercurius calcinatus and the red precipitate, I had got the same kind from *red lead* or *minium* [a red oxide of lead]. In this process, that part of the minium on which the focus of the lens had fallen, turned yellow. One third of the air, in this experiment, was readily absorbed by water [due to some carbon dioxide from carbonate mixed with the oxide], but, in the remainder, a candle burned very strongly, and with a crackling noise.

That fixed air [carbon dioxide] is contained in red lead I had observed before; for I had expelled it by the heat of a candle, and had found it to be very pure. See Vol. I, p. 192. I imagine it requires more heat than I then used to expel any of the other kind of air. [This is correct; the carbonate decomposes easily. However, Priestley assumes that his red lead is a homogeneous substance. His sample clearly was not, but contained some lead carbonate. One of the advantages of mercury oxide for preparing oxygen is that unlike many other oxides it is not contaminated with carbonate by any method of preparation.]

This experiment with *red lead* confirmed me more in my suspicion, that the *mercurius calcinatus* must get the property of yielding this kind of air from the atmosphere, the process by which that preparation, and this of red lead is made, being similar. As I never make the least secret of any thing that I observe, I mentioned this experiment also, as well as those with the mercurius calcinatus, and the red precipitate, to all my philosophical acquaintance at Paris, and elsewhere; having no idea, at that time, to what these remarkable facts would lead.

Presently after my return from abroad, I went to work upon the *mercurius calcinatus*, which I had procured from Mr. Cadet; and, with a very moderate degree of heat, I got from about one fourth of an ounce of it, an ounce-measure of air [the relation of weight to volume of air is of no particular significance], which I observed to be not readily imbibed, either by the substance itself from which it had been expelled (for I suffered them to continue a long time together before I transferred the air to any other place) or by water, in which I suffered this air to stand a considerable time before I made any experiment upon it.

In this air, as I had expected, a candle burned with a vivid flame; but what I observed new at this time, (Nov. 19,) and which surprized me no less than the fact I had discovered before, was, that, whereas a few moments agitation in water will deprive the modified nitrous air of its property of admitting a candle to burn in it; yet, after more than ten times as much agitation as would be sufficient to produce this alteration in the nitrous air, no sensible change was produced in this. A candle still burned in it with a strong flame. . . [The "nitrous air" here mentioned is nitrous oxide or laughing gas which, as already stated, is soluble in water. Priestley's preparation of this gas from nitric oxide resulted in a mixture; agitation with water removed the nitrous oxide.]

But I was much more surprized, when, after two days, in which this air had continued in contact with water (by which it was diminished about one twentieth of its bulk) I agitated it violently in water about five minutes, and found that a candle still burned in it as well as in common air. The same degree of agitation would have made phlogisticated nitrous air [laughing gas] fit for respiration indeed, but it would certainly have extinguished a candle [because most of the laughing gas would have been dissolved in the water; the difference in solubility of laughing gas and oxygen in water gave Priestley his first hint].

These facts fully convinced me, that there must be a very material difference between the constitution of the air from mercurius calcinatus, and that of phlogisticated nitrous air [laughing gas], notwithstanding their resemblance in some particulars. But though I did not doubt that the air from *mercurius calcinatus* was fit for respiration, after being agitated in water, as every kind of air without exception, on which I had tried the experiment, had been, I still did not suspect that it was respirable in the first instance; so far was I from having any idea of this air being, what it really was, much superior, in this respect, to the air of the atmosphere.

In this ignorance of the real nature of this kind of air, I continued from this time (November) to the 1st of March following; having, in the mean time, been intent upon my experiments on the vitriolic acid air above recited, and the various modifications of air produced by spirit of nitre, an account of which will follow. [These experiments are not relevant.] But in the course of this month, I not only ascertained the nature of this kind of air, though very gradually, but was led by it to the complete discovery of the constitution of the air we breathe.

Till this 1st of March, 1775, I had so little suspicion of the air from mercurius calcinatus, &c. being wholesome, that I had not even thought of applying to it the test of nitrous air [on this point Lavoisier was quicker on the trigger, for he applied this test at once, though, as we have seen, with unfortunate results]; but thinking (as my reader must imagine I frequently must have done) on the candle burning in it after long agitation in water, it occurred to me at last to make the experiment; and putting one measure of nitrous air to two measures of this air [the standard procedure devised by Priestley himself], I found, not only that it was diminished, but that it was diminished quite as much as common air [Priestley misses the quantitative difference at this time; see the next paragraph], and that the redness of the mixture was likewise equal to that of a similar mixture of nitrous and common air.

After this I had no doubt but that the air from mercurius calcinatus was fit for respiration, and that it had all the other properties of genuine common air. But I did not take notice of what I might have observed, if I had not been so fully possessed by the notion of there being no air better than common air, that the redness was really deeper, and the diminution something greater than common air would have admitted. [See p. 75 for explanation.]

Moreover, this advance in the way of truth, in reality, threw me back into error, making me give up the hypothesis I had first formed, viz. that the mercurius calcinatus had extracted spirit of nitre from the air; for I now concluded, that all the constituent parts of the air were equally, and in their proper proportion, imbibed in the preparation of this substance, and also in the process of making red lead. [As far as errors are concerned there is little to choose; both hypotheses, in fact, were wrong!] For at the same time that I made the above-mentioned experiment on the air from mercurius calcinatus, I likewise observed that the air which I had extracted from red lead, after the fixed air was washed out of it, was of the same nature, being diminished by nitrous air like common air: but, at the same time, I was puzzled to find that air from the red precipitate was diminished in the same manner, though the process for making this substance is quite different from that of making the two others. But to this circumstance I happened not to give much attention.

I wish my reader be not quite tired with the frequent repetition of the word *surprize*, and others of similar import; but I must go on in that style a little longer. For the next day I was more surprized than ever I had been before, with finding that, after the above-mentioned mixture of nitrous air and the air from mercurius calcinatus, had stood all night, (in which time the whole diminution must have taken place; and, consequently, had it been common air, it must have been made perfectly noxious, and intirely unfit for respiration or inflammation [i.e., would have been nitrogen]) a candle burned in it, and even better than in common air.

I cannot, at this distance of time, recollect what it was that I had in view in making this experiment; but I know I had no expectation of the real issue of it. Having acquired a considerable degree of readiness in making experiments of this kind, a very slight and evanescent motive would be sufficient to induce me to do it. If, however, I had not happened, for some other purpose, to have had a lighted candle before me, I should probably never have made the trial; and the whole train of my future experiments relating to this kind of air might have been prevented. [Priestley's critics have made much fun of this honest statement. Few experimenters are as frank about their lucky strikes.]

Still, however, having no conception of the real cause of this phenomenon, I considered it as something very extraordinary; but as a property that was peculiar to air extracted from these substances, and *adventitious*; and I always spoke of the air to my acquaintance as being substantially the same thing with common air. I particularly remember my telling Dr. Price, that I was myself perfectly satisfied of its being com-

> mon air, as it appeared to be so by the test of nitrous air; though, for the satisfaction of others, I wanted a mouse to make the proof quite complete.

Up to this point, Priestley is just where Lavoisier was, and at about the same time. If he had published his results as they stood, he would have given the world conclusions almost identical with those that Lavoisier was then preparing to communicate to the Academy (Easter 1775).

> On the 8th of this month I procured a mouse, and put it into a glass vessel, containing two ounce-measures of the air from mercurius calcinatus. Had it been common air, a full-grown mouse, as this was, would have lived in it about a quarter of an hour. In this air, however, my mouse lived a full half hour; and though it was taken out seemingly dead, it appeared to have been only exceedingly chilled; for, upon being held to the fire, it presently revived, and appeared not to have received any harm from the experiment.
>
> By this I was confirmed in my conclusion, that the air extracted from mercurius calcinatus, &c. was, *at least*, *as good* as common air; but I did not certainly conclude that it was any *better*; because, though one mouse would live only a quarter of an hour in a given quantity of air, I knew it was not impossible but that another mouse might have lived in it half an hour; so little accuracy is there in this method of ascertaining the goodness of air: and indeed I have never had recourse to it for my own satisfaction, since the discovery of that most ready, accurate, and elegant test that nitrous air furnishes. [This is an example of sound and careful reasoning about the tactics of experimentation.] But in this case I had a view to publishing the most generally-satisfactory account of my experiments that the nature of the thing would admit of.
>
> This experiment with the mouse, when I had reflected upon it some time, gave me so much suspicion that the air into which I had put it was better than common air, that I was induced, the day after, to apply the test of nitrous air to a small part of that very quantity of air which the mouse had breathed so long; so that, had it been common air, I was satisfied it must have been very nearly, if not altogether, as noxious as possible, so as not to be affected by nitrous air; when, to my surprize again, I found that though it had been breathed so long, it was still better than common air. [Here we come near to the crucial point, the examination of a residual gas after a test. If common air was at hand, the exhaustion of the oxygen by the respiration of the mouse would have yielded an air whose goodness by the "nitrous air test" would have been low.] For after mixing it with nitrous air, in the usual proportion of two to one, it was diminished in the proportion of 4½ to 3½; that is, the nitrous air had made it two ninths less than before, and this in a very short space of time; whereas I had never found that, in the longest time, any common air was reduced more than one fifth of its bulk by

any proportion of nitrous air, nor more than one fourth by any phlogistic process whatever. [The difference between two ninths and one fifth (one forty-fifth) was beyond the limits of accuracy of Priestley's measurements. The greatest change in volume by absorption of all the oxygen by combustion (a phlogistic process) yields a diminution of one fifth only if the experiment is carefully performed.] Thinking of this extraordinary fact upon my pillow, the next morning I put another measure of nitrous air to the same mixture, and, to my utter astonishment, found that it was farther diminished to almost one half of its original quantity. I then put a third measure to it; but this did not diminish it any farther: but, however, left it one measure less than it was even after the mouse had been taken out of it. [Here is the crucial experiment.]

Being now fully satisfied that this air, even after the mouse had breathed it half an hour, was much better than common air; and having a quantity of it still left, sufficient for the experiment, viz. an ounce-measure and a half, I put the mouse into it; when I observed that it seemed to feel no shock upon being put into it, evident signs of which would have been visible, if the air had not been very wholesome; but that it remained perfectly at its ease another full half hour, when I took it out quite lively and vigorous. Measuring the air the next day, I found it to be reduced from 1½ to ⅔ of an ounce-measure. And after this, if I remember well (for in my *register* of the day I only find it noted, that it was *considerably diminished* by nitrous air) it was nearly as good as common air. It was evident, indeed, from the mouse having been taken out quite vigorous, that the air could not have been rendered very noxious.

For my farther satisfaction I procured another mouse, and putting it into less than two ounce-measures of air extracted from mercurius calcinatus and air from red precipitate [red oxide prepared via nitric acid] (which, having found them to be of the same quality, I had mixed together) it lived three quarters of an hour. But not having had the precaution to set the vessel in a warm place, I suspect that the mouse died of cold. However, as it had lived three times as long as it could probably have lived in the same quantity of common air, and I did not expect much accuracy from this kind of test, I did not think it necessary to make any more experiments with mice.

Being now fully satisfied of the superior goodness of this kind of air, I proceeded to measure that degree of purity, with as much accuracy as I could, by the test of nitrous air; and I began with putting one measure of nitrous air to two measures of this air, as if I had been examining common air; and now I observed that the diminution was evidently greater than common air would have suffered by the same treatment. A second measure of nitrous air reduced it to two thirds of its original quantity, and a third measure to one half. Suspecting that the diminution could not proceed much farther, I then added only half a measure of nitrous air, by which it was diminished still more; but not much, and

> another half measure made it more than half of its original quantity; so that, in this case, two measures of this air took more than two measures of nitrous air, and yet remained less than half of what it was. Five measures brought it pretty exactly to its original dimensions. [It is assumed that the experiments are carried out over water, of course.]
>
> At the same time, air from the *red precipitate* was diminished in the same proportion as that from *mercurius calcinatus*, five measures of nitrous air being received by two measures of this without any increase of dimensions. Now as common air takes about one half of its bulk of nitrous air, before it begins to receive any addition to its dimensions from more nitrous air, and this air took more than four half-measures before it ceased to be diminished by more nitrous air, and even five half-measures made no addition to its original dimensions, I conclude that it was between four and five times as good as common air. It will be seen that I have since procured air better than this, even between five and six times as good as the best common air that I have ever met with.

These two paragraphs record the convincing experiments which showed that the gas at hand was not common air but a new substance. Pure "nitrous air" and pure oxygen when brought together over water combine in about the ratio of 2 to 1; the exact relation depends on the way the experiment is performed and the temperature. Priestley's results are the equivalent of a reaction between about 4 half measures or 2 volumes of nitrous air and 1 volume of oxygen. This indicates that his gases were quite pure. The final residual gas was the excess of nitrous air which was used. If he had used smaller increments he might have had almost no residue after the proper amount of nitrous air had been added over water. The effective discovery of oxygen by Priestley may be considered to have taken place when these experiments were made and interpreted.

> Being now fully satisfied with respect to the *nature* of this new species of air, viz. that, being capable of taking more phlogiston from nitrous air, it therefore originally contains less of this principle [a consistent use of the phlogiston terminology]; my next inquiry was, by what means it comes to be so pure, or philosophically speaking, to be so much *dephlogisticated*; and since the red lead yields the same kind of air with mercurius calcinatus, though mixed with common air, and is a much cheaper material, I proceeded to examine all the preparations of lead, made by heat in the open air, to see what kind of air they would yield, beginning with the *grey calx*, and ending with *litharge.*
>
> The red lead which I used for this purpose yielded a considerable quantity of dephlogisticated air, and very little fixed air; but to what circumstance in the preparation of this lead, or in the keeping of it, this difference is owing, I cannot tell. I have frequently found a very remarkable difference between different specimens of red lead in this respect,

> as well as in the purity of the air which they contain. [Here Priestley practically admits that his samples of red lead were not homogeneous, but neither then nor subsequently does he draw the correct conclusion. This is another illustration of the difficulties of correct interpretation of chemical "facts."] This difference, however, may arise in a great measure, from the care that is taken to extract the fixed air from it. In this experiment two measures of nitrous air being put to one measure of this air, reduced it to one third of what it was at first, and nearly three times its bulk of nitrous air made very little addition to its original dimensions; so that this air was exceedingly pure, and better than any that I had procured before.

Then there follows in Priestley's volume an account of many experiments with the oxides of lead. Of these there are a number containing, as we now know, different ratios of oxygen and lead atoms. They have different colors which serve to distinguish them from each other. As prepared by the various methods known to Priestley, they often contained not only a mixture of lead oxides but also lead carbonate and lead nitrate (if nitric acid was used in their preparation). Probably most, if not all, the oxygen that Priestley obtained from them came from the decomposition of the lead nitrate, for nitrates on heating frequently yield oxygen, an oxide of nitrogen, and an oxide of the metal. We need not pursue Priestley's investigation of these complications further except to note that he was led farther and farther from the right road by these subsequent inquiries. He began to confuse nitrates and carbonates and oxides and consequently developed the idea that a calx had imbibed "spirit of nitre," that is, nitric acid, from the air. *Not having any adequate criteria of purity and not operating with constant regard for changes in weight and in volume, he proceeded from one faulty experiment to another.* We need not follow his further work on calces, for he never arrived at a final conclusion. But he always had at his disposal some alleged fact, such as the statement that "some metallic calces yield fixed air on heating," to challenge Lavoisier's conceptual scheme and support the phlogiston theory. For the student of the history of the development of science, the importance of this part of the story, thus briefly summarized, is as follows: homogeneity of materials is as essential to the chemist as the control of such variables as temperature and pressure is to the physicist; furthermore, criteria for determining homogeneity are often extremely difficult to establish, and it was only slowly that such criteria were evolved. Only after Lavoisier's "principle of the balance sheet" became accepted among chemists could such criteria be found for many materials. A *complete quantitative* study of the decomposition by heat of various samples of red lead, for example, with and without the addition of charcoal, will yield the necessary information to tell the investigator whether two samples are identical in composition and whether carbonate or nitrate is also present.

5. NOTES ON PRECEDING SECTIONS

A study of the accounts by Lavoisier and Priestley of their first experiments with oxygen illustrates a number of general principles in the development of science. *First,* a contrast of the method of publishing the results and the reference to other works with early seventeenth-century practice on the one hand and twentieth-century procedure on the other, illustrates the growth of science as an organized activity. *Second,* the difficulties of chemical experimentation are exposed very clearly; the difficulties are sometimes those of interpretation of what is observed, sometimes the failure to try what now seems an obvious further experiment, often the failure to have homogeneous materials at hand. *Third,* the role of the accidental discovery is almost glorified by Priestley. *Fourth,* repeated use of the *limited* working hypothesis is evident. For example, every time a chemical test is applied, Priestley or Lavoisier is essentially saying, "If I do so and so, such and such will happen." Priestley's original faulty identification of oxygen as laughing gas and his failure to interpret the "nitrous air test" correctly shows how many hidden assumptions are involved in the interpretation of experimental results. *Fifth,* Priestley's blind adherence to the phlogiston theory in spite of his own effective discovery of oxygen and in spite of its obvious faults (such as the failure to account for the increase in weight on calcination) shows the hold that one conceptual scheme may have on the mind of an investigator. *Sixth,* the transformation of a broad working hypothesis into a new conceptual scheme is made evident by following Lavoisier's work. His broad working hypothesis was by 1778 well on its way to becoming a new conceptual scheme of revolutionary importance.

Long before Priestley and Lavoisier, the increase in weight of metals on calcination was recorded and at least one investigator had come close to an effective discovery of oxygen. Priestley's emphasis on the accidental nature of scientific discoveries should not deceive the reader into believing that scientific progress hangs on such accidents, nor should Lavoisier's brilliance lead one to conclude that science is solely the work of a few great men. Among the complex of conditions which determined that in the late eighteenth rather than in the late seventeenth century the time was ripe for an elucidation of combustion we may list the following: (*a*) the improvement in communications among scientific men, which made science more and more of a cooperative effort; (*b*) the accumulation of quantitative studies in physics that made unsatisfactory the concept of phlogiston, which implied a substance with a negative weight; (*c*) the accumulation of a century's work on the materials, apparatus, and techniques of chemistry.

6. THE COMPOSITION OF THE ATMOSPHERE

The discovery of oxygen was the central event in the overthrow of the phlogiston theory. But it must be remembered that it was the discovery that *oxygen was a constituent of the atmosphere* which provided the key to the riddle of combustion. The method of preparing the red oxide of mercury was an essential link in Lavoisier's argument. He was at some pains in his Easter Memoir to show that the red powder was a true calx; it was formed when mercury was heated in air. In this process the gain in weight was due to combination of either air or a constituent of air with the mercury. By 1777 Lavoisier was clear that the principle that combined with metals during calcination was "an eminently respirable air" which constituted only a part of common air. In his textbook, *Traité Élémentaire de Chimie* (Elements of Chemistry), published in 1789, he describes an experiment which taken together with the preparation of oxygen from the red oxide demonstrates the composition of the atmosphere by analysis. The following extract is from an English translation of this book by Robert Kerr (London, ed. 5, 1802), modernized by the editor of this Case.

Lavoisier's *Elements of Chemistry,* Chapter III

> It appears that our atmosphere is composed of a mixture of substances capable of retaining the gaseous state at common temperatures, and under the usual degrees of pressure. These gases constitute a mass, in some measure homogeneous, extending from the surface of the earth to the greatest height hitherto attained, of which the density continually decreases in the inverse ratio of the superincumbent weight. . . .
>
> It is our business to endeavor to determine, by experiments, the nature of the elastic fluids which compose the lower stratum of air which we inhabit. Modern chemistry has made great advances in this research; and it will appear, by the following details, that the analysis of atmospherical air has been more rigorously determined than that of any other substance of the class.
>
> Chemistry affords two general methods of determining the constituent principles of bodies, the method of analysis, and that of synthesis. When, for instance, by combining water with alcohol, we form the species of liquor called, in commercial language, brandy, or spirit of wine, we certainly have a right to conclude, that brandy, or spirit of wine, is com-

posed of alcohol combined with water. We can procure the same result by the analytical method; and in general it ought to be considered as a principle in chemical science, never to rest satisfied without both these species of proofs. We have this advantage in the analysis of atmospherical air; being able both to decompound it, and to form it anew in the most satisfactory manner. I shall, however, at present confine myself to recount such experiments as are most conclusive upon this head; and I may consider most of these as my own, having either first invented them, or having repeated those of others, intended for analyzing atmospherical air, in perfectly new points of view.

I took a flask of about 36 cubical inches capacity, having a long neck bent as shown in the figure [Fig. 3] and placed in the furnace in such a manner that the extremity of its neck might be inserted under a bell-glass, placed in a trough of quicksilver. I introduced four ounces of pure mercury into the flask and by means of a siphon, exhausted the air in the receiver so as to raise the quicksilver, and I carefully marked the height at which it stood, by pasting on a slip of paper. Having accurately noted the height of the thermometer and barometer, I lighted a fire in the furnace which I kept up almost continually during twelve days, so as to keep the quicksilver always very near its boiling point. Nothing remarkable took place during the first day: The mercury, though not boiling, was continually evaporating, and covered the interior surface of the vessel with small drops, which gradually augmenting to a sufficient size, fell back into the mass at the bottom of the vessel. On the second day, small red particles began to appear on the surface of the mercury; these, during the four or five following days, gradually increased in size and number, after which they ceased to increase in either respect. At the end of twelve days, feeling that the calcination of the mercury did not at all increase, I extinguished the fire, and allowed the vessels to cool.

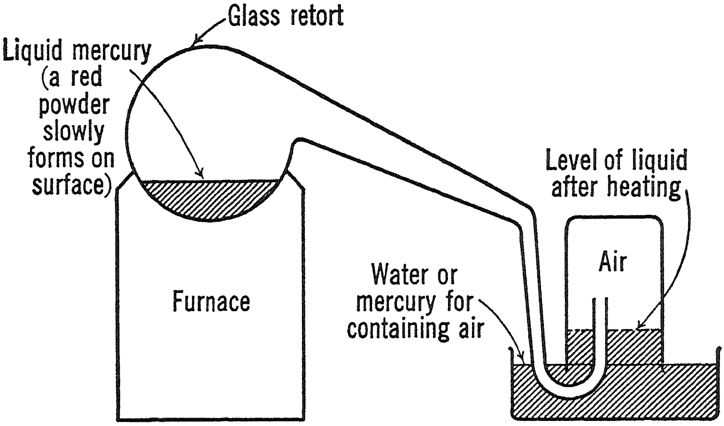

FIG. 3. Boiling mercury absorbs oxygen from the air.

> The bulk of air in the body and neck of the flask and in the bell-glass, reduced to a medium of 28 inches of the barometer and 54.5° of the thermometer, at the commencement of the experiment was about 50 cubical inches. At the end of the experiment the remaining air, reduced to the same medium pressure and temperature, was only between 42 and 43 cubical inches; consequently it had lost about 1/6 of its bulk. Afterwards, having collected all the red particles, formed during the experiment, from the running mercury in which they floated, I found these to amount to 45 grains.
>
> I was obliged to repeat this experiment several times, as it is difficult, in one experiment, both to preserve the whole air upon which we operate, and to collect the whole of the red particles, or calx of mercury, which is formed during the calcination. . . .
>
> The air which remained after the calcination of the mercury in this experiment, and which was reduced to 5/6 of its former bulk, was no longer fit either for respiration or for combustion: animals being introduced into it were suffocated in a few seconds, and when a taper was plunged into it, it was extinguished, as if it had been immersed in water.

This gas was commonly called "mephitic air." Lavoisier named it azote; in English the name nitrogen was introduced at this time.

Lavoisier then describes the famous experiment of the Easter Memoir but uses only the 45 grains of red oxide prepared in the preceding experiment. From this he obtains 7 to 8 cubic inches of gas and 41.5 grains of mercury. It is interesting to compare this result with those reported in 1775. The weight of the gas by difference is 3.5 grains, which gives a weight per cubic inch of about 0.5 or 0.44 grain (3.5 divided by 7 or 8). This figure is to be compared with the nearly 2/3 reported earlier (p. 82). At this point an analysis of the atmospheric air had been accomplished. By the aid of mercury, a furnace, and other equipment, 50 cubic inches of air had been separated into 42 to 43 cubic inches of air unfit for respiration or combustion (nitrogen) and 7 to 8 cubic inches of oxygen.

Lavoisier at this point draws the attention of the reader to the conclusion "that atmospheric air is composed of two elastic fluids (gases) of different and opposite qualities." He further adds, "As a proof of this important truth, if we recombine these two elastic fluids which we have separately obtained in the above experiment, viz. the 42 cubical inches of mephitic air [nitrogen] with the 8 cubical inches of highly respirable air, we reproduce an air precisely similar to that of the atmosphere, and possessing nearly the same power of supporting combustion and respiration, and of contributing to the calcination of metals." This is proof by synthesis as Lavoisier used the word in his book. Since air is a mixture and not a chemical compound, some chemists today would not speak of synthesizing air by mixing nitrogen and oxygen, for we generally reserve the word synthesis for the preparation of a chemical *compound*.

Lavoisier in the same chapter speaks of the "mutual adhesion of the two constituent parts of the atmosphere for each other." He thus seems to have something in the nature of a chemical compound in mind. And elsewhere he says that the method of analysis using boiling mercury is not accurate, for "the attraction of mercury to its respirable part of the air or rather to its base (i.e., the gas deprived of caloric fluid) is not sufficiently strong to overcome all the circumstances which oppose this union . . . In consequence, when the calcination ends, or is at least carried as far as is possible in a determinate quantity of atmospheric air, there still remains a portion of respirable air united to the mephitic air which the mercury cannot separate." These statements indicate that Lavoisier's picture of the atmosphere was somewhat different from what we have today. Yet we must recall that in the third paragraph of his Chapter III (see p. 105) he refers to mixing water and alcohol when speaking of a synthesis. The distinction between a mixture and a chemical compound was not yet quite clear. Only by the assiduous use of the "principle of the balance sheet" by hard-working investigators in the next two decades was it finally shown that elements unite in definite proportions to form a compound. A mixture, on the other hand, is characterized by the fact that a little more or less of one component will not greatly alter the properties, as in the case of mixtures of oxygen and nitrogen. Other criteria, of which Lavoisier was unaware, were later developed for distinguishing between mixtures and compounds.

Lavoisier was quite right about the difficulties of his method of analysis. However, the value he obtained of 16 parts by volume of oxygen and 84 of nitrogen is wrong. Dry air is composed of 21 percent of oxygen by volume, 78 percent of nitrogen, nearly 1 percent of the rare gases, and less than 0.05 percent of carbon dioxide. (The amount of moisture present depends on the temperature and the relative humidity. At room temperature the maximum amount of water by volume that can be present is a little over 2 percent. Therefore, the minimum value for the oxygen content in a sample of common air taken without drying, as Lavoisier did, would be about 20.5 percent by volume.) Accurate methods of determining the composition of air were developed shortly after Lavoisier's first experiments and were improved in the following century. In principle they are identical with his method but a chemical substance is employed (usually in solution) that will rapidly combine with the oxygen present at room temperature. The change in volume, as in Lavoisier's experiment, is a measure of the oxygen present.

7. THE FINAL COLLAPSE OF THE PHLOGISTON THEORY

Although Lavoisier's new conceptual scheme was clearly developed and well buttressed by experiments by 1778, he did not attack the prevailing doctrine directly until 1783. In that year the French chemist published his *Reflections on Phlogiston,* which marshaled the evidence for the new ideas and showed that the concept of phlogiston was not only unnecessary but self-contradictory. At just this time the composition of water was established by experiments of Henry Cavendish (1731–1810) which were immediately repeated by Lavoisier. Priestley had once again started a series of important experiments but had not in this case carried through to even a correct qualitative conclusion. Historians of chemistry still argue over who is entitled to the credit for the highly important discovery that water is composed of oxygen and hydrogen in the proportions by weight of approximately 8 to 1. Priestley, Cavendish, Lavoisier, and James Watt of steam-engine fame, are all contenders for the honor.

With the discovery that water was formed when hydrogen was burned in air, Lavoisier's scheme was complete. Water was clearly the oxide of hydrogen. Lavoisier at once proceeded to test an obvious deduction from this extension of his conceptual scheme, namely, that steam heated with a metal should yield a calx and hydrogen. It did. (The converse was likewise demonstrated at about the same time.)

$$\text{Hydrogen} + \text{Oxygen} \rightarrow \text{Water}$$
$$\text{Steam heated with metal} \rightarrow \underset{\text{(oxide)}}{\text{Calx}} + \text{Hydrogen}$$

These facts about the relation of water, hydrogen, oxygen, metals, and oxides would seem to leave no ground for the supporters of the phlogiston theory to stand on. But for a few years the new knowledge had the contrary effect. The believers in phlogiston were at last able to explain why a calx weighed more than the metal. This they did by a modification of the phlogiston theory which is illustrated by the following table:

Modified Phlogiston Theory
(about 1785)

Hydrogen = phlogiston (often carrying water);
Oxygen = dephlogisticated air;
Water = dephlogisticated air + phlogiston;
Nitrogen = completely phlogisticated air;
Common air = partially phlogisticated air carrying water;
Metal = calx + phlogiston − water;
Calx = the base of a pure earth + water;
Charcoal = phlogiston + ash + water.

If one studies this table it becomes clear that a fairly satisfactory account can be given of the simple chemical reactions. Thus in calcination the following process took place:

Metal heated in air → Phlogisticated air + Calx (water absorbed from the air).

The metal lost phlogiston to the air, which would mean a loss in weight, *but* the resulting "base of the pure earth" absorbed water from the air and the consequent gain in weight more than offset the loss in weight due to the loss of phlogiston!

The classic experiment with red oxide of mercury was formulated somewhat as follows: red oxide is a simple substance containing water; on heating, the phlogiston of the water combines with the simple substance (the pure earth) yielding the metal, while the rest of the water (dephlogisticated air) comes off and is collected. When mercury is heated in oxygen, the reverse process occurs; the phlogiston combines with the dephlogisticated air, forming water, which unites with the simple substance to form the calx.

Henry Cavendish, one of the great scientific figures of the period (though a most eccentric gentleman), was for a time an adherent of the modified phlogiston theory. In a famous article published in 1784 (in the *Philosophical Transactions of the Royal Society,* Vol. 74) he summarizes Lavoisier's new ideas quite fairly and then writes (pp. 151–152):

"It seems, therefore, from what has been said, as if the phenomena of nature might be explained very well on this [i.e., Lavoisier's] principle without the help of phlogiston; and indeed, *as adding dephlogisticated air to a body comes to the same thing as depriving it of its phlogiston and adding water to it,* and as there are, perhaps, no bodies entirely *destitute* of water, and *as I know no way by which phlogiston can be transferred from one body to another, without leav-*

ing it uncertain whether water is not at the same time transferred, it will be very difficult to determine by experiment which of these opinions is the truest; but as the commonly received principle of phlogiston explains all phenomena *at least as well* as Mr. Lavoisier's, I have adhered to that" [italics by the editor of this Case].

In retrospect, we can see that the adherents to the modified phlogiston theory were fighting a rear-guard action. Before Lavoisier's execution by the revolutionary tribunal in 1794, many chemists had come to accept his views. By the end of the century Priestley was almost alone in defending the doctrine of phlogiston. The story of the last days of the phlogiston theory is of interest, however, in illustrating a recurring pattern in the history of science. It is often possible by adding a number of new special auxiliary postulates to a conceptual scheme to save the theory — at least temporarily. Sometimes, so modified, the conceptual scheme has a long life and is very fruitful; sometimes, as in the case of the phlogiston theory after 1785, so many new assumptions have to be added year by year that the structure collapses. Most of the illustrations of this pattern, it should be pointed out, concern concepts and conceptual schemes of far less breadth than the phlogiston doctrine. They may be ideas that are useful in formulating merely some relatively narrow segment of physics, chemistry, astronomy, or experimental biology. What has just been said applies none the less.

The publication of Lavoisier's *Traité Élémentaire de Chimie,* with his exposition of the evidence in support of the new views and his new nomenclature, made the destruction of the phlogiston theory inevitable.

8. EIGHTEENTH-CENTURY REVOLUTIONS: CHEMICAL, INDUSTRIAL, POLITICAL, AND SOCIAL

The period 1770–1800 was a time of revolutions. The fact that the chemical revolution was contemporary with the American Revolution and preceded the French Revolution by a few years adds interest to the story. Priestley and Lavoisier were both involved in the French Revolution, the latter losing his life at the height of the terror, the former being driven from England because of his sympathies with the French revolutionists. During the same period the iron and steel industry was undergoing a major transformation that was the key to a series of events often called the industrial revolution of the late eighteenth century. The interconnections between these revolutions — scientific, industrial, political, and social — while many, are far from simple. A study of the lives of Priestley, Lavoisier, and Watt gives one a good picture of the status of scientific activity in this period. The important scientists are still for the most part amateurs, as they were in the days of Robert Boyle (mid-seventeenth century). Not until after the Napoleonic wars were the major contributions to the advance of chemistry (or physics) to come from the laboratories of the universities. The importance of the Royal Society and the French Academy as media of communication of scientific information is evident to all who have read the preceding section on the effective discovery of oxygen.

For those who are interested in the relation of science to technology, a study of the period in question will prove profitable. The advance in science and the progress in the practical arts are both rapid; yet the two borrow relatively little from each other in the way of concepts or new factual information. The cross connections are more evident than a century earlier and both activities have increased in importance since the seventeenth century. The application of science to industry, however, still lies in the future. One must not be misled by coincidences in time and place. For example, it is important to remember that the whole revolution of the making of iron and steel in the eighteenth century was based on purely empirical experimentation. The substitution of coke for charcoal, the invention of the crucible steel process, the improvements in iron-ore smelting that yielded pig iron, the development of the puddling process for making malleable iron (mild steel) were all accomplished without benefit of science. Not until after all these technical advances had been made did the impact of Lavoisier's new ideas enable people to recognize that the fundamental *chemical* distinction between iron and steel lay in the carbon content. The cut-and-try methods of practical men were for the time being far more effective in producing practical effects than the work of scientists.

The progress in the manufacture of all manner of products in this period made men alert to the possibilities of employing scientific discoveries. An improved process for manufacturing sulfuric acid yielded a material useful in the textile industry; James Watt recognized (1785) the possibilities of using chlorine gas (then recently discovered) in bleaching textiles. Pharmacists in this period were keenly interested in chemical developments and prepared chemicals for the use not only of doctors but of those interested in experimentation. The story of Cadet's red oxide of mercury (p. 96) is a case in point. One would like to know when yellow phosphorus first became available to a purchaser, for after its discovery in the seventeenth century its manufacture was more or less of a secret and each investigator had to prepare his own material. But Lavoisier in 1772 was able to purchase the theretofore rare substance. (The availability of new materials has often played an important role in the advance of chemistry; radioactive isotopes, which became readily available in the late 1940's, have stimulated a vast amount of work.) Scientists and inventors were in communication in this period and willingly learned from one another. However, the theoretical framework of physics and chemistry was so meager that the advances in science, except for mechanics, made little impact on the practical arts. Another fifty to seventy-five years of scientific work would be required before the applications of science were of prime importance.

The following chronological table may be of interest as a method of relating the various late-eighteenth-century revolutions to one another.

1760	George II dies; accession of George III.
1760	Smeaton improves blast furnaces for producing cast iron.
1760	Bridgewater canal completed; halves cost of coal in Manchester.
1760	Factory system and use of water-driven machinery firmly established in English silk industry.
1764	Hargreaves' spinning jenny introduced into English textile industry.
1765	Stamp Act.
1766	Cavendish (London) isolates and describes hydrogen gas (inflammable air).
1769	Watt's first steam engine. Arkwright greatly improves water-powered machines for textile industry.
1772	Lavoisier's experiments with sulfur and phosphorus. Priestley publishes his nitrous air test for the "goodness" of air.
1774	Death of Louis XV.
1775	Lavoisier's "Easter Memoir" on calcination. Priestley's effective discovery of oxygen.
1776	Declaration of American Independence.
1776	Publication of Adam Smith's *Wealth of Nations.*
1778	Lavoisier's revised memoir on calcination.
1779	Further improvements in textile machinery in England.
1781	Capitulation of British at Yorktown.
1782–1783	Composition of water established; spread of Lavoisier's ideas; last stand of phlogiston theory.
1783	Lavoisier and Laplace determine large number of specific heats.
1784	Cort's puddling process for making malleable iron from cast iron using coal as fuel.
1783	Peace between Great Britain and the United States.
1784	Watt's improved steam engine.

1786 Watt brings to England from France news of Berthollet's process for bleaching by the action of chlorine (then believed to be a compound); this knowledge utilized by English textile industry.

1787 Constitutional convention at Philadelphia.

1789 Publication of Lavoisier's *Traité Élémentaire de Chimie* setting forth results of the chemical revolution in clear and systematic form.

1789 Louis XVI summons the States General (January); third estate adopts title of National Assembly; fall of the Bastille (July).

1791 Birmingham mob burns Priestley's house.

1792 Attack on the Tuileries, Louis XVI a prisoner; French Republic proclaimed.

1793 Louis XVI executed; Committee of Public Safety in Paris; "Terror" in France begins.

1793 War between Great Britain and France, continues with only short truces until 1815.

1794 Execution of Lavoisier (May 8); fall and death of Robespierre (July); end of Terror.

1796 Production of cast iron in Great Britain 125,000 tons, double the figure of a decade earlier.

1798 Battle of the Nile. Nelson's victory assures supremacy of British fleet.

1798 Publication of *Essay on Population* by Malthus.

1799 Napoleon becomes First Consul.

SUGGESTED READING

1. Books Directly Related to the Effective Discovery of Oxygen

Torch and Crucible, The Life and Death of Antoine Lavoisier, by Sidney J. French (Princeton University Press, 1941). A popular account of Lavoisier's work; combination of a biography and exposition of the chemical revolution. Recommended for students of this Case.

Three Philosophers (Lavoisier, Priestley, and Cavendish), by W. R. Aykroyd (London, 1935; out of print).

Antoine Lavoisier, by Douglas McKie (Philadelphia, 1935; out of print).

The Eighteenth Century Revolution in Science: The First Phase, by A. U. Meldrum (Calcutta: Longmans, Green, 1930). This pamphlet, which is difficult to obtain, is an authoritative scholarly review of the work of Lavoisier and Priestley.

Elements of Chemistry, by Antoine Lavoisier (English translation by Robert Kerr, 1793; many editions). The first four or five chapters can be read with profit by students of this Case.

Historical Introduction to Chemistry, by T. M. Lowry (London: Macmillan, 1936). A good guide to those interested in an elementary presentation of any phase of the history of chemistry since 1700.

Lectures on Combustion, by Joseph Priestley and John MacLean, edited by William Foster (Princeton University Press, 1929). Throws interesting light on Priestley's last stand in defense of the phlogiston theory.

2. The Eighteenth-Century Background

Among the vast number of books dealing with the political and social history of the last half of the eighteenth century, the following may have special relevance for the student of this Case.

Life of Joseph Priestley, by Anne Holt (Oxford, 1931).

The Eighteenth Century Background, by Basil Willey (London, 1940). Chapter X on Priestley is recommended.

Science and Social Welfare in the Age of Newton, by G. N. Clark (Oxford: Clarendon Press, 1937). Although this little volume deals with an earlier period, it is recommended for students of this Case as providing a picture of the economic and cultural factors involved in the interaction of science and technology.

Iron and Steel in the Industrial Revolution, by T. S. Ashton (1924). Too detailed and technical for the average student, but contains a great deal of interesting material.

CASE 3

The Early Development of the Concepts of Temperature and Heat

The Rise and Decline of the Caloric Theory

PREPARED BY

DUANE ROLLER

CASE 3

The Early Development of the Concepts of Temperature and Heat

THE RISE AND DECLINE OF THE CALORIC THEORY

The development of thermometry, of methods for measuring heat, and of concepts about the nature of heat in the seventeenth and eighteenth centuries can be understood with little or no previous knowledge about science. The reason is that the growth of thermal science constitutes an epoch in scientific history that occurred almost independently of basic developments in other parts of experimental science. Nevertheless, because these early developments in thermal science were far from being superficial in character, one can gain from the study of them a rather deep insight into the ways in which a fundamental, though limited, body of scientific knowledge came into being.

As the present Case History will show, quantitative studies of phenomena connected with heat became possible only after the invention of the thermometer. Section 1 is a brief outline of important steps in the early development of this instrument, which will give the reader an appreciation of the difficulties that are likely to be encountered in the development of a satisfactory measuring instrument, and will also enable him to formulate for himself some general principles applicable to many instruments of this class.

Section 2, which is based on excerpts from the published lectures of Joseph Black, shows how the thermometer made possible new concepts of fundamental importance, and how it led in turn to the invention of a new type of thermal instrument — the calorimeter. Here the reader may be able to decide whether Sir Humphry Davy (Sec. 5) was correct in an assertion which he once made that "nothing tends so much to the advancement of knowledge as the application of a new instrument."

Speculations current during the sixteenth and seventeenth centuries on the nature of heat had little effect on thermometry and the measurement of heat. However, Black described various views (Sec. 2), and the last three sections of this Case History describe how the most useful of these eighteenth-century conceptual schemes — the caloric theory —

was subjected to experimental tests by Count Rumford and by Davy, and make clear the role of their experiments in weakening the foundations of that theory.

The final downfall of the caloric theory and the subsequent correlation of the sciences of heat and mechanics did not occur until near the middle of the nineteenth century and is not treated in detail here. But the reader will be able to see how, from thermometry through heat measurements to early speculations about what heat is, the thread of scientific history here followed finally led to the development of the modern theory of heat as a mode of motion. It also led to the enunciation of one of the great generalizations of physical science — the principle of conservation of energy.

1. EVOLUTION OF THE THERMOMETER

The earliest forms of the thermometer appear to have been suggested by a sixteenth-century revival of interest in various mechanical devices and toys invented during the Hellenic period, particularly by Philo of Byzantium and Hero of Alexandria. Certain of these ancient devices depended for their operation upon the expansion of air when heated. But the idea of adapting them to the purpose of indicating "degrees of hotness," or temperature, seemingly occurred to no one in ancient or medieval times.

Galileo's barothermoscope, ca. 1592–1603. Although it is not known with certainty who first conceived the idea of trying to measure temperatures, the adaptation of the ancient devices to this purpose is generally attributed to Galileo Galilei. He seems not to have appreciated the invention, for his own writings, so far as they have survived, contain only one incidental reference to the principle of the instrument. However, records left by several of his friends and students indicate that he devised and used it shortly after 1592.

The instrument was merely a glass bulb containing air and having a long stem which extended downward into a vessel of water. As the temperature changed, the air in the bulb expanded or contracted and the water in the stem fell or rose. Thus air was the *temperature-indicating substance*, and its expansion served as the *temperature-indicating property*. Galileo appears also to have added to the device a scale, which probably consisted of a long narrow strip of paper attached to the stem and marked off in degrees "at pleasure." One such scale was divided into eight large spaces, and each of these into 60 smaller ones, a scheme possibly suggested by the graduation of astronomical instruments into degrees and minutes.

Since there was no thought of basing these scales on standard, reproducible temperatures, the temperature indications were at best only semiquantitative. Thus Galileo's instrument is usually referred to as a *thermoscope*, a term that first came into use in 1617, rather than as a *thermometer*, a term that was not coined until 1624. More accurately speaking, his instrument was a "barothermoscope," for it indicated changes in atmospheric pressure as well as temperature; but this fact apparently was not clearly recognized until some time after the invention of the barometer (1643).

One of Galileo's colleagues, Sanctorius, who was professor of medicine at the University of Padua, applied Galileo's barothermoscope to the detection of fevers and other physiologic studies. Recognizing that fiducial points are needed for a satisfactory measuring device, Sanctorius made marks on his scale to indicate the two readings obtained when the bulb of the instrument was exposed, first to snow, and then to the flame of a candle.

First liquid-expansion thermoscopes, 1632–1641. The expansion of a liquid was probably first employed for estimating temperatures by Jean Rey, a French physician, in 1631. His instrument, which he used for taking the temperature of patients, was a glass bulb and stem similar to Galileo's, except that it was inverted and partly filled with water. The upper end of the stem was left open, so the readings were influenced by evaporation of the water, although not to an appreciable extent by changes in atmospheric pressure.

The first thermoscope with the end of the stem sealed, and also utilizing the expansion of alcohol instead of water (Plate I, *1*, *2*), was developed in 1641 by the Grand Duke Ferdinand II of Tuscany, who was soon to become one of the founders of the Florentine Accademia del Cimento (Academy of Experiment). Ferdinand used this instrument for meteorologic purposes and in experiments on the artificial hatching of eggs. He also invented an entirely new type of thermoscope (Plate I, 5), consisting of a number of blown glass bubbles suspended in alcohol, their weights being adjusted so that first one and then another would sink as the temperature rose and the density of the alcohol decreased.

The Accademia del Cimento, during its brief existence from 1657 to 1667, manufactured many temperature-measuring devices, mainly of the alcohol-in-glass expansion type. They were marvels of glass blowing (Plate I, 4) and were long used for meteorologic and other purposes in different parts of the world. The divisions on the scale were marked by minute glass beads of different colors attached to the stem, and the scale on the stem was constructed by dividing into a number of equal parts the space between the two marks indicating "the most severe winter cold" and "the greatest summer heat." Since these two extreme

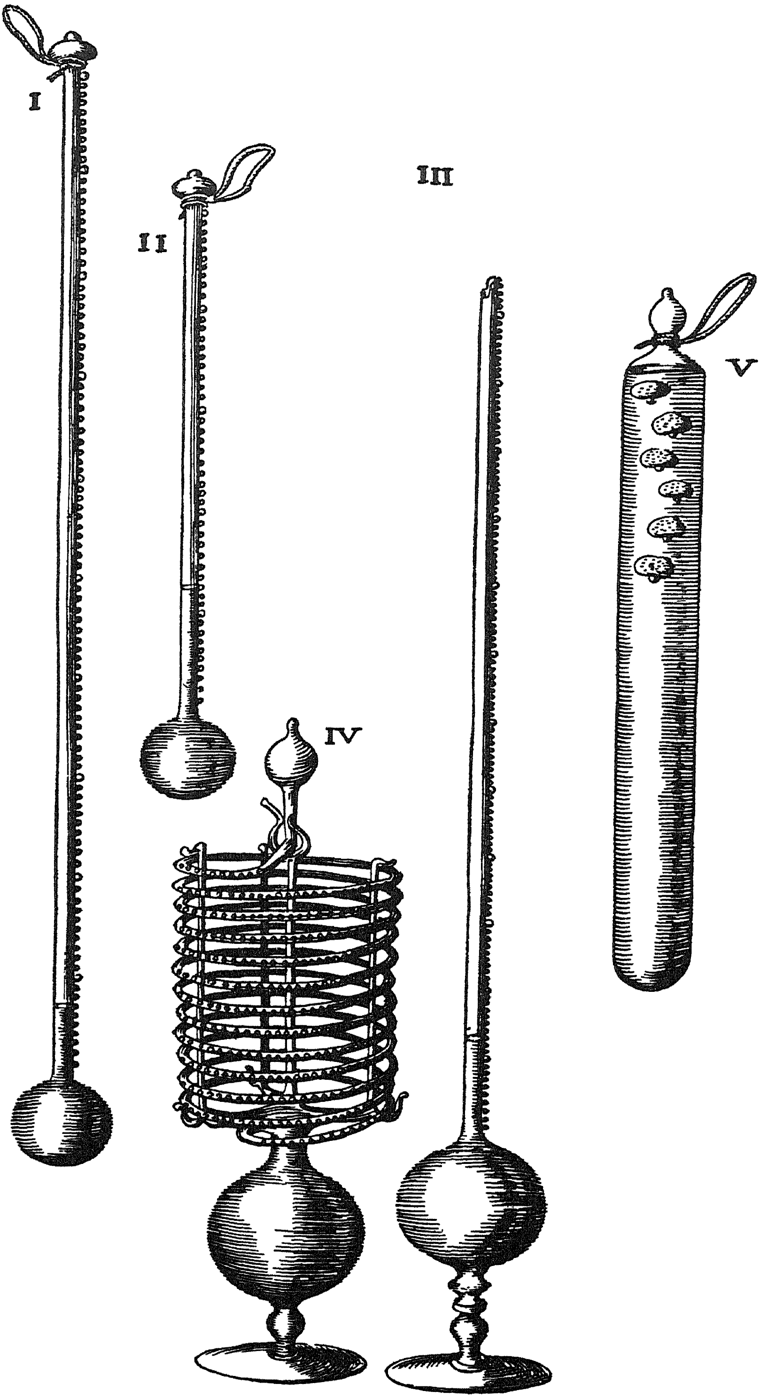

Plate I. Thermometers of the Accademia del Cimento.

temperatures could not be determined with any precision, no standard thermometric system was established by their use. However, this Florentine scheme for constructing a scale eventually made possible a universally comparable measure of temperature. The main problem, it turned out, was to find temperatures for determining the fixed marks that could be reproduced experimentally with precision.

The one-fixed-point method of calibration, 1665. Another method of calibration affording a universally comparable measure of temperature was independently proposed in 1665 by Robert Boyle, Robert Hooke, and Christiaan Huygens. This is to mark on the thermometer stem a *single* fixed point, which is to be determined experimentally and is to serve as a starting point; and then to place "degree" marks on the stem, each of them corresponding to an expansion or contraction of a certain fraction — say 1/1000, or 1/10,000 — of the volume of the thermometric substance when at the temperature corresponding to the fixed point. For the temperature to be used in establishing the single fixed point, Boyle suggested the freezing temperature of oil of aniseed; Hooke, the freezing temperature of water; and Huygens, either the freezing or the boiling temperature of water.

The two-fixed-point method of calibration, 1669–1694. The method used on Florentine thermometers, in which the space between *two* fixed marks is divided into a number of equal parts, or "degrees," is called the *two-fixed-point method.* In 1669, Honoré Fabri, a Jesuit who had been a corresponding member of the Accademia del Cimento, adopted the temperature of melting snow to determine the lower fixed point; but for the upper fixed point he retained the indefinite "greatest summer heat."

Dalencé, in 1688, suggested that the temperature for the upper fixed point be changed to the melting temperature of butter, thus affording greater precision and more nearly comparable readings. He assigned the respective values $-10°$ and $+10°$ to his two fixed points, and divided the interval between them into 20 equal parts.

In 1694, the freezing and the boiling temperatures of water were proposed as the two fixed-point temperatures by Carlo Renaldini, a professor at Padua and a former member of the Accademia del Cimento. He divided the interval between these fixed points into 12 equal parts, possibly because the number 12 is easily subdivided or because there are 12 inches to the foot.

Eventually it became clear that both the melting temperature of ice and the boiling temperature of water are influenced by changes in the atmospheric pressure. So it was agreed that these two temperatures when the pressure is one standard atmosphere shall be used to establish the fixed points; these points are referred to as the *ice point* and the *steam point.*

First air thermometer, 1699–1702. The first air thermometer that was not at the same time a barometer was developed by Guillaume Amontons, a French physicist. In one form of this instrument, the pressure of the air is kept constant, and temperatures are measured by observing changes in the volume of the air. In another form — the one first developed by Amontons — the volume of the air is kept constant, and temperatures are measured by observing changes in the pressure of this air, instead of in its volume. In other words, air is here the thermometric substance, and either its volume or its pressure is the thermometric property.

Origin of the Fahrenheit system, 1702–1717. Ole Roemer (Rømer), the Danish astronomer, proposed in 1702 that the temperature of a certain mixture of ice and salt be made the lower fixed point and assigned the value 0°, and that the steam point be made the upper fixed point and assigned the value 60°. Thus this was a sexagesimal system. G. D. Fahrenheit, who was a celebrated maker of meteorologic instruments, visited Roemer in Copenhagen in 1708 and subsequently undertook the calibration of thermometers along similar lines. In 1717 he proposed a scheme essentially like the one that is today called the "Fahrenheit system," in which the values 32°F and 212°F are assigned to the ice and steam points, respectively.

Fahrenheit was the first to use a cylindrical rather than a spherical bulb in thermometers, and contributed in other important ways to the art of thermometry by his improved methods of making reliable alcohol-in-glass and mercury-in-glass thermometers. Mercury had previously been used in barometers and, to some extent, as a thermometric substance, but no one before Fahrenheit seems to have thoroughly appreciated its advantages over other liquids for this purpose.

Origin of the centigrade system, 1710–1743. What today is known as the "centigrade system," in which the values 0°C and 100°C are assigned to the ice and steam points, is believed to have been first suggested as early as 1710 by Elvius, a Swede. It was later proposed, seemingly independently, by the eminent Swedish botanist, Linnaeus, in 1740, and by Christian of Lyons in 1743. This system is often credited to Anders Celsius, a Swedish astronomer, possibly because of a casual association suggested by the "C" for centigrade, coupled with the fact that Celsius used a centesimal system as early as 1742. However, Celsius' system was inverted with respect to the centigrade in that he assigned the values 100° and 0° to the ice and steam points.

Some recent developments. It eventually became clear that the properties of different substances are not generally the same functions of temperature and, therefore, that thermometers constructed from different substances do not agree exactly with one another at temperatures other than the fixed points. So it was desirable that a particular thermometric substance, together with some particular property of this substance, be chosen to serve as the ultimate standard in practical thermometry. In the nineteenth century, H. V. Regnault showed that the constant-volume hydrogen thermometer was highly suitable for this purpose; it was adopted as the practical standard and was so used until 1927.

Because of experimental difficulties in the use of any gas thermometer, the Seventh General Conference on Weights and Measures, with a representation of 31 nations, adopted in 1927 a standard working scale designated as the *international temperature scale.* This scale is defined by a series of fixed points, which have been determined by gas-thermometer measurements, and by the specification of suitable thermometers for interpolating between the fixed points and extrapolating to higher temperatures. For example, the platinum electrical-resistance thermometer is used in the range -190° to 660°C, and for higher temperatures thermoelectric and optical thermometers are employed.

Among liquids, mercury is found to agree fairly closely with the gas scale, and mercury-in-glass thermometers are still used in cases where facility of observation is more important than the highest attainable degree of precision.

2. JOSEPH BLACK'S DISCOVERIES OF SPECIFIC AND LATENT HEATS

The invention of the thermometer provided the means for developing not only thermometric measurements but an entirely new science — that of *heat measurements*; and the pioneer in the latter development was Joseph Black (1728–1799). Black, as a young man, studied medicine, first at the University of Glasgow, and then at the University of Edinburgh, where he received the M.D. degree in 1754. It was during these years that he started his researches in chemistry and probably also began to form his new ideas about heat.

In 1756 Black returned to Glasgow as a professor. It was here, during the three years between 1759 and 1762, that he made his main discoveries in heat. In 1766 he returned to Edinburgh, where he occupied the chair of medicine and chemistry until his death. During all these years he also engaged extensively in the private practice of medicine.

Until Black made his discoveries, there was no clear distinction in people's minds between the concepts of "quantity of heat" and "degree of hotness," or "temperature." The qualitative idea of "heat" as a "something" concerned with thermal phenomena had long existed, of course. The simple fact that an object close to a fire warms up, which surely was known from the time when man discovered fire, must have suggested that something passes from the fire to the object. But to these early people, this something that passes might well have been thought to be temperature, or degree of hotness, itself; or, again, it might be a separate something, called "heat," this heat and the resulting increase in hotness of the object seeming to play the respective roles of cause and effect.

To have clarified these ideas would have been almost impossible as long as people had to depend mainly on their thermal sense organs for a knowledge of thermal phenomena. The thermal sense organs, as is now known, generally afford us judgments that depend not on temperature alone but on a blend of several thermal properties of a body. For instance, if we touch metal and wood in cold weather, the metal will "feel" colder than the wood, even though a thermometer applied to these objects will show them to be at the same temperature.

The clarification started only after the invention of the thermometer, near the beginning of the seventeenth century. Thus Francis Bacon (1620) and, after the middle of the seventeenth century, the members of the Florentine Academy, showed evidence of distinguishing between temperature and heat. But it was Black who, in the middle of the eighteenth century, made the distinction sharp and who, moreover, was the first to conceive clearly of heat as a *measurable* physical quantity, distinct from, although related to, the quantity indicated by a thermometer and called *temperature.*

Black never published his great discoveries on heat, although he taught them in his academic lectures. These lectures, which also incorporated his chemical researches, were published in 1803, after his death, being written out by John Robison from Black's notes and those taken by some of his students. "Black's heavy duties, ill health, lack of initiative, and almost morbid horror of generalization prevented him from going further than forming a plan" for a book.

Robison dedicated the *Lectures* to James Watt (1736–1819) in a letter, printed at the beginning of volume I, of which the following is a part:

> Dear Sir:
>
> By placing your name in the front of this edition of the Lectures of our excellent Master, I think that I pay my best respects to his memory, and also do a service to the Public. By thus turning the Reader's attention to Dr. Black's most illustrious Pupil, I remind him of the important services derived from his discoveries: for surely nothing in modern times

> has made such an addition to the power of man as you have done by your improvements on the steam engine, which you profess to owe to the instructions and information you received from Dr. Black. . . .
>
> I show the Reader, in your example, that there is no preëminence in scientific attainment which he may not hope to reach by rigidly adhering to the sober plan of experimental inquiry, so constantly inculcated by Dr. Black; and turning a deaf ear to all the fascinating promises of splendid theories. The spark, which I thus throw out, may chance to light among suitable materials — some *felices animæ, quibus hæc cognoscere curæ est* — minds perhaps unconscious of their own powers. Even yours might have lain dormant, had not Dr. Black discovered its latent fire. . . .

Early in his lectures, Black mentions the various theories that had been devised to explain the nature of heat — what heat "really is." But he warns his listeners that one cannot properly understand these theories, or how they are applied, until one has become acquainted with the effects of heat and with some discoveries that preceded the theories and gave occasion to them:

> Our first business must, therefore, necessarily be to study the facts belonging to our subject, and to attend to the manner in which heat enters various bodies, or is communicated from one to another, together with the consequences of its entrance, that is, the effects that it produces on bodies. These particulars, when considered with attention, will lead us to some more adequate knowledge and information upon the subject — which again will enable you to examine and understand the attempts that have been made to explain it, and put you in the way to form a judgment of their validity.

The part of the *Lectures* devoted to the subject of heat covers some 225 printed pages. Thus the excerpts that appear in the present document represent only a very small fraction of the whole. However, they have been selected so as to bring out Black's main discoveries.

[Excerpts from Volume I of]

LECTURES ON THE ELEMENTS OF CHEMISTRY

Delivered in the University of Edinburgh

by the late

Joseph Black, M.D.

Professor of Chemistry in that University
Physician to His Majesty for Scotland; Member
of the Royal Society of Edinburgh, of the
Royal Academy of Sciences at Paris,

and the Imperial Academy of
Sciences at St. Petersburgh

Now published from his Manuscripts
by
John Robison, LL.D.
Professor of Natural Philosophy in the University
of Edinburgh
1803

Of the Distribution of Heat

An improvement in our knowledge of heat, which has been attained by the use of thermometers, is the more distinct notion we have now than formerly of the *distribution* of heat among different bodies. Even without the help of thermometers, we can perceive a tendency of heat to diffuse itself from any hotter body to the cooler ones around it, until the heat is distributed among them in such a manner that none of them is disposed to take any more from the rest. The heat is thus brought into a state of equilibrium.

This equilibrium is somewhat curious. We find that, when all mutual action is ended, a thermometer applied to any one of the bodies undergoes the same degree of expansion. Therefore the temperature of them all is the same. No previous acquaintance with the peculiar relation of each body to heat could have assured us of this, and we owe the discovery entirely to the thermometer. We must therefore adopt, as one of the most general laws of heat, the principle that *all bodies communicating freely with one another, and exposed to no inequality of external action, acquire the same temperature, as indicated by a thermometer.* All acquire the temperature of the surrounding medium.

By the use of thermometers we have learned that, if we take a thousand, or more, different kinds of matter — such as metals, stones, salts, woods, cork, feathers, wool, water and a variety of other fluids — although they be all at first of different temperatures, and if we put them together in a room without a fire, and into which the sun does not shine, the heat will be communicated from the hotter of these bodies to the colder, during some hours perhaps, or the course of a day, at the end of which time, if we apply a thermometer to them all in succession, it will give precisely the same reading. The heat, therefore, distributes itself upon this occasion until none of these bodies has a greater demand or attraction for heat than every other of them has; in consequence, when we apply a thermometer to them all in succession, after the first to which it is applied has reduced the instrument to its own temperature, none of the rest is disposed to increase or diminish the quantity of heat which that first one left in it. This is what has been commonly called an "equal heat," or "the

> equality of heat among different bodies"; I call it the *equilibrium of heat.*
>
> The nature of this equilibrium was not well understood until I pointed out a method of investigating it. Dr. Boerhaave imagined that when it obtains, there is an equal quantity of heat in every equal volume of space, however filled up with different bodies; and Professor Musschenbroeck, in his *Physica,* expressed his opinion to the same purpose: "Est enim ignis æqualiter per omnia, non admodum magna, distributus, ita ut in pede cubico auri et aëris et plumarum, par ignis sit quantitas." ["For the heat is distributed through all (the bodies), not in proportion to their (weight), so that in a cubic foot of gold and of air and of feathers, there will be an equal quantity of heat.] The reason they give for this opinion is that, to whichever of those bodies the thermometer be applied, it gives the same reading.
>
> But this is taking a very hasty view of the subject. It is confounding the quantity of heat in different bodies with its intensity [temperature], though it is plain that these are two different things, and should always be distinguished, when we are thinking of the distribution of heat. . . .

Hermann Boerhaave (1668–1738) was a great teacher of medicine at the University of Leiden who performed a useful service by collecting and classifying the scientific knowledge of his period and publishing it in textbooks on medicine (1708) and on chemistry (1732). Pieter van Musschenbroeck (1692–1761) went to Leiden in 1740 as professor of philosophy; he also wrote extensively on physical science.

As Black says, Boerhaave and Musschenbroeck thought that, if a number of different objects were placed in, say, a room and allowed to remain there until all had acquired the same temperature, as indicated by a thermometer, then this meant that heat was also distributed uniformly throughout the room and its contents—that every cubic inch of space in the room, whether it be occupied by wood, metal, air, or anything else, contained the same quantity of heat. On the contrary, asserts Black, when the various objects have come to the same temperature, there exists, not an equal distribution of heat throughout the room, but what he calls an "equilibrium of heat," meaning that there is no longer any flow of heat among the objects. Notice that *temperatures* are *observed* with a thermometer, whereas Black's notion that a something called *heat* passes from bodies of higher temperature to those of lower temperature is of the character of a hypothesis.

In the section that follows, on "Capacities for Heat," Black investigates the question of the quantities of heat needed to increase the temperatures of different bodies by the same amount. He says that it was formerly supposed that these required quantities of heat were directly proportional to the "quantities of matter" in the bodies; or, since the "quantities of matter" in different bodies can be compared by comparing the weights of the bodies when they are in the same locality, that the required quantities of heat were supposed to be directly proportional to the weights of the bodies. If this hypothesis were correct, the quantity of heat needed to warm 1 lb of mercury through, say, one Fahrenheit degree would be the same as that needed for 1 lb of water; and to produce the same temperature change in 2 lb of mercury would require twice as much heat as for 1 lb of water, or of mercury, or of any other substance.

Black subsequently shows that this hypothesis is not generally valid. The argument that he uses will perhaps be made easier to follow if we first restate the hypothesis in algebraic language, which he did not use. Let the symbol H_1 signify the quantity of heat that must be added to a body of weight w_1 in order to increase its temperature by an amount Δt. (The Greek capital letter delta is used to express a difference between two values of the quantity symbolized by the letter that follows it — in this case t for temperature; for instance, if water is warmed from its freezing temperature, 32°F, to its boiling temperature, 212°F, then Δt is equal to 212°F − 32°F, or 180°F.) Similarly, let H_2 signify the quantity of heat needed to produce the *same* temperature change Δt in another body of weight w_2. By using these symbols, the foregoing hypothesis may now be expressed in the form

$$\frac{H_1}{H_2} = \frac{w_1}{w_2}. \qquad \text{(For the same temperature change } \Delta t\text{)} \qquad (1)$$

We shall see (p. 23) that Black finds it useful to restate this faulty hypothesis in another, alternative way, namely, that the quantities of heat needed to produce the same temperature change in bodies of the same *volume* are proportional to the densities of the bodies. To convert our Eq. (1) to this alternative form, recall, first, that the weight-density D of any object is, by definition, the weight w of the object divided by its volume V; that is, $D = w/V$. Now, multiply both members of this defining equation by V, thus changing it to the form $w = DV$. Finally, replace w_1 in Eq. (1) by D_1V, and w_2 by D_2V, thus giving

$$\frac{H_1}{H_2} = \frac{D_1V}{D_2V} = \frac{D_1}{D_2}. \qquad \text{(For the same temperature change } \Delta t \text{ in bodies of the same volume)} \qquad (2)$$

For instance, the density of mercury is about 14 times that of water. Therefore, according to Eq. (2), the quantity of heat needed to warm mercury through, say, one Fahrenheit degree should be 14 times that needed for equal warming of the same volume of water. As we shall see, Black finds that this prediction is far from being in accord with experiment.

In our subsequent notes, we shall find it convenient to refer to the hypothesis expressed by either Eq. (1) or Eq. (2) as the "weight hypothesis."

Capacities for Heat

It was formerly a common supposition that the quantities of heat required to increase the temperatures of different bodies by the same number of degrees were directly proportional to the quantities of matter in them [and thus to their weights]; and therefore, when the bodies were of equal volumes, that the quantities of heat were proportional to their densities [and thus to their weights per unit volume]. But very soon after I began to think on this subject (*anno* 1760), I perceived that this opinion was a mistake, and that the quantities of heat which different kinds of matter must receive to raise their temperatures by an equal number of degrees are not in proportion to the quantity of matter in each, but in proportions widely different from this, and for which no general principle or reason could yet be assigned.

This opinion was first suggested to me by an experiment described by Dr. Boerhaave in his *Elementa Chemiæ* [1732]. After relating an experiment on the mixing of hot and cold water which Fahrenheit made at his desire, Boerhaave also tells us that Fahrenheit agitated together quicksilver [mercury] and water of initially different temperatures. From the Doctor's account, it is quite plain that the quicksilver, though it has more than 13 times the density of water, had less effect in heating or cooling the water with which it was mixed than would have been produced by an equal volume of water. He says expressly that the quicksilver, whether it was applied hot to cold water, or cold to hot water, never produced more effect in heating or cooling an equal volume of the water than would have been produced by water of the same initial temperature as the quicksilver, and only two-thirds of its volume. He adds that is was necessary to mix three volumes of quicksilver with two of water in order to produce the same middle temperature that is produced by mixing equal volumes of hot and cold water.

To make this plainer by an example in numbers, let us suppose the water to be at 100°F and that an equal volume of warm quicksilver at 150°F is suddenly mixed and agitated with it. We know that the temperature midway between 100° and 150°F is 125°F, and we know that this middle temperature would be produced by mixing cold water at 100°F with an equal volume of warm water at 150°F, the temperature of the warm water being lowered by 25 degrees while that of the cold is raised just as much. But when warm quicksilver is used in place of warm water, the temperature of the mixture turns out to be only 120°F, instead of 125°F. The quicksilver, therefore, has cooled through 30 degrees, while the water has become warmer by 20 degrees only; and yet the quantity of heat which the water has gained is the very same as that which the quicksilver has lost. This shows that the same quantity of heat has more

> effect in warming quicksilver than in warming an equal volume of water, and therefore that a smaller *quantity* of it is sufficient for increasing the temperature of quicksilver by the same number of degrees.
>
> This is true, whatever way we vary the experiment. Thus, if the water is the warmer mass, and the equal volume of quicksilver the cooler one, by the aforementioned difference, the temperence of the mixture will be 130°F; the water, in this case, cools through 20 degrees, while the heat it has given to the quicksilver makes this warmer by 30 degrees. And lastly, if we take 3 volumes of quicksilver to 2 of water, it does not matter which of them is the hotter; the temperature of the mixture always will be the middle temperature between the two. Here it is manifest that the quantity of heat which makes 2 volumes of water warmer by, say, 25 degrees is sufficient to make 3 volumes of quicksilver warmer by the same number of degrees. Quicksilver, therefore, has less *capacity for heat* (if I may be allowed to use this expression) than has water; a smaller quantity of heat is needed to raise its temperature by the same number of degrees.

G. D. Fahrenheit (1668–1736) seemingly never published an account of the mixing experiments which Boerhaave attributed to him. Boerhaave, in his *Elementa Chemiæ*, said that Fahrenheit first mixed *equal volumes* of cold and hot water, and found the temperature of the resulting mixture to be midway between the two initial temperatures. For instance, when the initial temperatures were 40° and 80°F, the temperature of the mixture turned out to 60°F.

Let us see what light is thrown on this experimental result of Fahrenheit's by the weight hypothesis. Fahrenheit found that when equal volumes of the *same* liquid are mixed, the rise in temperature Δt of the cold liquid is numerically equal to the drop in temperature Δt of the warm liquid. Moreover, since the two liquids are the same, their densities D_1 and D_2 are the same. So our Eq. (2) becomes for this case,

$$\frac{H_1}{H_2} = \frac{D_1}{D_2} = 1,$$

or $H_1 = H_2$. According to this result, the quantity of heat H_1 *gained* by the cold liquid is equal to quantity H_2 *lost* by the warm liquid during the mixing. The same conclusion was reached in similar experiments on the mixing of *unequal* volumes of cold and hot water, made at about this time (*ca.* 1723) by Brook Taylor; he found that the temperature of the mixture could be successfully predicted on the assumption that the heat gained by the cold liquid is equal to that lost by the warm liquid.

This assumption was extended by Black to explain the effects of mixing, not only the same liquids, but any volumes of different liquids;

for he says (p. 23), "and yet the quantity of heat which the water has gained is the very same as that which the quicksilver has lost." Actually, two assumptions are involved in his and all subsequent explanations of mixing experiments, namely, (i) that heat is neither created nor destroyed during the mixing and (ii) that account must be taken of any heat lost to or gained from the air or other bodies in contact with the mixture. The first of these assumptions is called the "principle of conservation of heat." This principle seemed to be plausible for, as we shall eventually see, it was rather generally believed in Black's day that heat was a material substance, having many of the properties of ordinary matter; and since the time of the Greeks the idea had persisted that matter was uncreatable and indestructible. However, it is important to note that the possibility of using this principle in calculations of mixture temperatures first became apparent through consideration of the weight hypothesis [Eq. (1) or (2)]. Yet, as Black has shown in the preceding pages, the weight hypothesis predicts correct mixture temperatures only when the *same* substances are mixed, whereas the principle of conservation of heat is assumed by him to apply in all mixing experiments. The weight hypothesis is less generally valid than the new principle that it has suggested.

As Black says, the results obtained by Fahrenheit in mixing water and mercury indicate that the quantities of heat needed to produce the same temperature change in different substances depends, not merely on their weight, but also on their different capacities for heat, the mercury evidently having a smaller capacity for heat than the water.

> The inference that Dr. Boerhaave drew from Fahrenheit's experiment is very surprising. Observing that heat is not distributed among different bodies in proportion to the quantity of matter in each [and therefore the weight of each], he concluded that it is distributed in proportion to the *volume* of each body — a conclusion contradicted by this very experiment. Yet Musschenbroeck has followed him in this opinion.

Boerhaave saw for himself that the weight hypothesis — our Eq. (1) — did not correctly predict the mixture temperature when two different substances, such as mercury and water, are mixed. So he advanced another hypothesis, namely, that the quantities of heat needed to produce the same temperature change in any two bodies were directly proportional to the *volumes* of the bodies, or, in algebraic language, that

$$\frac{H_1}{H_2} = \frac{V_1}{V_2}. \qquad \text{(For the same temperature change } \Delta t\text{)} \qquad (3)$$

This "very surprising" inference, which we shall call the "volume hypothesis," is seen to have the same limited validity as the weight hypothesis; that is, it predicts results in accord with experiment only when two liquids of the same kind are mixed, for instance, water and water, or mercury and mercury. But, for equal volumes of *different* liquids, the volume hypothesis predicts that equal quantities of heat should be needed to produce the same temperature changes. Yet Fahrenheit's experiments indicated that equal quantities of heat produced the same temperature changes, not in equal volumes of water and mercury, but in two volumes of water and three of mercury.

> As soon as I understood this experiment [of Fahrenheit's] in the manner I have now explained it, I found a remarkable agreement between it and some experiments described by Dr. Martine, in his "Essay on the heating and cooling of bodies" [1740]. His experiments appeared at first very surprising and unaccountable, but, being compared with this one, may be explained by the same principle. Dr. Martine placed before a good fire, and at equal distances from it, some water and an equal volume of quicksilver, each of them contained in equal and similar glass vessels, and each having a delicate thermometer immersed in it. He then carefully observed the celerity with which each of these liquids was heated by the fire, as indicated by the thermometers. He found, by repeated trials, that the quicksilver was warmed by the fire almost twice as fast as the water; and after each trial, having heated these two liquids to the same temperature, he placed them in a stream of cold air and found that the quicksilver always cooled much faster than the water. Before these experiments were made, it was supposed [on the basis of the weight hypothesis] that the time needed for the quicksilver to heat or cool would be longer than for an equal volume of water, in the proportion of 13 or 14 to one.
>
> But, from the view I have given of Fahrenheit's experiment with quicksilver and water, the foregoing experiment of Dr. Martine's is easily explained. We need only to suppose that the fire communicated equal quantities of heat to both liquids, but that, as less of it was required for warming the quicksilver than for warming the water, the quicksilver necessarily was warmed the faster of the two. And when both, being raised to the same temperature, were exposed to the cold air, the air at first received heat from them equally fast, but the quicksilver, by losing the same quantity of heat as the water, became cold much faster than the water. These experiments of Dr. Martine's, in thus agreeing so well with Fahrenheit's, plainly show that quicksilver, notwithstanding its larger density, requires less heat to produce a given temperature rise than is necessary for an equal volume of water. The quicksilver, therefore, may be said to have less capacity for the matter of heat. And we are thus taught that, in cases in which we may have occasion to investigate the capacities of different bodies for heat, we can learn them only by making experiments. Some have accordingly been made, both by myself and others.

George Martine (1702–1741), a physician who served for a time in the British Army in America, was a skilful experimenter who published a number of scientific papers in a volume entitled *Essays, Medical and Philosophical* (London, 1740). In the experiment just described, he made use of what has since come to be called "the method of constant heat supply." The substance to be heated is exposed to a fire or other source of heat that is sufficiently steady to warrant the assumption that heat is supplied at a constant rate; in other words, that the quantity of heat H absorbed by the substance is directly proportional to the time T during which the substance is exposed to the source. One is reminded here of the inverse, ancient practice of measuring the passage of time by observing the rate at which a candle burns away.

If the weight hypothesis — our Eq. (2) — were correct, mercury, whose density is 13.6 times that of water, should rise in temperature only 1/13.6 as fast as the same volume of water, when both are exposed to the same fire. But Martine found, "contrary to the common opinion," that the mercury actually warmed about twice as fast as the water.

Nor could Martine's result be predicated by Boerhaave's volume hypothesis — our Eq. (3). According to it, equal volumes of mercury and water should warm through the same temperature interval in the same time.

Martine made similar experiments with other pairs of unlike liquids, noting the time needed for them to warm, and also to cool after being warmed, and in no case was the result in accord with either the weight or the volume hypothesis. In his essay describing these experiments, Martine said that, contrary to all our fine theories, quicksilver, the most dense ordinary fluid in the world, excepting only melted gold, is, however, the most ticklish next to air; it heats and cools sooner than water, oil, or even rectified spirits of wine itself; and he was moved to say that he knew "no stronger instance than this of the weakness, or, if I may venture to say so, of the presumptuousness of the human understanding, in pronouncing too hastily concerning the nature of things from some general preconceived theories."

Although Black says (p. 134) that he carried out experiments to determine what he called the "capacity for heat" of various substances, he does not describe them anywhere in his lectures. However, Robison states in his "Notes and Observations by the Editor," at the end of volume I, that Black made many such experiments prior to 1765 and was assisted in them by William Irvine (1743–1787), who studied under him and later became Lecturer in Chemistry at Glasgow. Robison says that these experiments were carried out by the *method of mixtures*, which both Fahrenheit and Brook Taylor (p. 132) had used to a limited extent, but which Black developed so as to be able to measure "capacities for heat."

Later, Martine's method of constant heat supply was also used for this purpose. By putting different weights w of a particular substance in a vessel and exposing each of them to a steady fire for varying periods of time, Black found that the time of heating, and therefore the quantity of heat H added, is directly proportional both to the weight w of substance and to the rise in temperature Δt; that is, $H \propto w\Delta t$ for a given substance. Now any statement of proportionality, such as this, may be converted into an equation by introducing a *proportionality factor*. Denoting this factor in the present case by the symbol s and inserting it in the foregoing expression, we obtain

$$H = sw\Delta t. \tag{4}$$

Black's great achievement here was to show that the value of this factor s is different for every different substance. He and Irvine referred to the factor variously as "affinity for heat," "faculty for receiving heat" and "appetite for heat," but finally settled on the term "capacity for heat." Later experimenters, such as Adair Crawford, the author of a well-known book entitled *Experiments and Observations on Animal Heat* (1779), and J. C. Wilcke (1781), a Swedish physicist, used various other terms; but Wilcke finally adopted *specific heat* for the factor s, and this is the term most widely used today.

Nothing has yet been said about units for measuring heat H and specific heat s. Richard Kirwan, a contemporary of Black's, seemingly was the first to suggest that the specific heats of various substances be measured with respect to that of water taken as a *standard*, and this is the practice still followed today. However, the early methods of expressing specific heats were varied and somewhat complicated, and thus we will find it better to introduce modern units at this point.

The unit for quantity of heat H called the *British thermal unit* (symbol, Btu) is defined as the quantity of heat that enters or leaves 1 lb of *water* when it undergoes a temperature change of one Fahrenheit degree. In other words, when Eq. (4) is applied to water, H is 1 Btu when w is 1 lb and Δt is 1 Fahrenheit degree; thus

$$1 \text{ Btu} = s_{\text{water}} \times 1 \text{ lb} \times 1\,^{\circ}\text{F},$$

or

$$s_{\text{water}} = 1 \text{ Btu/lb }^{\circ}\text{F}.$$

Notice that the specific heat s of any substance is, by definition, the quantity of heat that enters or leaves 1 lb of the substance when its temperature changes by one Fahrenheit degree. For water, the specific heat is 1 Btu/lb °F, by definition. For other substances, as Black points out (p. 134), the specific heats must be found by experiment. For instance, experiment shows that the specific heat of mercury is 0.033 Btu/lb °F.

Liquefaction

Our experience of freezing of liquids when exposed to more or less powerful degrees of cold is almost universal. The exceptions are very few. The strongest spirit of wine [alcohol] and a few subtle and volatile oils are the only substances that have not yet been solidified by any degree of cold hitherto known. As these, however, are so few in number, it appears unreasonable to believe them to be so different in nature and constitution from all other bodies that liquidity is in them an essential quality, of which they cannot be deprived by any diminution of their heat. We have no certain knowledge of what is the lowest possible temperature, but, on the contrary, shall have reason hereafter to be persuaded that the most violent cold which has yet been observed is very far short of the most extreme degree. So it is reasonable to suppose that these few substances differ from others only in having a much greater *disposition* to liquidity, so that we have never yet known a degree of cold sufficient for solidifying them; but that they would undoubtedly freeze, like other liquids, were they exposed to a sufficiently low temperature.

Quicksilver was, not long since, one of this small number of substances, which, having never been seen in any other than a liquid state, was considered as naturally and essentially liquid, and incapable of being reduced to a solid form, until experiments were made with it, first in different parts of the Russian Empire, since the year 1760, and verified afterwards in other places. By these experiments, every person must be convinced that quicksilver is a metal that can become solid and malleable like the rest, but that it freezes at a lower temperature [now known to be about − 38°F] than has ever been observed over the greater part of the surface of this earth. In the same manner may we consider all other liquids as solids melted by heat.

Some philosophers, however, have offered many objections to this general proposition concerning the nature of liquids. They thought it necessary to suppose that water is an exception. They could not be persuaded that its liquidity is the effect of heat, but supposed this quality to be an essential one of the water, depending on the spherical form and polished surface of its particles, and that the freezing of it depended on the introduction of some extraneous, subtle matter. This opinion is defended by Professor Musschenbroeck, in his *Physica*, and he has collected all the reasons and arguments which have been devised for supporting such an opinion.

But when we consider these reasons and arguments with due attention, we find that none of them are valid. Many of them are alleged facts, adduced to prove that water sometimes freezes under circumstances

> such that Mr. Musschenbroeck did not comprehend how it could have been cooled to the temperature reckoned necessary for its solidification; and he therefore concludes that the freezing of it must have been due to some cause other than the diminution of its temperature to the proper degree.
>
> But had he applied a good thermometer to the water, he would have found that it was actually cooled to the usual temperature [32°F] in every case in which it froze. For the truth of this we may depend on the testimony of Dr. Martine, who, with the assistance of his friends, had experiments made in many distant parts of the world and at different times, with thermometers on which he could entirely rely. There is no doubt that many mistakes have been committed by using bad thermometers, or by the want of skill to use them properly., But the truth is that, in the facts adduced by Musschenbroeck, no thermometer whatever was applied to the water itself, but only vague reasoning was employed to make it appear probable that it was not cooled to the proper temperature. We may, therefore, pass over the greater number of his reasons, and take some notice of a few of his facts that are surprising in themselves, that could not be explained by any principles then known, and that, besides, are so stated by him as to make them appear uncommonly perplexing.

In several pages that we are omitting, Black discusses various phenomena cited by Musschenbroeck — for instance, the fact that water expands when it freezes — and shows that the latter was mistaken in thinking that they supported his views.

> Thus many of Professor Musschenbroeck's reasons for his opinion on the congelation of water are quite inconclusive, none of them giving any satisfactory proof that the liquidity of water is an essential quality or that any new matter is introduced when it is frozen. The propensity of many people to imagine water as naturally and essentially liquid is a prejudice contracted from the habit of seeing it much oftener in this state than in the solid state. . . .
>
> In considering the effect of heat in producing liquefaction, we should first remark that innumerable experiments made with thermometers show that the change of a particular substance from solid to liquid occurs only when the temperature is increased to a certain value. Above this temperature the substance is a liquid. If the liquid is cooled back down to this temperature, it becomes solid, and it remains solid at all lower temperatures. This at least may be stated as the general fact.
>
> There are, however, many substances [now called *amorphous substances*] in which the transition is not so sudden. These, within a certain range of temperatures, are reduced to an intermediate state — one of softness — and pass through all the degrees of it while heat is being added to change them from solid to liquid. We have examples of this in beeswax, resin, tallow, glass, and many other substances. But even in these,

every degree of softness depends on a corresponding temperature, which has the power to produce it; and in most of these bodies there is also a remarkable step from the greatest degree of softness to perfect liquidity, which always depends on a certain temperature necessary to the complete liquefaction of that particular body.

Thus, in general, each different kind of matter must be heated to a particular temperature to render it liquid, and below this temperature it is either solid or has some degree of solidity. This temperature is therefore called the FREEZING or the MELTING POINT of the substance. It is called the freezing point of such substances as exist commonly in the liquid state, and the melting point of those that are solid under ordinary circumstances. When we compare different kinds of matter, there is all the variety that can be imagined between those that require for their fusion the highest temperatures and those for which the freezing point is so low that they always appear, in ordinary circumstances, in the liquid form. . . .

I must now add that the foregoing general account of liquefaction as an effect of heat is not complete and satisfactory, if this effect is interpreted in terms of certain common opinions that have been entertained about it — opinions that are inconsistent with many remarkable phenomena. As these phenomena show, when attentively considered, liquefaction is produced by heat in a very different manner from that which has commonly been imagined — yet in a manner which, when understood, enables us to explain many particulars relating to heat or cold that formerly appeared to be quite perplexing and unaccountable.

Melting had been universally considered as produced by the addition of a very small quantity of heat to a solid body, once it had been warmed up to its melting point; and the return of the liquid to the solid state, as depending on a very small diminution of the quantity of its heat, after it had cooled to the same degree. It was believed that this small addition of heat during melting was needed to produce a small rise in temperature, as indicated by a thermometer placed in the resulting liquid; and that, when the melted body was again made to solidify, it suffered no greater loss of heat than that corresponding to a drop in temperature of the resulting solid, indicated also by the application to it of the same instrument.

This was the universal opinion on the subject, so far as I know, when I began to read my lectures in the University of Glasgow in the year 1757. But I soon found reason to object to it, as inconsistent with many remarkable facts, when attentively considered; and I endeavored to show that these facts are convincing proofs that liquefaction is produced by heat in a very different manner.

The opinion I formed from attentive observation of the facts and phenomena is as follows. When ice or any other solid susbtance is melted, I am of the opinion that it receives a much larger quantity of heat than what is perceptible in it immediately afterwards by the thermometer. A large quantity of heat enters into it, on this occasion, without making it apparently warmer, when tried by that instrument. This heat must be added in order to give it the form of a liquid; and I affirm that this large addition of heat is the principal and most immediate cause of the liquefaction induced.

On the other hand, when we freeze a liquid, a very large quantity of heat comes out of it, while it is assuming a solid form, the loss of which heat is not to be perceived by the common manner of using the thermometer. The apparent temperature of the body, as measured by that instrument, is not diminished, or not in proportion to the loss of heat which the body actually suffers on this occasion; and it appears, from a number of facts, that the state of solidity cannot be induced without the abstraction of this large quantity of heat. And this confirms the opinion that this quantity of heat, absorbed, and, as it were, concealed in the composition of liquids, is the most necessary and immediate cause of their liquidity. . . .

If we attend to the manner in which ice and snow melt when exposed to the air of a warm room, or when a thaw succeeds to frost, we can easily perceive that, however cold they might be at first, they soon warm up to their melting point and begin to melt at their surfaces. And if the common opinion had been well founded — if the complete change of them into water required only the further addition of a very small quantity of heat — the mass, though of a considerable size, ought all to be melted within a very few minutes or seconds by the heat incessantly communicated from the surrounding air. Were this really the case, the consequences of it would be dreadful in many cases; for, even as things are at present, the melting of large amounts of snow and ice occasions violent torrents and great inundations in the cold countries or in the rivers that come from them. But, were the ice and snow to melt suddenly, as they would if the former opinion of the action of heat in melting them were well founded, the torrents and inundations would be incomparably more irresistible and dreadful. They would tear up and sweep away everything, and this so suddenly that mankind would have great difficulty in escaping from their ravages. This sudden liquefaction does not actually happen. The masses of ice or snow require a long time to melt, especially if they be of a large size, such as are the collections of ice and wreaths of snow formed in some places during the winter; these, after they begin to melt, often require many weeks of warm weather before they are totally changed into water . . . In the same manner does snow continue on many mountains during the whole summer, in a melting state, but melting so slowly that the whole of that season is not a sufficient time for its complete liquefaction. . . .

If any person entertain doubts of the entrance and absorption of heat in the melting ice, he needs only to touch it; he will instantly feel that it rapidly draws heat from his warm hand. He may also examine the bodies that surround or are in contact with it, all of which he will find deprived by it of a large part of their heat; or if he suspend ice by a thread in a warm room, he may perceive with his hand, or by a thermometer, a stream of cold air descending constantly from the ice; for the air in contact is deprived of a part of its heat, and thereby contracts and is made denser than the warmer air of the rest of the room; it therefore falls, and its place round the ice is immediately taken by some of the warmer air; but this, in its turn, is soon deprived of some heat, and so descends in like manner; and thus there is a constant flow of warm air from around to the sides of the ice, and a descent of the same after cooling, during which operation the ice must necessarily receive a large quantity of heat.

It is evident, therefore, that the melting ice receives heat very fast, but the only effect of this heat is to change it into water, which is not in the least sensibly warmer than the ice was before. A thermometer applied to the drops of water, immediately as they come from the melting ice, will indicate the same temperature [32°F] as when it is applied to the ice itself, or, if there is any difference, it is too small to deserve notice. A large quantity, therefore, of the heat which enters into the melting ice produces no effect other than to give it liquidity, without augmenting its sensible heat; it appears to be absorbed and concealed within the water, so as not to produce any effect discoverable by the application of a thermometer.

In order to understand better this absorption of heat by the melting ice, and concealment of it in the water, I made the following experiments. . . .

I chose two thin globular glasses, 4 inches in diameter, and very nearly of the same weight. I poured 5 ounces [apothecaries' weight, equivalent to 5.5 oz avoirdupois] of pure water into one of them, and then set it in a mixture of snow and salt until the water was frozen into a small mass of ice. It was then carried into a large empty hall, in which the air was not disturbed or varied in temperature during the progress of the experiment. The glass was supported, as it were, in mid-air, by being set on a ring of strong wire, which had a 5-inch tail issuing from the side of it, the end of which was fixed in the most projecting part of a reading desk or pulpit.

I now set up the other globular glass precisely in the same way, and at the distance of 18 inches to one side, and into this I poured 5 ounces of water, previously cooled almost to the freezing point — actually to 33°F. Suspended in it was a very delicate thermometer, with its bulb in the center of the water, and its stem so placed that I could read it without touching the thermometer. I then began to observe the ascent of this thermometer, at suitable intervals, in order to learn with what celerity the water received heat; I stirred the water gently with the end of a feather about a minute before each observation. The temperature of the air, examined at a little distance from the glasses, was 47°F.

The thermometer assumed the temperature of the water in less than half a minute, after which, the rise of it was observed every 5 or 10 minutes, during half an hour. At the end of that time, the water was 7

> degrees warmer than at first; that is, its temperature had risen to 40°F.
>
> The glass containing the ice was, when first taken out of the freezing mixture, 4 or 5 degrees colder than melting snow, which I learned by applying the bulb of the thermometer to the bottom of it; but after some minutes, it had gained from the air enough heat to warm it those 4 or 5 degrees, and the ice was just beginning to melt. After an additional 10½ hours, only a very small and spongy mass of the ice remained unmelted, it being in the center of the upper surface of the water, but this also was totally melted in a few minutes more. Introducing the bulb of the thermometer into the water, near the sides of the glass, I found that the water there had warmed to 40°F. . . .
>
> It appears that the ice-glass had to receive heat from the air of the room during 21 half-hours in order to melt the ice and then warm the resulting water to 40°F. During all this time it was receiving heat with the same celerity (very nearly) as had the water-glass during the single half-hour in the first part of the experiment . . . Therefore, the quantity of heat received by the ice-glass during the 21 half-hours was 21 times the quantity received by the water-glass during the single half-hour. It was, therefore, a quantity of heat, which, had it been added to liquid water, would have made it warmer by (40 — 33) × 21, or 7 × 21, or 147 degrees. No part of this heat, however, appeared in the ice-water, except that which produced the temperature rise of 8 degrees; the remaining part, corresponding to 139 or 140 degrees, had been absorbed by the melting ice and was concealed in the water into which it was changed. . . .

In this experiment, Black has used Martine's method of constant heat supply (p. 134), the constant source of heat here being the air of the room. Let us repeat Black's calculation in terms of modern units and using Eq. (4), p. 136. To simplify the calculation, we will assume that the contents of each glass weighed 1 lb avoirdupois, instead of 5 oz apothecaries' weight. This will not change the final result, but means merely that the room temperature would have to be considerably higher than was Black's in order for the temperature changes and time-intervals to be the same as he observed.

In the water-glass, 1 lb of water underwent a temperature rise Δt of 7 Fahrenheit degrees in 1 half-hour. Since the specific heat of water is 1 Btu/lb °F, the quantity of heat H that passed from the air into this water in 1 half-hour was

$$H = sw\Delta t = 1\,\frac{\text{Btu}}{\text{lb }^\circ\text{F}} \times 1\text{ lb} \times 7^\circ\text{F} = 7\text{ Btu}.$$

For the ice-glass, the quantity of heat absorbed by its contents in 21 half-hours was $21H$, or 21 × 7 Btu, or 147 Btu. Some of this heat served to warm the 1 lb of melted ice through 8 Fahrenheit degrees, this part evidently amounting to 8 Btu. The remainder, or 139 Btu, "had been absorbed by the melting ice and was concealed in the water into which it was changed."

This discovery of Black's suggested that it would be useful to define a new physical quantity, which has come to be called the *heat of fusion* of a substance, symbol h_f. It is defined as the quantity of heat required to melt unit weight of a solid substance without any change of temperature taking place. Thus Black's present experiment yields a value of 139 Btu/lb for the heat of fusion of ice. The modern value is 144 Btu/lb.

In the next experiment, Black uses the method of mixtures to obtain data for another determination of the heat of fusion of ice.

> Another obvious method of melting ice occurred to me, in which it would be still easier to perceive the absorption and concealment of heat, and this was by the action of warm water. . . .
>
> If equal weights of hot and cold water are mixed together, the temperature of the mixture is halfway between that of the hot and that of the cold. No part of the heat disappears on this occasion, so far as we can perceive, only the intensity of it [the temperature] being diminished by the heat's being diffused through a larger quantity of matter. It was obvious, therefore, that if a quantity of heat is absorbed and disappears in the melting of ice, this would easily be perceived when the ice is melted by mixing it with warm water.
>
> To make this experiment, I first froze some water in the neck of a broken retort, in order to have a mass of ice of an oblong form. At the same time I heated some water, nearly equal in weight to the ice, in a very thin globular glass, the mouth of which was sufficiently wide to admit the piece of ice. The water was heated by a small spirit-of-wine lamp; it was also often stirred with the end of a feather, and had a thermometer hung in it.
>
> While the water was heating, the mass of ice was taken out of the mould and was exposed to the air until it was beginning to melt over the whole of its surface. I then put a woolen glove on my left hand and, taking hold of the ice, wiped it quite dry with a linen towel, laid it in the pan of a balance on a piece of flannel, and hastily counterpoised it with sand in the opposite pan, so that I might examine its weight afterwards. I immediately plunged it into the hot water, and at the same time extinguished the lamp. The lamp being small, the temperature of the water had been increasing very slowly, and had almost ceased to increase; immediately before I put the ice into it, this temperature was found to be just 190°F. The ice was all melted in a few seconds and produced a mixture, the temperature of which was 53°F. . . .
>
> The melting of the ice was effected, not only by the heat from the hot water, but also by that from the glass. From other experiments I learned that 16 parts [by weight] of hot glass have no more power in heating

> cold bodies than do 8 parts of equally hot water; we may therefore substitute, in place of the 16 half-drams of warm glass, 8 half-drams of warm water, which, added to the 135 half-drams of warm water, make up 143 half-drams. . . .

Since the calculations to which Black now proceeds are carried out in a somewhat complicated fashion, we are replacing them here by the simpler method in common use today. Moreover, we are substituting more convenient values for the weights of the materials and are expressing them in pounds avoirdupois, instead of apothecaries' units. These weights are: for the hot water, 1.03 lb; for the glass, 0.07 lb; for the ice, 0.89 lb.

Our method of finding the quantity of heat absorbed by the ice in melting will be to compute the heat lost by the hot water and hot glass in cooling to the temperature of the mixture, and from this sum to subtract the heat gained by the cold water (melted ice) in warming to the mixture temperature. The assumptions involved here are that the heat is conserved in the process of mixing and that none of it is gained from or lost to any objects except the water, glass and ice.

(1) The *hot water* of weight 1.03 lb and specific heat 1 Btu/lb °F cooled from 190° to 53°F, the mixture temperature. So it *lost* a quantity of heat H_1 equal to

$$H_1 = sw\Delta t = 1 \frac{\text{Btu}}{\text{lb °F}} \times 1.03\text{ lb} \times (190 - 53)\text{°F} = 141\text{ Btu}.$$

(2) The *glass* weighed 0.07 lb and cooled through the same temperature interval as the hot water; its specific heat, as can be seen from Black's statement, was half that of water, or 0.5 Btu/lb °F. So the heat H_2 *lost* by the glass was

$$H_2 = sw\Delta t = 0.5 \frac{\text{Btu}}{\text{lb °F}} \times 0.07\text{ lb} \times (190 - 53)\text{°F} = 4.8\text{ Btu}.$$

(3) The *cold water* (melted ice) weighed 0.89 lb and warmed from 32° to 53°F. So the quantity of heat H_3 *gained* by it was

$$H_3 = sw\Delta t = 1 \frac{\text{Btu}}{\text{lb °F}} \times 0.89\text{ lb} \times (53 - 32)\text{°F} = 18.7\text{ Btu}.$$

(4) Let H_4 represent the heat *gained* by the 0.89 lb of ice of temperature 32°F in changing into water of the same temperature. Then it follows from our assumption that $H_1 + H_2 = H_3 + H_4$, or $H_4 = H_1 + H_2 - H_3 = (141 + 4.8 - 18.7)\text{ Btu} = 127\text{ Btu}$.

Thus the value for the heat of fusion of ice yielded by this experiment is 127 Btu/0.89 lb, or 143 Btu/lb.

In this experiment we see Black taking into account the heat capacity of the *vessel* containing the mixture. This had not been done by Brook Taylor, Fahrenheit, or any previous experimenter.

> The result of this experiment coincides sufficiently with that of the former; the difference [between the values 139 and 143 Btu/lb] is not larger than what may be expected in similar experiments, and might arise from the accident of the central parts of the mass of ice being one or two degrees colder than its surface.
>
> These two experiments, and the reasoning which accompanies them, were read by me in the Philosophical Club, or Society of Professors and others in the University of Glasgow, in the year 1762, and have been described and explained in my lectures, there and in Edinburgh, every year since. . . .
>
> It is, therefore, proved that the various phenomena attending the melting of ice are inconsistent with the common opinion previously held on this subject, and that they support the one which I have proposed. . . .
>
> In the ordinary process of freezing water, the extrication and emergence of the *latent heat*, if I may be allowed to use these terms, is performed by such minute steps, or rather with such a smooth progress, that many may find difficulty in apprehending it; but I shall now mention another example in which this extrication of the concealed heat becomes manifest and striking.
>
> This example is an experiment, first made by Fahrenheit [*Philosophical Transactions of the Royal Society*, vol. 33 (1724), p. 78], but since repeated and confirmed by many others. He wished to freeze water from which the air had been carefully expelled. This water was contained in a small glass globe, about one-third filled, and sealed to prevent the return of the air into it. The globe was exposed to the air in frosty weather until he felt satisfied that it had cooled down to the temperature of the air, which was 6 or 7 Fahrenheit degrees below the freezing point of water. The water, however, still remained liquid, so long as the globe was left undisturbed; but, when the globe was taken up and shaken a little, the water instantly solidified.
>
> Others have since found that the experiment will succeed even when the water is not deprived of its air, and that the most essential circumstances are that it be contained in a vessel of small size and preserved carefully from the least disturbance . . . In these circumstances, it may be cooled to 6, 7, or 8 degrees below the freezing point without being frozen. But, if it be then disturbed, there is a sudden solidification, not of the whole, but of a small part only; this forms into feathers of ice, traversing the water in every direction and forming a spongy contexture of ice, that contains the water in its vacuities, so as to give to the whole the appearance of being frozen. But the most remarkable fact is that,

> while this happens (and it happens in a moment of time), this mixture of ice and water suddenly becomes warmer, and a thermometer immersed in it indicates a rise to the freezing point.
>
> Nothing can be more inconsistent with the old opinion concerning the cause of congelation than the phenomena of this experiment. It shows that the loss of a little more heat, after the water is cooled down to the freezing point, is not the most necessary and inseparable cause of its congelation, since the water can be cooled 6, 7, or 8 degrees below that point without being congealed.

This phenomenon, in which a liquid is cooled to a temperature below its ordinary freezing point, is now known to be exhibited by many substances in addition to water. The undercooled liquid is unstable; it will immediately begin to solidify if disturbed, or if even the tiniest crystal of the solid is dropped into it. As Black indicates, this phenomenon of *undercooling* provides a striking example of the "latent heat" evolved when a solid freezes; the undercooled liquid retains this heat in latent form until solidification starts, and then gradually releases it as the solidification proceeds. It is this released heat that warms the substance up to its ordinary freezing temperature.

In addition to his measurements of the heat absorbed by melting ice, Black performed the converse experiment of measuring the heat released by the resulting water upon freezing. The thought of making this important experiment occurred to him during the summer of 1761; but, "as there was no ice house then in Glasgow, he waited with impatience for the winter, and in December . . . made the decisive experiment." The quantities absorbed and released turned out to be equal, which convinced him of the soundness of his conjecture that the large amount of heat absorbed during melting is not destroyed, but remains latent and can be completely recovered from the liquid by freezing it. In other words, he could now confidently extend the principle of conservation of heat to include this latent heat as well as sensible heat. Indeed, it is only by assuming the validity of the principle in this extended form that one is able to calculate heats of fusion from experiments made either by the method of mixtures or by the method of constant heat supply.

Black also studied the melting of other substances than ice, but did not describe them in his lectures; for, as Robison says, "in this elementary course, intended for the instruction of the uninformed hearer, he chose to confine his proofs to the most familiar observations." At Black's request, Irvine determined the heats of fusion of beeswax, spermaceti, and tin. For tin the heat of fusion is 26 Btu/lb, this therefore being the quantity of heat required to convert 1 lb of solid tin at 450°F (its melting point) to liquid tin of the same temperature.

Vaporization

When we heat a large quantity of liquid in a vessel, in the ordinary manner, by setting it on the fire, we have an opportunity to observe some phenomena that are very instructive. The liquid gradually warms, and at last attains that temperature which it cannot pass without assuming the form of vapor. In these circumstances, we always observe that the water is thrown into violent agitation, which we call *boiling*. This agitation continues as long as we keep adding heat to the liquid, and its violence increases with the celerity with which the heat is supplied.

Another peculiarity attends this boiling of liquids which, when first observed, was thought very surprising. However long and violently we boil a liquid, we cannot make it in the least hotter than when it began to boil. The thermometer always points at the same degree, namely, the vaporific point of that liquid. Hence the vaporific point of a liquid is often called its *boiling point*.

When these facts and appearances were first observed, they seemed surprising, and different opinions were formed with respect to the causes on which they depend. Some thought that this agitation was occasioned by that part of the heat which the water was incapable of receiving, and which forced its way through, so as to occasion the agitation of boiling. Others imagined that the agitation proceeded from the air which water is known to contain and which is expelled during boiling. . . .

A more just explanation will occur to any person who will take the trouble to consider this subject with patience and attention. In the ordinary manner of heating water, the source of heat is applied to the lower parts of the liquid. If the pressure on the surface of the water [such as that due to the atmosphere] be not increased, the water will soon acquire the highest temperature that it can attain without assuming the form of vapor. Any subsequent addition of heat must therefore convert into vapor that part of the water which it enters. As this added heat all enters at the bottom of the liquid, elastic vapor [steam] is constantly produced there, which, because it weighs almost nothing, must rise through the surrounding water and appear to be thrown up to the surface with violence, and from thence it is diffused through the air. The water is thus gradually wasted away, as the boiling continues, but its temperature is never increased, at least in that part which remains after long-continued and violent boiling. The parts, indeed, in contact with the bottom of the vessel may be supposed to have received a little more heat, but this is instantly communicated to the surrounding water through which the steam rises.

This has the appearance of being a simple, plain, and complete account of the production of vapor and the boiling of liquids; and it is the only account that was given of this subject before I began to deliver these lectures. But I am persuaded that it is by no means a full account. It used to be taken for granted that, after a liquid was heated up to its boiling point, nothing further was necessary but the addition of a little more heat to change it into vapor. It was also supposed that when this vapor was so far cooled as to be ready for condensation, this condensation, or return to the liquid state, would happen at once, in consequence of the vapor's losing only a very small quantity of heat.

But I can easily show, in the same manner as in the case of liquefaction, that a very large quantity of heat is necessary for the production of vapor, although the body be already heated to that temperature which it cannot pass, by the smallest possible degree, without being so converted. The undeniable consequence of this, if the old view were correct, should be an explosion of the whole water with a violence equal to that of gunpowder. But I can show that this large quantity of heat enters into the vapor gradually, while it is forming, without making this vapor hotter. Thus steam, if examined with a thermometer, is found to have exactly the same temperature as the boiling water from which it arose. The water must be raised to a certain temperature [212°F] because at that temperature only, is it disposed to absorb heat [that becomes latent]; and it is not instantly exploded, because, in that instant, there cannot be had a sufficient supply of heat throughout the whole mass.

On the other hand, I can show that when the steam is condensed back into water, the very same large quantity of heat comes out of it into the colder, surrounding matter by which it is condensed; and the water into which it is changed does not become sensibly colder by the loss of this large quantity of heat. . . .

In the ordinary course of such experiments in this climate, it requires about six times the number of minutes to boil off a small quantity of water that it takes to bring it [from room temperature] to the boiling point. I can scarcely remember the time in which I had not some confused idea of this disagreement of the fact with the common opinion; and I presume that it has come across the mind of almost every person who has attended to the boiling of a pot or pan. But the importance of the surmise never struck me with due force till after I had made my experiments on the melting of ice. The regular procedure in that case, and its similarity to what appears here, encouraged me to expect a similar regularity in the boiling of water, if my conjecture was well founded. But it appeared to me difficult, if at all possible, to procure a source of heat that would be tolerably uniform, or to ascertain its irregularities. And this discouraged me from making an experiment that would in all probability be so anomalous. But I was one day told by a practical distiller that, when his furnace was in good order, he could tell to a pint what quantity of liquor he would get in an hour. I immediately set about boiling off small quantities [weights] of water, and I found that it was accomplished in times very nearly proportional to these quantities, even although the fire was sensibly irregular.

I, therefore, set seriously about making experiments, conformable to the suspicion that I entertained concerning the boiling of liquids. My

> conjecture, when put into form, was to this purpose. I imagined that, during the boiling, heat is absorbed by the water and enters into the composition of the steam produced from it, in the same manner as it is absorbed by ice in melting and enters into the composition of the resulting water. And, as the ostensible effect of the heat in this latter case consists, not in warming the surrounding bodies, but in converting the ice into water; so, in the case of boiling, the heat absorbed does not warm surrounding bodies, but converts the water into steam. In both cases, considered as the cause of warmth, we do not perceive its presence: it is concealed, or latent, and I gave it the name of LATENT HEAT.
>
> I shall now describe a few of the experiments, which, I apprehend, will fully establish the justice of my conjecture.
>
> *Experiment 1.* I procured some cylindrical tin-plate vessels, about 4 or 5 inches in diameter, and flat bottomed. Putting a small quantity of water into them, of temperature 50°F, I set them upon a red-hot kitchen table — that is, a cast-iron plate with a furnace of burning fuel below it — taking care that the fire should be pretty regular. After 4 minutes the water began sensibly to boil, and in 20 minutes more, it was all boiled off. This experiment was made on 4th October 1762. . . .
>
> I reasoned from it in the following manner. The temperature rose 162 Fahrenheit degrees in 4 minutes, or 40½ degrees each minute. Therefore, on the assumption that the heat entered the water equally fast during the whole ebullition, we must suppose that the quantity of heat absorbed by the water, and contained in its vapor, was equivalent to that which would raise the temperature of water through 40½ × 20, or 810 degrees. [This is equivalent to saying that 810 Btu were absorbed by each pound of water boiled away.] Since this vapor [steam] is no hotter than boiling water, the heat is contained in it in a latent state. Its presence is sufficiently indicated, however, by the vaporous or expansive form which the water has now acquired.
>
> In experiments 2 and 3 [the descriptions of which we are omitting here], the quantities of heat absorbed, and rendered latent, seem to be about 830 and 750 [Btu/lb] . . . There are reasons for believing that this smallest value resulted from an irregularity in the fire. Upon the whole, the conformity of these results with my conjecture was sufficient to confirm me in my opinion of its justice. In the course of further experiments made both by myself and by some friends, and in which the utmost care was taken to procure uniformity in the rate at which the heat was applied, the absorption was found extremely regular, and amounted at an average to about 810 [Btu/lb]. . . .

From this work on vaporization emerged the conception of still another new physical quantity — the *heat of vaporization* of a substance, symbol h_v. It is defined as the quantity of heat required to vaporize unit weight of a liquid without any change of temperature taking place. The modern value for the heat of vaporization of water is 970 Btu/lb.

Robison, in his Preface to volume I, says that Black taught the doctrine of latent heat of vaporization in 1761, "before he had made a single experiment on the subject . . . He thought that what we may observe every day was sufficient for settling the main questions." Seeing that there was much in common between the phenomena of melting and of vaporization, he was able to form his ideas of latent heats of vaporization by analogy with those developed earlier for melting. But he delayed making quantitative experiments for about a year because he thought it would be difficult to obtain a steady source of heat (p. 148).

In the experiments that finally were made, he was assisted, first by Irvine, and then by James Watt. Robison says: "Fortunately for Dr. Black, and for the world, he had now gotten a pupil who was as keenly interested in this scientific question as the Professor. This was Mr. James Watt, then employed in fitting up the instruments in the McFarlane Observatory of the University . . . He chanced to have in his hand, for repairs, a model of Newcomen's steam engine, belonging to the Natural Philosophy Class, and was delighted with the opportunity which this small machine gave him for trying experiments connected with the theory of ebullition, which he had just learned from Dr. Black . . . This gentleman, attached to Dr. Black by every tie of respect, esteem and affection, supplied him with proofs and illustrations in abundance, of all the points on which the Professor wanted information. These were always recited in the class, with the most cordial acknowledgment of obligation to Mr. Watt."

Concerning Theories of Heat

Heat is plainly something extraneous to matter. It is either something superadded to ordinary matter or some alteration of it from its most spontaneous state. Having arrived at this conclusion, it may perhaps be required of me, in the next place, to express more distinctly this something — to give a full description, or definition, of what I mean by the word *heat* in matter. This, however, is a demand that I cannot satisfy entirely. I shall mention, by and by, the supposition relating to this subject that appears to me the most probable. But our knowledge of heat is not brought to that state of perfection that might enable us to propose with confidence a theory of heat or to assign an immediate cause for it.

Some ingenious attempts have been made in this part of our subject, but none of them has been sufficient to explain the whole of it. However, this should not give us much uneasiness. It is not the immediate manner of acting, dependent on the ultimate nature of this peculiar substance, or this particular condition of common matter, that most interests us. We are far removed as yet from that extent of chemical knowledge which makes this a necessary step for further improvement. We have still before us an abundant field of research in the various general facts and laws of action, which constitute the real objects of pure chemical science. And I apprehend that it is only when we have nearly completed this catalogue that we shall have a sufficient number of resembling facts to lead us to a clear knowledge of the behavior peculiar to this substance or modification of matter called heat; and, when we have at last attained it, I presume that the discovery will not be chemical but mechanical. It would, however, be unpardonable to pass without notice some of the most ingenious attempts which have had a certain currency among the philosophical chemists.

The first attempt I think was made by Lord Verulam [Francis Bacon, in 1620]; next after him, Mr. Boyle [Robert Boyle, in 1665 and 1673] gave several dissertations on heat; and Dr. Boerhaave, in his lectures on chemistry [1732], endeavored to prosecute the subject still further, and to improve on the two former authors.

Lord Verulam's attempt may be seen in his treatise *De forma Calidi* [1620], which he offered to the public as a model of the proper manner of prosecuting investigations in natural philosophy. In this treatise he enumerated all the principal facts then known about heat and its production, and endeavored, after a cautious and mature consideration of these, to form some well-founded opinion of its cause.

The only conclusion, however, that he was able to draw from the whole of his facts is a very general one, namely, that heat is *motion*. This conclusion was founded chiefly on the consideration of several means by which heat is produced, or made to appear, in bodies, such as the percussion of iron, the friction of solid bodies, the collision of flint and steel.

The first of these examples is a practice to which blacksmiths have sometimes recourse for kindling a fire; they take a rod of soft iron, half an inch or less in thickness, and, laying the end of it upon their anvil, turn and strike that end very quickly on its different sides with a hammer; it very soon becomes red hot and can be employed to kindle shavings of wood or other very combustible matter. The heat producible by the strong friction of solid bodies occurs often in some parts of heavy machinery when proper care has not been taken to diminish that friction as much as possible by the interposition of lubricating substances. Thick forests are said to have taken fire sometimes because of the branches rubbing one another in stormy weather. Savages in different parts of the world have recourse to the friction of pieces of wood for kindling their fires.

In all these examples, heat is produced or made to appear suddenly in bodies that have not received it in the usual way of communication from others, the only cause of its production being a mechanical force or impulse, or mechanical violence. It was, therefore, very natural for Lord Verulam to conclude that the most usual, nay, perhaps the sole effect of mechanical force or impulse applied to a body is to produce some sort of motion of that body.

Although this eminent philosopher has had a great number of followers on this subject, his opinion has been adopted with two different modifications. The greater number of the English philosophers suppose this motion to be in the small particles of the heated bodies, and imagine that it is a rapid tremor, or vibration, of these particles among one another. Mr. Macquer and Mons. Fourcroy both incline, or did incline, to this opinion. I acknowledge that I myself cannot form a conception of this internal tremor which has any tendency to explain even the more simple effects of heat, and I think that Lord Verulam and his followers have been contented with very slight resemblances indeed between those most simple effects of heat and the legitimate consequences of a tremulous motion. I also see many cases in which intense heat is produced in this way, but where I am certain that the internal tremor is incomparably less than in other cases of percussion, similar in all other respects. Thus the blows that make a piece of soft iron intensely hot produce no [easily observable] hotness in a similar piece of very elastic steel.

But the greater number of French and German philosophers, and Dr. Boerhaave, have held that the motion of which they suppose heat to consist is not a tremor, or vibration, of the particles of the hot body itself, but of the particles of a subtle, highly elastic, and penetrating fluid matter, which is contained in the pores of hot bodies, or interposed among their particles — a matter that they imagine to be diffused through the whole universe, pervading with ease the densest bodies. Some suppose that this matter, when modified in different ways, produces light and the phenomena of electricity.

But neither of these suppositions has been fully and accurately considered by their authors, or applied to explain the whole of the facts and phenomena relating to heat. They have not, therefore, supplied us with a proper *theory* or *explication* of the nature of heat.

A more ingenious attempt has lately been made, the first outlines of which, so far as I know, were given by the late Dr. Cleghorn, in his inaugural dissertation on the subject of heat, published here [at the University of Edinburgh, in 1779]. He supposed that heat depends on the abundance of that subtle elastic fluid which had been imagined before by other philosophers to be present in every part of the universe and to be the cause of heat. But these other philosophers had assumed, or supposed, one property only as belonging to this subtle matter, namely, its great elasticity, or strong repulsion of its particles for one another; whereas, Dr. Cleghorn has supposed it to have still another property, namely, a strong attraction for the particles of the other kinds of matter in nature, which have in general more or less [gravitational] attraction for one another. Thus he supposed that the ordinary kinds of matter consist of particles having a strong attraction both for one another and for the matter of heat; whereas the subtle elastic matter of heat is self-repelling,

> its particles having a strong repulsion for one another while they are attracted by the other kinds of matter, and that with different degrees of force. . . .
>
> Such an idea of the nature of heat is the most probable of any that I know; and an ingenious attempt to make use of it has been published by Dr. Higgins, in his book on vegetable acid [any organic acid] and other subjects. It is, however, altogether a supposition.

In passages not included here, Black says that his discovery that different substances have different capacities for heat are very unfavorable to the opinion that heat is "a tremulous, or other, motion of the particles of matter." If that theory were correct, he contends, then the more dense substances ought to have the larger specific heats, whereas in many cases this is not true; for instance, mercury is more dense than water, but has a much smaller specific heat. "I do not see how this objection can be evaded."

More than half a century elapsed before it became clear that this objection of Black's is invalid and can be evaded; but to see this required a much better knowledge of the weights and velocities of the particles (atoms and molecules) of different substances than was available in his day.

In another place Black points out how the fact that bodies expand in volume when heated had led many to suppose that the addition of heat to a body increased its weight. He reviews experiments made by Boerhaave, Buffon, Whitehurst ("who is distinguished by his accuracy and ingenuity in the construction of very nice and delicate balances"), Roebuck (who "made his experiments with the most scrupulous accuracy") and, lastly, Dr. Fordyce (see Sec. 3). Although finding the results of these various experiments to be contradictory, he concludes "that if heat depends on the presence of a subtle matter introduced into bodies, this matter lacks any perceptible degree of gravitation."

> It has not, therefore, been proved by any experiment that the weight of bodies is increased by their being heated, or by the presence of heat in them. This may be thought very inconsistent with the idea of the nature or cause of heat that I lately mentioned as the most plausible: I mean the notion that heat depends on the abundance of a subtle matter — highly elastic, or self-repellent — which easily enters into all bodies and penetrates them throughout, being strongly attracted by the matter of those bodies. It must be confessed that the afore-mentioned fact may be stated as a strong objection against this supposition.
>
> Some have attempted to remove this objection by supposing the matter of heat to be so subtle and tenuous that no quantity of it which we can collect together can have any sensible weight. Others have thought that it might be the matter which causes the gravitation of other bodies

> and so could not be supposed to gravitate like them, but, on the contrary, might have an opposite tendency.
>
> These attempts to remove the objection are ingenious, but they are not satisfactory. We find too much difficulty in attempting to comprehend them. And this has contributed more than any direct arguments to confirm in their opinion those who, with Lord Verulam, assert that heat . . . is not a material substance, transferable from one body to another, but a mere state or condition in which the matter comprising all bodies may be found. Yet, notwithstanding this difficulty, I imagine that, as we proceed, you will find yourselves more and more impressed with the belief that heat is the effect of a peculiar substance. . . .
>
> When we perceive that what we call heat disappears in the liquefaction of ice, and reappears in the congelation of water, and a number of analogous phenomena, we can hardly avoid thinking it a subtance that may be united with the particles of water in the same manner as [for example] the particles of Glauber's salt [sodium sulfate] are united with them in solution, and may be separated as these are. But, since heat has never been observed by us in a separate state, all our notions of this union must be hypothetical. Moreover, this hypothesis must be combined with some other hypothesis concerning the unions of those other substances; for it must be acknowledged that our notions of those more palpable and familiar combinations are all hypothetical. We think that we can conceive how a particle of common salt can draw around it, and attach to itself, particles of water, and how they may adhere and compose a saline crystal. We transfer this notion to the relation between bodies and heat and — without much reflection, or distinct conception — suppose that, in like manner, a particle of a body attaches itself to a number of particles of heat. Heat is, therefore, supposed to be somehow contained or lodged in the pores of bodies, and we endeavor to account for observable changes in bodies, such as increase of volume, or fusion, or vaporization, by showing some resemblance between these appearances and those that occur in chemical unions or mixtures.
>
> Many have been the speculations and views of ingenious men about this union of bodies with heat. But, as they are all hypothetical, and as the hypothesis is of the most complicated nature, being in fact a hypothetical application of another hypothesis, I cannot hope for much useful information by attending to it. A nice adaptation of conditions will make almost any hypothesis agree with the phenomena. This will please the imagination, but does not advance our knowledge. I therefore avoid such speculations, as taking up time which may be better employed in learning more of the general laws of chemical operations. . . .

The idea that heat might be a material substance stems from the Greeks, and so is much older than Black indicates. It was invoked by Robert Boyle (*Essays of Effluviums,* 1673) in an attempt to explain the gain in weight shown by metals on calcination. In the eighteenth century it came into general use, and indeed proved to be much more helpful in explaining the thermal phenomena known at that time than was the rival and relatively undeveloped view that heat is something associated with the motions of the particles of ordinary matter.

In 1779, William Cleghorn, who is mentioned by Black (p. 152), extended the material theory to take into account Black's discoveries of specific and latent heats. The main properties that Cleghorn and later investigators ascribed to "matter of heat" — or "caloric," as Lavoisier called it in 1787 — may be summarized for our purposes in the form of "postulates of the caloric theory" as follows:

(i) Caloric is an elastic fluid, the particles of which repel one another strongly.

(ii) The particles of caloric are attracted by the particles of ordinary matter, the magnitude of the attraction being different for different substances and for different states of aggregation.

(iii) Caloric is indestructible and uncreatable. (This "principle of conservation of heat" was from the first regarded as plausible; for, from the time of the Greeks onward, the idea had existed that matter was indestructible and, if heat were matter, then it ought to be indestructible. But with the development of the method of mixtures and also of the concept of latent heat, this postulate became an indispensable part of the caloric theory.)

(iv) Caloric can be either sensible or latent, and in the latter state is combined "chemically" with the particles of matter to form the liquid or vapor. (Sensible caloric, which increases the temperature of a body to which it is added, was supposed to form an "atmosphere" around the particles of the body. But latent caloric supposedly was combined with these particles in a manner similar to the chemical combinations of particles (atoms) themselves; this supposedly produced a new compound — the liquid or the vapor — and took place, as do ordinary chemical reactions, only in definite proportions and under definite circumstances.

(v) Caloric does (does not) have appreciable weight (see Sec. 3).

3. COUNT RUMFORD'S INVESTIGATION OF THE WEIGHT ASCRIBED TO HEAT

Count Rumford (1753–1814), whose family name was Benjamin Thompson, carried out an experimental study of "the weight ascribed to heat" as part of an extensive program of research designed by him primarily to throw light on the question of the ultimate nature of heat.

Although Rumford was tremendously versatile and gained international fame as a philanthropist, administrator, and authority on military problems, his most consuming interest and perhaps greatest skill lay in physical experimentation, especially in the field of heat. Of this interest, he wrote, in his *Mémoire sur la Chaleur* (1804):

> To engage in experiments on heat was always one of my most agreeable employments. This subject had already begun to excite my attention, when, in my seventeenth year, I read Boerhaave's admirable *Treatise on Fire*. Subsequently, indeed, I was often prevented by other matters from devoting my attention to it, but whenever I could snatch a moment I returned to it anew, and always with increased interest. Even now this object of my speculations is so present to my mind, however busy I may be with other affairs, that everything taking place before my eyes, having the slightest bearing upon it, immediately excites my curiosity and attracts my attention.

In Rumford's time, the caloric, or material, theory of heat was well established and generally accepted by most scientists. Indeed, as a conceptual scheme serving to correlate most of the facts then known about heat, and as a convenient way to think about these facts or even to predict new ones, it was proving itself to be far more useful than the opposing and then relatively undeveloped doctrine that heat is a form of motion. Rumford, however, came to regard the mode-of-motion view as basically the sounder one, and he continually reiterated this belief in many of the 72 papers and essays which he wrote on a wide variety of subjects. Most of his experiments were concerned with thermal phenomena and, in devising them, his primary object was to try to attack the caloric theory from as many different points of view as seemed possible.

According to the caloric theory (p. 155), heat was a material substance. Now, *material substance*, or *matter*, is ordinarily defined as that which occupies space and has weight. Hence, if heat were matter, in the ordinary sense of the word, it should have weight — that is, it should be attracted gravitationally by the earth as well as by the particles of all other matter.

Attempts to detect this weight ascribed to heat had been made at various times during the eighteenth century by a number of excellent experimenters. Up to about 1776, the experiments were carried out with solid metals, such as iron, copper, gold, and silver. The usual procedure was to weigh the metal when it was cold and then when it was hot — usually red-hot, or even white-hot, so that the quantity of heat added would be large. The results varied widely. In some cases the metal appeared to weigh more when cold; in other cases, to weigh more when hot; in a few cases, not to change in weight. That the results were conflicting is not surprising, in view of the difficult character of such experiments. Although good balances for weighing were available, there are many other possible sources of error when the same object is weighed at widely different temperatures. Moreover, the methods that had to be used to heat the metals were crude. For instance, one experimenter heated his metal in charcoal by means of a candle and a blowpipe.

Most of these early experimenters were aware that the effects which they had observed might be due, not to any supposed weight of heat, but to accidental factors, such as a current of air rising above the hot metal (a *convection current*, as it later came to be called), or a difference in the lengths of the two balance arms resulting from thermal expansion, or a chemical change occurring in the heated metal. For instance, when a piece of iron is heated in air, loose flakes of iron oxide form on its surface and may fall off during the course of the experiment.

In the last quarter of the century, the modes of attack on this problem began to be influenced by Joseph Black's discoveries of specific and latent heats (Sec. 2). Black had found, for one thing, that the quantity of heat needed to change 1 lb of ice at 32°F into water at the same temperature is equal to that which must be added to 1 lb of water to raise its temperature through 141 (now known to be more nearly 144) Fahrenheit degrees. This suggested that, if heat did have weight, it might be easier to detect it by melting or freezing a substance, for then the quantity of heat added or subtracted would be much larger than in the earlier experiments in which solid metals were merely changed in temperature. In truth, some experiments of this kind had been made nearly a century earlier by Robert Boyle, who reported in his *New Experiments and Observations Touching Cold* (1665) that water weighed first when frozen and then when unfrozen showed "not one grain difference." On the other hand, it was also Boyle who was among the first to lend encouragement to the idea that heat might be a substance having weight, for, in his *Essays of Effluviums* (1673), he showed that a metal gains weight upon calcination and suggested that this might be due to the addition to it of "the material particles of fire."

In 1785, George Fordyce, a British physician who was acquainted with Black's discoveries, carried out careful experiments to determine whether there was any change of weight when water is frozen. Fordyce put some water in a glass globe, sealed and cleaned the globe, and weighed it on a very sensitive balance. He then put the globe in a freezing mixture of ice and common salt and, just when the water was ready to freeze, removed and dried the globe, and weighed it. Replacing the globe in the freezing mixture and waiting until some of the water had frozen, he again removed and weighed it and found an *increase* in weight of about 1 part in 129,000. He repeated this procedure five times; each time more water had frozen and more weight had been gained. When the ice subsequently was allowed to melt, this additional weight was gradually lost.

Count Rumford was much interested in these experiments of Fordyce's and in 1787 set out to repeat them. Twelve years later he described his results in a paper published in the *Philosophical Transactions of the Royal Society*, vol. 89 (1799), p. 179. The edited and annotated version that follows is based on this paper as it is reprinted in *The Complete Works of Count Rumford* (American Academy of Arts and Sciences, Boston, 1870–75), vol. II, pp. 1–16.

AN INQUIRY CONCERNING THE WEIGHT ASCRIBED TO HEAT

by

Benjamin Thompson (Count Rumford)

The various experiments which have hitherto been made with a view to determine the question, so long agitated, relative to the weight which has been supposed to be gained, or to be lost, by bodies upon their being heated, are of a very delicate nature and are liable to many errors, not only on account of the imperfections of the instruments used, but also because of effects, much more difficult to appreciate, arising from the vertical [convection] currents in the atmosphere, caused by the hot or cold body which is placed in the balance. It is not at all surprising that opinions have been so much divided, relative to a fact so very difficult to ascertain.

It is a considerable time since I first began to meditate upon this subject, and I have made many experiments with a view to its investigation; and in these experiments I have taken all those precautions to avoid errors which a knowledge of the various sources of them, and an earnest desire to determine a fact which I conceived to be of importance to be known, could inspire; but though all my researches tended to convince me more and more that *a body acquires no additional weight upon being heated*, or, rather, that heat has no effect whatever on the weights of bodies, I have been so sensible of the delicacy of the inquiry that I was for a long time afraid to form a decided opinion upon the subject.

Being much struck with the experiments recorded in the [*Philosophical*] *Transactions of the Royal Society*, vol. LXXV [1785], made by Dr. Fordyce, on the weight said to be acquired by water upon being frozen; and being possessed of an excellent balance, belonging to his Most Serene Highness the Elector Palatine Duke of Bavaria; early in the beginning of the winter of the year 1787 — as soon as the cold was sufficiently intense for my purpose — I set about to repeat those experiments, in order to convince myself whether the very extraordinary fact related by Dr. Fordyce might be depended on. With a view to removing, as far as was in my power, every source of error and deception, I proceeded in the following manner.

Having provided a number of glass bottles, of the form and size of what in England is called a Florence flask — blown as thin as possible — and of the same shape and dimensions, I chose from amongst them two, which, after using every method I could imagine of comparing them, appeared to be so much alike as hardly to be distinguished from each other.

Into one of these bottles, which I shall call *A*, I put 4107.86 grains [about 0.59 lb avoirdupois] of pure distilled water, which filled it about half full, and into the other, *B*, I put an equal weight of weak spirit of wine [alcohol]. After sealing both bottles hermetically, I washed them, and wiped them perfectly clean and dry on the outside. I then hung them from the arms of the balance and placed the balance in a large room, which for some weeks had been regularly heated every day by a German stove, and in which the air was kept up to the temperature of 61°F, with very little variation. Having suffered the bottles, with their contents, to remain in this situation till I conceived they must have acquired the temperature of the circumambient air, I wiped them afresh, with a very clean, dry cambric handkerchief, and brought them into the most exact equilibrium possible, by attaching a small piece of very fine silver wire to the arm of the balance holding the lighter bottle.

Having suffered the apparatus to remain in this situation about 12 hours longer, and finding no alteration in the relative weights of the bottles — they continuing all this time to be in the most perfect equilibrium — I now removed them to a large uninhabited room, fronting the north, in which the air, which was very quiet, was at the temperature of 29°F, the air outdoors being at the same time at 27°F; and going out of the room, and locking the door after me, I suffered the bottles to remain 48 hours, undisturbed, in this cold room, attached to the arms of the balance as before.

As the expiration of that time, I entered the room — using the utmost caution not to disturb the balance — and, to my great surprise, found that bottle *A* very sensibly preponderated. The water in this bottle was completely frozen into one solid body of ice; but the spirit of wine, in bottle *B*, showed no signs of freezing.

I now very cautiously restored the equilibrium by adding small pieces of the very fine wire of which gold lace is made to the arm of the balance from which bottle *B* was suspended, and I found that bottle *A* had augmented its weight by 1/35,904 part of its whole weight at the beginning of the experiment. The initial weight of the bottle and contents was 4811.23 grains (the bottle weighed 703.37 grains), and it now required 134/1000 part of a grain, added to the opposite arm of the balance, to counterbalance it.

Having had occasion, just at this time, to write to my friend, Sir Charles Blagden, upon another subject, I added a postscript to my letter, giving him a short account of this experiment, and telling him how *"very contrary to my expectation"* the result of it had turned out; but I soon after found that I had been too hasty in my communication. Sir Charles, in his answer to my letter, expressed doubts respecting the fact; but, before his letter had reached me, I had learned from my own experience how very dangerous it is in philosophical investigations to draw conclusions from single experiments.

Having removed the balance, with the two bottles attached to it, from the cold to the warm room (which still remained at the temperature of 61°F), I waited until the ice in bottle *A* had been totally reduced to water and had acquired the temperature of the surrounding air. The two bottles, after being wiped perfectly clean and dry, were found to weigh as at the beginning of the experiment, before the water was frozen.

This experiment, being repeated, gave nearly the same result — the water appearing when frozen to be heavier than in its liquid state. But some irregularity in the manner in which the water lost this additional weight when it was afterward thawed, and also a sensible difference in the weight apparently acquired in the different trials, led me to suspect that the experiment could not be depended on for deciding the fact in question. I therefore set about to repeat it, with some variations and improvements. But before I give an account of my further investigations relative to this subject, it may not be amiss to mention the method I pursued for discovering whether the appearances mentioned in the foregoing experiments might not arise from the imperfections of my balance.

My suspicions respecting the accuracy of the balance arose from a knowledge — which I acquired from the maker — of the manner in which it was constructed. The three principal points of the balance having been determined, as nearly as possible, by measurement, the axes of motion were firmly fixed in their places, in a straight line. After the beam was finished and its two arms brought into equilibrium, the balance was proved [tested] by hanging weights, which were known to be exactly equal, from the ends of its arms.

If with these weights the balance remained in equilibrium, this was considered as a proof that the beam was just; but if one arm was found to preponderate, the other was gradually lengthened, by beating it upon an anvil, until the difference of the lengths of the arms was reduced to nothing, or until the balance remained in equilibrium when equal weights were suspended from the two arms. Care was taken before each trial to bring the two ends of the beam into equilibrium by reducing with a file the thickness of the arm that had been lengthened.

By this method of constructing balances one may obtain the most perfect equality in the lengths of the arms, and consequently the greatest possible accuracy, especially if the balance is used at a time when the temperature of the air is the same as when the balance was made. But it may have happened that, in order to bring the arms of the balance to the same length, one of them had to be hammered much more than the

> other, and I suspected that the texture of the metal forming the two arms might possibly be rendered so far different by this operation as to occasion a difference in their amounts of expansion when heated. This difference might occasion a sensible error in the balance when, being charged with a large weight, it should be exposed to a considerable change of temperature.
>
> To determine whether the apparent augmentation of weight in the afore-mentioned experiments arose in any degree from this cause, I had only to repeat the experiment, causing the two bottles *A* and *B* to exchange places upon the arms of the balance; but, as I had already found a sensible difference in the results of different repetitions of the same experiment, made as nearly as possible under the same circumstances, and as it was above all things of importance to ascertain the accuracy of my balance, I preferred making a particular experiment for that purpose.

In a passage omitted here, Rumford says that, in planning this test of the balance, his first idea had been to use two equal glass globes, filled with mercury. But he feared that, despite all his precautions, moisture had deposited on the glass flasks in the preceding experiments. So he decided to use two equal, solid brass globes, "well gilt and burnished"; for he had previously found that moisture did not deposit on a metal surface that had been gilded.

Having suspended these brass globes from the two arms of the balance by fine wires, he let them stand for a day in the room at 61°F, then carefully balanced them and, finally, removed them to a room at 26°F, where they were left all night.

> The result of this trial furnished the most satisfactory proof of the accuracy of the balance; for, upon entering the cold room, I found the equilibrium as perfect as at the beginning of the experiment. Having thus removed my doubts respecting the balance, I now resumed my investigations relative to the augmentation of weight which liquids have been said to acquire upon being frozen.
>
> In my experiments, I had, as I then imagined, guarded as much as possible against every source of error and deception. The bottles being of the same size, neither any occasional alteration in the pressure of the atmosphere during the experiment, nor the necessary and unavoidable difference in the densities of the air in the hot and in the cold rooms in which they were weighed, could affect their apparent weights; and their shapes and surface areas being the same, and as they remained for such a considerable length of time at the high and low temperatures to which they were exposed, I flattered myself that the quantities of moisture remaining attached to their surfaces could not be so different as sensibly to affect the results of the experiments. But, in regard to this last circumstance, I afterwards found reason to conclude that my opinion was erroneous.

> Admitting the fact stated by Dr. Fordyce — and which my experiments had hitherto rather tended to corroborate than to contradict — I could not conceive any other cause for the augmentation of the apparent weight of water upon freezing than the loss of so large a proportion [144 Btu/lb] of its latent heat as that liquid is known to evolve when it freezes; and I concluded that, if the loss of latent heat added to the weight of one body, it must of necessity produce the same effect on another, and consequently, that the augmentation of the quantity of heat must in all bodies and in all cases diminish their apparent weights.

Rumford says (p. 160) that he began these experiments with a tendency toward the conviction that heat had no effect whatever on the weights of objects. Now we find him consciously shifting to the opposite point of view; he accepts Fordyce's result, which his own experiment has seemed to confirm, and proceeds to generalize it so as to apply to any body heated or cooled in any manner whatever.

It seems to be a fairly common belief that a well-trained scientist always approaches his scientific problems with an entirely open mind — without preconceived opinions and prejudices. Was Rumford in this respect a poor scientist? Or is it possible that no inquiry, of any kind, can be planned or gotten under way until some selection of subject matter has been made; and that such selection requires some assumption, or preconception, or prejudice, which both guides the inquiry and delimits its subject matter? Is it possible that preconceived opinions about, say, certain relations may increase our chances of discovering these relations, if they exist? However, if the answer is in the affirmative, certainly we would want to add that the investigator must be willing to abandon his preconceived opinions if they are not supported by the results of subsequent observation and experiment.

Having adopted, at least tentatively, the assumption that water gains in weight upon freezing, Rumford next sets out to determine whether liquids change in weight when they lose heat merely by cooling, without freezing. Here he is returning to a method similar to that employed by the early eighteenth-century experimenters (p. 156). But again the work of Black has suggested an improved and more sensitive test. Instead of weighing a single substance, as did the early experimenters, Rumford compares the weights, before and after cooling, of *two* substances — water and mercury — that have *widely different specific heats.*

> To determine whether this is actually the case or not, I made the following experiment. Having provided two bottles, as nearly alike as possible, and in all respects similar to those made use of in the preceding experiments, into one of them I put 4012.46 grains [about 0.57 lb

> avoirdupois] of water, and into the other an equal weight of mercury. Sealing them hermetically and suspending them from the arms of the balance, I suffered them to acquire the temperature of my room, 61°F. After bringing them into a perfect equilibrium with each other, I removed them into a room in which the air was at the temperature of 34°F, where they remained 24 hours. But there was not the least appearance of either of them acquiring or losing any weight.
>
> Here it is very certain that the quantity of heat lost by the water was considerably larger than that lost by the mercury, for the specific heats of water and mercury have been determined to be to each other as 1000 to 33; but this difference in the quantities of heat lost produced no sensible difference in the weights of the liquids in question.
>
> Had any difference of weight really existed, had it been no more than *one millionth* part of the weight of either of the liquids, I should certainly have discovered it; and had it amounted to so much as 1/700,000 part of that weight, I should have been able to have measured it, so sensitive and so very accurate is the balance which I used in these experiments.

There is no indication that Rumford repeated this experiment. Surely he must have, in view of his earlier comment on "how very dangerous it is . . . to draw conclusions from single experiments" and because of his willingness (expressed in the next paragraph) again to question the validity of his earlier, freezing experiments, which, as we know, he repeated at least once.

This readiness to question the earlier experiments also suggests that Rumford actually had not shifted wholeheartedly to Fordyce's view that heat had weight. A scientist, such as Rumford, is even in his science still a human being. Logical considerations may lead him to change to and even act upon a belief that is repugnant to him, but wholehearted conversion is difficult because of the emotional factors involved.

> I was now much confirmed in my suspicions that the apparent augmentation of the weight of the water upon its being frozen, in the experiments before related, arose from some accidental cause; but I was not able to conceive what that cause could possibly be, unless it were either a larger quantity of moisture deposited on the external surface of the bottle containing the water than on the surface of that containing the spirit of wine, or some vertical current or currents of air caused by the bottles, or one of them not being exactly at the temperature of the surrounding atmosphere.
>
> I had foreseen and, as I thought, guarded sufficiently against these accidents by making use of bottles of the same size and form, which were blown of the same kind of glass and at the same time, and by exposing them during the experiments for a considerable length of time to the different temperatures which alternately they were made to acquire.

> However, I did not know the relative conducting powers of ice and of spirit of wine with respect to heat — in other words, the degrees of facility of difficulty with which they acquire the temperature of the medium in which they are exposed, or the time taken up in that operation. Consequently, I was not *absolutely certain* as to the equality of the temperatures of the contents of the bottles at the time when their weights were compared. So I determined now to repeat the experiments, with such variations as should put the matter in question out of all doubt.

By *conduction* of heat is meant the transfer of heat from places of higher to places of lower temperature, occurring either through a body or from one body to another in contact with it, and without any visible movement of the parts of the bodies. It is to be distinguished from *convection*, which occurs only in liquids and gases, and in which the fluid moves as a result of pressure differences, thus carrying its heat with it. The pressure differences may be brought about in many different ways; a common cause is the local changes of density that result from unequal warming or cooling of the fluid.

A way to measure the relative rates at which heat is conducted through various *solid* substances was first suggested by Benjamin Franklin, and measurements by his method were made in 1789 by J. Ingenhausz. But it was Rumford, in an essay published in 1797, who showed that water and various other *nonmetallic liquids* are poor conductors of heat, and that the transfer of heat through them occurs mainly by convection. Because of the disturbing effects of convection, it is much more difficult to investigate conduction in liquids and gases than in solids.

> I was more anxious to assure myself of the real temperatures of the bottles and their contents because any difference in their temperatures might vitiate the experiment, not only by causing unequal currents in the air, but also by causing, at the same time, a larger or smaller quantity of moisture to remain attached to the glass. To remedy these evils, and also to render the experiment more striking and satisfactory in other respects, I proceeded in the following manner.
>
> Having provided three bottles, *A*, *B*, and *C*, as nearly alike as possible, and resembling in all respects those already described, into the first, *A*, I put 4214.28 grains [about 0.60 lb avoirdupois] of water and a small thermometer, made on purpose for the experiment and suspended in the bottle in such a manner that its bulb remained in the middle of the mass of water; into the second bottle, *B*, I put a like weight of spirit of wine, with a like thermometer; and into the bottle *C* I put an equal weight of mercury.
>
> These bottles, being all hermetically sealed, were placed in a large room, in a corner far removed from the doors and windows, and where

the air appeared to be perfectly quiet. After they had remained there for more than 24 hours — the temperature of the room being kept at 61°F during all that time with as little variation as possible — the contents of bottles *A* and *B* appeared, by their inclosed thermometers, to be exactly at the same temperature. The bottles were then wiped with a very clean, dry, cambric handkerchief and were afterwards suffered to remain exposed to the free air of the room a couple of hours longer, in order that any inequalities in the quantities of heat or of the moisture attached to their surfaces, which might have been occasioned by the wiping, would be corrected by the operation of the atmosphere by which they were surrounded. Then all were weighed, being brought into the most exact equilibrium with each other by attaching small pieces of very fine silver wire to the necks of those bottles that were the lighter.

This being done, the bottles were taken to a room in which the air was at 30°F. Bottles *A* and *B* were hung from the arms of the balance, and bottle *C* was hung, at an equal height, from the arm of a stand constructed for that purpose and placed as near the balance as possible, a very sensitive thermometer being suspended beside it.

At the end of 48 hours, I reëntered the room, opening the door very gently for fear of disturbing the balance. I had the pleasure of finding that the three thermometers (that in bottle *A* was now inclosed in a solid cake of ice) all stood at the same point, 29°F, and that bottles *A* and *B remained in the most perfect equilibrium.*

To assure myself that the play of the balance was free, I now approached it very gently and caused it to vibrate; and I had the satisfaction of finding, not only that it moved with the utmost freedom, but also, when its vibration ceased, that it rested precisely at the point from which it had set out.

I now removed bottle *B* from the balance, and put bottle *C* in its place; and I found that it likewise had the same apparent weight as at the beginning of the experiment, being in the same perfect equilibrium with bottle *A* as at first.

I afterwards removed the whole apparatus into a warm room and, causing the ice in bottle *A* to thaw, let the three bottles remain there till they and their contents had acquired the exact temperature of the surrounding air. I then wiped them very clean and, comparing them, found that their weights remained unaltered.

This experiment I afterwards repeated several times, and always with precisely the same result — the water *in no instance* appeared to gain, or to lose, the least weight upon being frozen or upon being thawed; nor were the relative weights of the liquids in either of the other bottles in the least changed by the various temperatures to which they were exposed.

If the bottles were weighed at a time when their contents were *not precisely of the same temperature*, they would frequently appear to have gained, or to have lost, some weight; but this doubtless was due to the vertical [convection] currents which they produced in the atmosphere

> upon being heated or cooled in it, or to unequal quantities of moisture attached to the surfaces of the bottles, or to both these causes operating together.
>
> As I knew that the conducting power of mercury with respect to heat is considerably larger than that of either water or spirit of wine, while its specific heat is much less than that of either of them, I did not think it necessary to inclose a thermometer in the bottle *C*, which contained the mercury; for it was evident that, when the contents of the other two bottles should appear, by their thermometers, to have arrived at the temperature of the medium in which they were exposed, the contents of the bottle *C* could not fail to have acquired it also, and even to have arrived at it before them; for the time needed to heat or to cool any body increases, *caeteris paribus*, *directly* with the specific heat of the body, and *inversely* with its conducting power.

The specific heats of water, alcohol and mercury are 1, 0.6 and 0.03 Btu/lb °F, respectively. After Rumford's time, Joseph Fourier (1822) showed that the "conducting power" of a substance, now usually called its *thermal conductivity*, can be most usefully defined as the quantity of heat, expressed in British thermal units, that will be transferred each second between opposite faces of a cube of that substance 1 ft on an edge when the temperature difference of the opposite faces is 1°F. The thermal conductivities of water, alcohol, and mercury are now known to be in the ratios of 1.0 to 0.35 to 12. Other things being equal, the *time* required to raise or lower the temperature of an object by some given amount is directly proportional to the specific heat and inversely proportional to the thermal conductivity of the substance comprising the object.

> The bottles were attached to the balance arms by silver wires about 2 inches long, with hooks at the ends of them; and, in removing and changing the bottles, I took care not to touch the glass. I likewise avoided upon all occasions, and particularly in the cold room, coming near the balance with my breath, or touching it, or any part of the apparatus, with my naked hands.
>
> Having determined that water does not acquire or lose any weight upon being changed from a state of liquid to that of ice, and *vice versa*, I shall now take my final leave of a subject which has long occupied me, and which has cost me much pains and trouble; for I am fully convinced, from the results of the afore-mentioned experiments, that if heat be in fact a *substance*, or matter — a fluid *sui generis*, as has been supposed — which, passing from one body to another, and being accumulated, is the immediate cause of the phenomena we observe in heated bodies, it must be something so infinitely rare, even in its most condensed state, as to baffle all our attempts to discover its weight. And if the opinion which

> has been adopted by many of our ablest philosophers, that heat is nothing more than an intestine [internal] vibratory motion of the constituent parts of heated bodies, should be well founded, it is clear that the weights of bodies can in no wise be affected by such motion.
>
> It is, no doubt, upon the supposition that heat is a substance distinct from the heated body, and which is accumulated in it, that all the experiments have been undertaken with a view to determine the weight which bodies have been supposed to gain or to lose upon being heated or cooled; and it is toward this supposition — but without, however, adopting it entirely, as I do not conceive it to be sufficiently proved — that all my researches have been directed.
>
> The experiments with *water* and with *ice* were made in a manner which I take to be perfectly unexceptionable, in which no foreign cause whatever could affect the results of them; and since the quantity of heat which water is known to part with upon freezing is so considerable, if this loss has no effect upon its apparent weight, it may be presumed that we shall never be able to contrive an experiment by which we can render the weight of heat sensible.

We omit the concluding paragraphs, in which Rumford explains in some detail why he believed his experiments with ice and water to be the most favorable that could be contrived for detecting the weight of heat. Part of his argument is similar to that given in our comments on page 49. He closes the paper with the remark that follows.

> I think we may safely conclude that ALL ATTEMPTS TO DISCOVER ANY EFFECT OF HEAT UPON THE APPARENT WEIGHTS OF BODIES WILL BE FRUITLESS.

One may question whether Rumford was justified in making a conclusion of such breadth and finality. For instance, A. Tilloch, in the *Philosophical Magazine*, vol. 9 (1801), p. 158, of which periodical he was then the editor, tried to show that Rumford's experiments, as well as the earlier direct attempts to weigh heat, involved a fallacy and were not conclusive. Tilloch's criticism was based on the fact that all the weighings were made in air, which, as is well known, exerts a buoyant effect on any object immersed in it. This vertically upward, or buoyant, force is, in accordance with Archimedes' principle of buoyancy, equal in magnitude to the weight of the air displaced by the object. When an object is weighed on a balance, both the object and the balancing weights are of course buoyed up by the air. However, if the volume of air displaced by the object differs from that displaced by the weights, the buoyant effects upon the two sides of the balance are different. Under this circumstance, the balancing weights do not accurately represent the *true weight* of the object, that is, its weight in a vacuum. For instance, a bundle of feathers that weighs 1 lb in a vacuum has an *apparent weight* of about 0.99 lb in air.

Tilloch illustrated his argument by citing the example of objects immersed in water. If a bit of cork is attached to a piece of metal, the true weight of the combination will of course be larger than that of the metal alone. But if this combination of metal and cork is weighed when immersed in water, its apparent weight will be found to be *smaller* than that of the metal alone. One can show that this will always be true when one object of the combination is of larger density, and the other is of smaller density, than the water. If the material attached to the immersed metal has the *same* density as water, the apparent weight of the combination will be the same as that of the metal alone.

Now, argued Tilloch, suppose that heat actually does have weight, but that its density is less than that of air. Then, when heat is removed from an object, as in cooling or freezing it, the weight of the object in air would appear to increase, just as the weight of the metal in water would appear to increase if the cork were detached from it. This was precisely what Fordyce had observed: the weight of his liquid appeared to increase when heat was removed from it. It should be noted that Tilloch had here provided a way to explain an increase in the weight of an object upon losing heat without having to resort to the *ad hoc* assumption that heat has *negative* weight. However, his argument is not valid unless it is assumed that the volume of air displaced by an object containing heat is larger than the volume displaced after some of the heat has been removed.

Rumford, in his final and very accurate experiments, observed no change in the weight of a liquid when heat was subtracted from or added to it. But Tilloch could also explain this result, simply by assuming that the density of heat was equal to, and not smaller than, the density of air.

Tilloch's ingenious argument provides a good illustration of how difficult it is to devise a simple type of experiment that will settle a question, such as that about the weight of heat, in a conclusive and unambiguous manner. However, his argument involved assumptions that Rumford could have questioned, in view of the procedure that he had used in his final weighings. Moreover, Tilloch's essential objection could have been removed by repeating the weighings in a vacuum, although such experiments would not have been easy to carry out.

Even if Rumford had made the weighings in a vacuum, the calorists could still have argued either that heat was "weightless," and yet had all the other properties characteristic of a material substance, or else that it was too "subtle" for its weight to be detected. This raises the important question whether it is useful and meaningful to assume the existence of any entity or property, once it has become clear that there is no way whatever to detect it.

Joseph Black had been of the opinion that heat did not have weight, and he had considered this to be one of the chief objections to the caloric theory (p. 153). But to many other scientists and philosophers of the eighteenth century, this would not have been regarded as a serious objection. It was currently believed that there was a small class of "imponderable substances," which at the time included light, electricity and magnetism, that, unlike ordinary matter, were not subject to gravitational attraction, at least to any observable extent. Yet, on the assumption that these "substances" exhibited certain other familiar properties of ordinary matter, the various phenomena known at the time could be connected fairly satisfactorily, and new phenomena often could be successfully predicted. Thus, the question whether heat had weight was deemed less critical in trying to distinguish between the caloric and mode-of-motion theories than was, for example, the question of the validity of the principle of conservation of heat, which was the most basic postulate of the caloric theory. Rumford was able to throw some light on this latter question in other experiments (Sec. 4) carried out as part of his program of attack on the caloric theory.

Although Rumford's experiments on the weight of heat may not have been completely conclusive, they undoubtedly were the best of all the experiments carried out on this subject. Indeed, the present paper has been characterized as describing a magnificent experimental technique and a classic example of what scientific investigation is at its best.

4. COUNT RUMFORD'S EXPERIMENTS ON THE SOURCE OF THE HEAT THAT IS EXCITED BY FRICTION

The most celebrated experiments carried out by Count Rumford were those concerned with the heat produced during the boring of cannon. The caloric theory had been found especially helpful in explaining and predicting phenomena in which heat passes from one body to another by conduction — as when liquids are mixed or when a substance placed over a fire is warmed, melted, or vaporized. For such phenomena, it is worth noting, one can safely assume that there is no creation or destruction of heat during its passage from one object to another, or from a fire to an object.

But whence comes the heat when an object is warmed, not by fire, but by rubbing or hammering it? The supporters of the caloric theory believed that they could also answer this question satisfactorily, and still retain their principle that heat can be neither created nor destroyed.

But there were other investigators who thought that the mode-of-motion theory offered a better explanation. As early as 1620, Francis Bacon, in the Second Book of his *Novum Organum*, expressed the idea that *new* heat comes into existence when an object is rubbed or hammered, and from this he concluded that "heat itself, its essence and quiddity, is motion and nothing else." The same view was expressed later in the seventeenth century by Boyle and by Hooke, and also by many philosophers of the period. Early in the eighteenth century, the philosopher John Locke, in his *Elements of Natural Philosophy* (1722), supported the idea that heat is a kind of motion by citing various ways in which it is produced; for example, "the axle-trees of carts and coaches are often made hot, and sometimes to a degree that it sets them on fire, by the rubbing of the naves of the wheels upon them." "On the other side," he said, "the utmost degree of cold is the cessation of that motion of the insensible particles."

Rumford carried out his cannon-boring experiments at the military arsenal in Munich, of which he was in charge. He reported them in a paper entitled "An Inquiry Concerning the Source of Heat which is Excited by Friction," which he read at a meeting of the Royal Society in January 1798 and later published in the *Philosophical Transactions*, vol. 88 (1798), p. 80. The edited and annotated version that follows is based on the paper as it was reprinted in *The Complete Works of Count Rumford* (American Academy of Arts and Sciences, 1870), vol. I, pp. 471–493.

AN INQUIRY CONCERNING THE SOURCE OF THE HEAT WHICH IS EXCITED BY FRICTION

by

Benjamin Thompson (Count Rumford)

It frequently happens that in the ordinary affairs and occupations of life, opportunities present themselves of contemplating some of the most curious operations of Nature; and very interesting philosophical experiments might often be made, almost without trouble or expense, by means of machinery contrived for the mere mechanical purposes of the arts and manufactures.

I have frequently had occasion to make this observation; and am persuaded that a habit of keeping the eyes open to everything that is going on in the ordinary course of the business of life has oftener led — as it were by accident, or in the playful excursions of the imagination, put into action by contemplating the most common appearances — to useful doubts and sensible schemes for investigation and improvement than all

> the more intense meditations of philosophers in the hours expressly set apart for study.
>
> It was by accident that I was led to make the experiments of which I am about to give an account; and, though they are not perhaps of sufficient importance to merit so formal an introduction, I cannot help flattering myself that they will be thought curious in several respects, and worthy of the honor of being made known to the Royal Society.
>
> Being engaged lately in superintending the boring of cannon in the workshops of the military arsenal at Munich, I was struck with the very considerable degree of heat [temperature] that a brass gun acquires in a short time in being bored, and with the still higher temperature (much higher than that of boiling water, as I found by experiment) of the metallic chips separated from it by the borer.
>
> The more I meditated on these phenomena, the more they appeared to me to be curious and interesting. A thorough investigation of them seemed even to bid fair to give a farther insight into the hidden nature of heat; and to enable us to form some reasonable conjectures respecting the existence, or nonexistence, of an *igneous fluid* — a subject on which the opinions of philosophers have in all ages been much divided.

As Rumford says, he began these experiments "by accident," that is, as the result of what he observed while engaged in his regular work as superintendent of the arsenal at Munich. One might ask whether the making of such experiments would be likely to have occurred accidentally to a person unfamiliar with the currently known facts, experimental methods, and theories about heat or to a person who lacked Rumford's "habit of keeping the eyes open to everything that is going on in the ordinary course of the business of life."

There was nothing extraordinary about his mere observation that heat is produced during the boring of a gun. Since the earliest times it had been known that heat could be developed by friction — as when primitive people made a fire by rapidly rotating a pointed stick inserted in a hole drilled in dry wood. Rumford's feats here were that he noticed the very high temperature quickly acquired by the gun during the boring and saw how further study of this phenomenon might throw new light on the "hidden nature of heat."

By "igneous fluid" Rumford means the "subtle elastic fluid" which, according to the caloric theory, constituted heat. In the literature of his period, the terms "igneous fluid," "heat fluid," "matter of heat," "caloric," "calor," and "heat" were used more or less interchangeably. The term "caloric" actually was not introduced until comparatively late in the history of the conception of heat as a substance, having been coined in 1787 by Lavoisier and other French scientists during a revision of chemical terminology which they carried out at that time. The term "calorimeter," which is still used today to refer to any apparatus for measuring quantities of heat, was coined by Lavoisier in 1789.

> In order that the Society may have clear and distinct ideas of the speculations and reasonings to which these appearances gave rise in my mind, and also of the specific objects of philosophical investigation they suggested to me, I must beg leave to state them at some length, and in such manner as I shall think best suited to answer this purpose.
>
> From *whence comes* the heat actually produced in the mechanical operation above mentioned?
>
> Is it furnished by the metallic chips which are separated by the borer from the solid mass of metal? If this were the case, then, according to the modern doctrines of latent heat and of caloric, the *specific heat* of the parts of the metal, so reduced to chips, ought not only to be changed, but the change undergone by them should be sufficiently large to account for *all* the heat produced.
>
> But no such change had taken place; for I found, upon taking equal weights of these chips and of thin slips separated from the same block of metal by means of a fine saw, and putting them at the same temperature (that of boiling water) into equal weights of cold water initially at the temperature of 59½ °F, the portion of water into which the chips were put was not, to all appearance, heated either less or more than the other portion in which the slips of metal were put. This experiment being repeated several times, the results were always so nearly the same that I could not determine whether any, or what, change had been produced in the metal, *in regard to its specific heat*, by being reduced to chips by the borer.

In boring a cannon, or whenever one solid object is rubbed against another, the rubbing surfaces are abraded, that is, rubbed or cut into dust or chips. Might these chips possibly be the source of the large quantity of heat produced during the boring? If so, asserts Rumford, it follows from the "modern" caloric theory that the specific heat of the chips should be different from that of the metal in bulk. Suppose it were found that the specific heat of the chips was smaller than that of the metal in bulk. Then this could be interpreted to mean that the attractive force was smaller between the chips and caloric than between the bulk metal and caloric, and hence that caloric would be set free during the abrasion. Indeed, this was one way in which the calorists had tried to explain heat produced by friction; yet no one prior to Rumford seemingly had made experiments to determine whether there was any difference in the specific heats of the abraded and the bulk metal.

To find the specific heat of the cannon metal, Rumford here has made use of the technique in calorimetry known as the *method of* *mixtures* (Sec. 2). He took slices of the bulk metal, determined their weight w_b and initial temperature t_b, and then put them in a known weight w_w of water initially at a known temperature t_w. Let t be the observed, equilibrium temperature of the mixture of metal and water. Then the heat lost by the bulk metal is given by the expression $s_b w_b (t_b - t)$, where s_b is the unknown specific heat of the metal; and the heat gained by the water is given by $s_w w_w (t - t_w)$, where s_w is the specific heat of water. Assuming the experiment to have been so devised that the heat lost by the metal was equal to the heat gained by the water, we can write the equation

$$s_b w_b (t_b - t) = s_w w_w (t - t_w). \tag{5}$$

Rumford next repeated this whole method-of-mixtures experiment, this time substituting *chips* bored from the same block of cannon metal for the bulkier slices, but keeping the weights and the initial temperatures the same as before; and he observed the temperature of the mixture of chips and water again to be t, the same as in the preceding experiment. If s_c denotes the specific heat of the metal chips, the equation for this second experiment is

$$s_c w_b (t_b - t) = s_w w_w (t - t_w). \tag{6}$$

By comparing Eqs. (5) and (6) we can conclude, as did Rumford, that the specific heats s_b and s_c are equal.

Suppose it had been found that the specific heat of the chips was not equal to that of the metal in bulk. Then, as Rumford points out, the next question for investigation would have been whether this change in specific heat upon abrasion was "sufficiently large to account for *all* the heat produced." Often an explanation or a hypothesis will turn out to be admissible *qualitatively*, but not *quantitatively*. As a simple example, a very early hypothesis as to the source of solar energy was that the sun is a mass of fuel, such as coal, which is burning and thus emitting energy. This hypothesis passed the qualitative test in that it is true that a burning fuel emits energy. But when, later, our knowledge of fuels, of the size and distance of the sun, and of the energy given off by it was sufficiently complete to make even rough calculations possible, it became clear that the sun, if it were simply a ball of burning fuel, would have been completely consumed long ago. The hypothesis met the qualitative but not the quantitative test.

> As these experiments [on the specific heats of the abraded and bulk metal] are important, it may perhaps be agreeable to the Society to be made acquainted with them in their details. One of them is as follows:
>
> To 4590 grains [0.66 lb] of water, at the temperature of 59½°F (in-

> cluded in this weight was an allowance, reckoned in terms of water, for the heat capacity of the containing tin vessel), were added 1016⅛ grains [0.16 lb] of cannon metal in thin slips, these being at 210°F, the temperature of boiling water at Munich. When they had remained together 1 minute, and had been well stirred about by means of a small rod of light wood, the temperature of the mixture was found to be 63°F. From this experiment the specific heat of the metal, calculated according to the rule given by Dr. Crawford, turns out to be 0.1100 [Btu/lb °F], that of water being 1.0000 [Btu/lb °F].
>
> An experiment was afterwards made with the metallic chips as follows. To the same weight of water as was used in the afore-mentioned experiment, at the same temperature (59½°F), and in the same cylindrical tin vessel, were now put 1016⅛ grains of metallic chips bored out of the same gun from which the slips used in the foregoing experiment were taken, and at the same temperature (210°F). The temperature of the mixture at the end of 1 minute was 63°F, as before. Consequently, the specific heat of these metallic chips is 0.1100 [Btu/lb °F]. Each of the foregoing experiments was repeated three times, and always with nearly the same results.

The "rule given by Dr. Crawford," which Rumford says he used in calculating the specific heats, is essentially the one for the method of mixtures described in our note on page 173; that is, one writes an equation which contains in one member all the quantities representing heat *gained* by the warming bodies and, in the other member, all the quantities representing heat *lost* by the cooling bodies. In the present experiment, the water and its containing vessel are the warming bodies, and the cannon metal is the cooling body. Rumford probably found this rule in Crawford's *Experiments and Observations on Animal Heat, etc.* (ed. 1, 1779; ed. 2, 1788). Although most of the features of the method of mixtures were developed earlier by Black and Irvine (Sec. 2), at least one improvement was made by Crawford; he suggested that the transfer of heat to and from the surrounding air can be reduced by so choosing the values of the initial temperatures of the warming and cooling bodies that the temperature of the mixture will be approximately the same as that of the surrounding air.

Strictly speaking, Rumford's demonstration that the chips and bulk metal have the same specific heat at the same temperature did not constitute a complete refutation of the calorists' explanation of how heat was developed by friction. To show that the two specific heats are equal may have been *necessary*, but it was not *sufficient*. For a more conclusive test, it was still necessary to show that equal weights of the chips and bulk metal always contained equal *quantities of heat* when at the same temperature. The calorists could have said that, even though the chips and bulk metal had the same specific heats at the same temperature, yet the bulk metal contained more latent heat than the chips, the difference having been evolved during abrasion. A possible test of this contention would have been to measure the quantities of heat needed to *melt* equal weights of chips and of bulk metal. If these quantities of heat were found equal, and if it were granted that the resulting liquids were in all respects exactly the same, then one could conclude that equal weights of the chips and bulk metal contained equal quantities of heat at the same temperature. However, we shall see that Rumford did not bother to carry out such an experiment; a possible reason for this is suggested in our note on page 188.

One supporter of the caloric theory asserted, in 1830, that none of the afore-mentioned experiments on specific heats had any significance in determining whether or not the heat evolved during boring came from the metal chips. He contended that this heat could have come, not from the chips, but from the layer of bulk metal in contact with the borer. The large force to which this layer was subjected would tend to compress it and increase its density; and it had long been known that when any piece of metal is compressed, as by hammering it, heat is evolved. This heat, the calorists said, was squeezed out of the metal as a result of the compression. Thus, in the boring of the cannon, successive fresh layers of cannon metal were exposed to compression as the result of the abrasion, and hence each layer in succession would release a certain quantity of heat. If any changes in density or specific heat occurred, it would therefore be confined to the surface layer of the bulk metal, and this Rumford did not test.

The passages that follow will be easier to interpret if it is remembered that Rumford and some other scientists of his period used the expression "latent heat" to refer, not solely to heats of fusion and vaporization, as Black had done (Sec. 2), but also to heat which the calorists assumed was stored in an inactive form in any substance and released upon rubbing or hammering it.

> It is evident that the heat produced could not possibly have been furnished at the expense of the latent heat of the metallic chips. But, not being willing to rest satisfied with these trials, however conclusive they appeared to me to be, I had recourse to the following still more decisive experiments.
>
> Taking a cannon (a brass six-pounder), cast solid, and rough as it came from the foundry (see Fig. 1 in Plate II), and fixing it horizontally in the machine used for boring, and at the same time finishing the outside of the cannon by turning (see Fig. 2), I caused its extremity to be cut off and the metal in that part to be turned down to form a solid cylinder, 7¾ inches in diameter and 9⁸⁄₁₀ inches long. This cylinder, when fin-

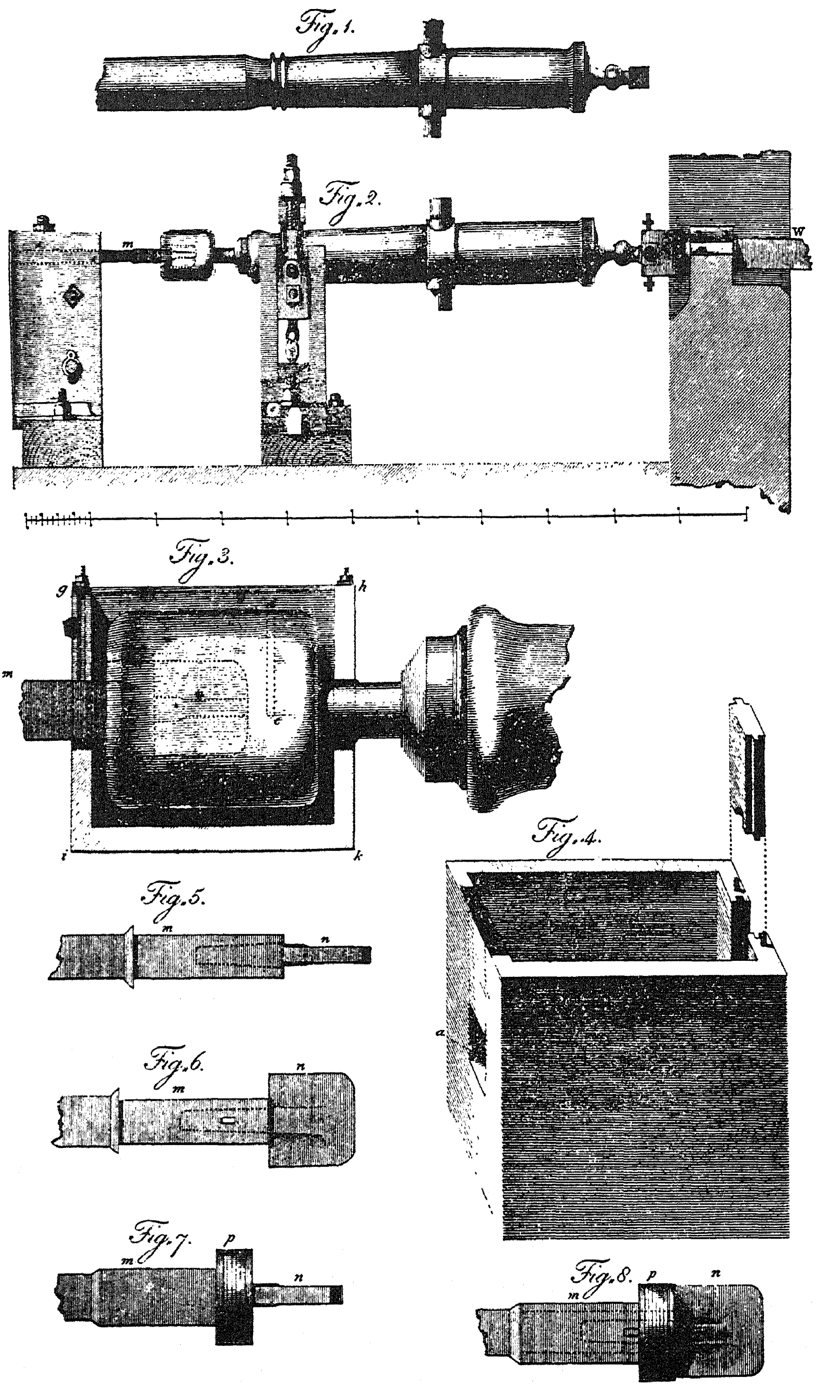

PLATE II. Rumford's diagrams of his apparatus.

> ished, remained joined to the rest of the metal (that which, properly speaking, constituted the cannon) by a small cylindrical neck only 2⅕ inches in diameter and 3⁸⁄₁₀ inches long.
>
> This short cylinder, which was supported in its horizontal position and could be turned round its axis by means of the neck that united it to the cannon, was now bored with the horizontal borer used in boring cannon; but its bore, which was 3.7 inches in diameter, instead of being continued through its whole length (9.8 inches) was only 7.2 inches in length; so that a solid bottom was left to this hollow cylinder, which bottom was 2.6 inches in thickness. This cavity is represented by dotted lines in Fig. 2 and also in Fig. 3, where the cylinder is represented on an enlarged scale.
>
> This cylinder was designed for the express purpose of generating heat *by friction*, by forcing a blunt borer against the solid bottom of the cylinder at the same time that the latter was turned round its axis by the force of horses. In order that the temperature of the cylinder might from time to time be measured, a small round hole (see *de*, Fig. 3), only 0.37 inch in diameter and 4.2 inches in depth, was made in it for the purpose of introducing a small cylindrical mercurial thermometer. This hole was on one side, in a direction perpendicular to the axis of the cylinder, and ended in the middle of the solid bottom.
>
> The volume of the hollow cylinder, exclusive of the cylindrical neck by which it remained united to the cannon, was 385¾ cubic inches, English measure, and it weighed 113.13 lb avoirdupois; this I found on weighing it at the end of the course of experiments, and after it had been separated from the cannon.
>
> *Note.* For fear I should be suspected of prodigality in the prosecution of my philosophical researches, I think it necessary to inform the Society that the cannon I made use of in this experiment was not sacrificed to it. The short hollow cylinder which was formed at the end of it was turned out of a cylindrical mass of metal, about 2 feet in length, projecting beyond the muzzle of the gun, called in the German language the *verlorner kopf* (the head of the cannon to be thrown away) and which is represented in Fig. 1. This original projection, which is cut off before the gun is bored, is always cast with it, in order that, by means of its weight on the metal in the lower part of the mould during the time it is cooling, the gun may be the more compact in the neighborhood of the muzzle, where, without this precaution, the metal would be apt to be porous, or full of honeycombs.

The reader who is acquainted with the general history of this period may be able to suggest reasons why Rumford seems to feel it necessary to explain that the cannon was not destroyed in the course of these philosophical researches. By "philosophical research" he means what we, today, often call "pure research," as distinguished from research in engineering and technology.

Experiment No. 1

This experiment was made in order to ascertain how much heat was actually generated by friction when the blunt steel borer was so forcibly shoved (by means of a strong screw) against the bottom of the bore of the cylinder that the pressing force on it was equivalent to the weight of about 10,000 lb avoirdupois and the cylinder was being turned round on its axis (by the force of horses) at the rate of about 32 times in a minute. This machinery, as it was put together for the experiment, is represented by Fig. 2. Here *w* is a strong horizontal iron bar, connected with proper machinery carried round by horses, by means of which the cannon was made to turn round its axis.

To prevent, as far as possible, the loss of any part of the heat that was generated in the experiment, the cylinder was well covered up with a fit coating of thick and warm flannel, which was carefully wrapped round it, and defended it on every side from the cold air of the atmosphere. This covering is not shown in Fig. 2.

I ought to mention that the borer was a flat piece of hardened steel, 0.63 of an inch thick, 4 inches long, and nearly as wide as the cavity of the bore of the cylinder, namely, 3½ inches. Its corners were rounded off at its end, so as to make it fit the hollow bottom of the bore; and it was firmly fastened to the iron bar *m* which kept it in its place. The area of the surface by which its end was in contact with the bottom of the bore of the cylinder was nearly 2⅓ square inches. This borer, which is distinguished by the letter *n*, is represented in most of the figures.

At the beginning of the experiment, the temperature of the air in the shade, as also that of the cylinder, was 60°F. At the end of 30 minutes, when the cylinder had made 960 revolutions about its axis, the horses being stopped, a cylindrical mercurial thermometer, whose bulb was $^{32}/_{100}$ of an inch in diameter and 3¼ inches in length, was introduced into the hole *de* in the side of the cylinder; the mercury rose almost instantly to 130°F.

The heat could not be supposed to be quite equally distributed in every part of the cylinder, yet, as the length of the bulb of the thermometer was such that it extended from the axis of the cylinder to near its surface, the temperature indicated by it could not be very different from the *mean temperature* of the cylinder; and it was on this account that a thermometer of that particular form was chosen for this experiment.

To see how fast the heat escaped from the cylinder (in order to be able to make a probable conjecture respecting the quantity given off by it during the time the heat generated by the friction was accumulating), the machinery standing still, I suffered the thermometer to remain in its place nearly three quarters of an hour, observing and noting down, at small intervals of time, the temperature indicated by it. [See Table 1.]

As Rumford states, the boring in experiment No. 1 was carried on for 30 min, during which time the temperature of the cylinder rose from

60° to 130°F. The cylinder was wrapped in flannel, but as the cooling data in Table 1 show, some of the heat evolved during the boring escaped to the surrounding objects and atmosphere. From these cooling data, Rumford could have estimated how much above 130°F the final temperature of the cylinder would have been if it had been perfectly insulated from the surroundings. However, we see from Table 1 that, at the highest temperatures, the time-rate of cooling never exceeded one degree per minute, and at temperatures near that of the air (60°F) the rate was much smaller. So he does not bother to complete the calculations or to comment further on these cooling data.

[TABLE 1. Cooling data.]

Total time, in minutes, since machinery was stopped	Temperature, in degrees Fahrenheit, as shown by the thermometer
[0]	[130°]
4	126°
5	125°
7	123°
12	120°
14	119°
16	118°
20	116°
24	115°
28	114°
31	113°
34	112°
37½	111°
41	110°

Having taken away the borer, I now removed the metallic dust, or, rather, scaly matter, which had been detached from the bottom of the cylinder by the blunt steel borer. I carefully weighed this dust and found its weight to be 837 grains.

Is it possible that the very considerable quantity of heat produced in this experiment (a quantity which actually raised the temperature of above 113 lb of gun metal at least 70 Fahrenheit degrees, and which, of course, would have been capable of melting 6½ lb of ice) could have been furnished by so inconsiderable a quantity of metallic dust? And this merely in consequence of *a change* of its specific heat?

As the weight of this dust (837 grains) amounted to no more than 1/948th part of that of the cylinder, the dust would have had to give up a quantity of heat equal to that which it would lose in cooling through 948 Fahrenheit degrees to have been able to raise the temperature of the

> cylinder 1°; and consequently it would have had to give up a quantity corresponding to a cooling through 66,360 Fahrenheit degrees to have produced the effects that were actually observed in the experiment!

Rumford had previously found the specific heat of the cannon metal to be 0.11 Btu/lb °F. The cylinder weighed 113 lb, and its temperature during boring increased *at least* (130–60) °F, or 70 Fahrenheit degrees. So the quantity of heat entering the cylinder during boring was *at least* (0.11 Btu/lb °F) × 113 lb × 70°F, or 870 Btu.

That this really is a considerable quantity of heat is strikingly illustrated by Rumford's remark that it is sufficient to melt 6.5 lb of ice. Using the modern value of the heat of fusion of ice, namely, 144 Btu/lb, we see that the weight of ice that would be melted by 870 Btu of heat is 870 Btu/(144 Btu/lb), or about 6.0 lb. Rumford, in arriving at the larger figure of 6.5 lb for the weight of ice that would be melted, probably took into account the fact that, if a correction for cooling had been made, the value for the final temperature of the cylinder would have exceeded 130°F. Moreover, in his day the heat of fusion of ice was often taken to be Black's value of 141 Btu/lb, instead of the more correct modern value of 144 Btu/lb.

In saying that the metallic dust would have had to cool through 66,360 Fahrenheit degrees to have produced the effects observed, Rumford is not implying that the dust is to be thought of as actually having undergone this drop in temperature. The British thermal unit had not yet come into use and so Rumford, like Black (Sec. 2), had to express quantity of heat in some other way — for instance, in terms of the temperature change that it would produce in some specified substance. If the British thermal unit had been available to him, he very likely would have stated his argument somewhat as follows. The quantity of heat evolved in 30 min was at least 870 Btu. To gain an idea of the magnitude of this quantity, notice that it would be sufficient to melt more than 6 lb of ice or, as another illustration, sufficient to produce a temperature change of 66,360 Fahrenheit degrees in 837 grains of metallic dust.

This temperature change can be computed as follows. The quantity of heat H_m absorbed by the bulk metal was equal to $sw \times 70°\text{F}$, where s and w are the specific heat and weight of this metal, respectively. The quantity of heat H_d needed to produce a temperature change Δt in the dust is given by $s(w/948)\Delta t$, on the assumption that the specific heat of the dust is practically equal to that of the bulk metal. If $H_m = H_d$, *then*

$$sw \times 70°\text{F} = s\,(w/948)\,\Delta t,$$

or

$$\Delta t = 948 \times 70°\text{F} = 66{,}360°\text{F}.$$

Incidentally, there is no justification for retaining five significant figures in this result. Rumford was not always consistent in his use of significant figures.

If Rumford could have used modern units, he might have continued his argument in this fashion. If the release of 870 Btu of heat actually had been due to a change in the specific heat of the metal upon abrasion, this would mean that "so inconsiderable a quantity" of metal as 837 grains (0.1197 lb) must have released 870 Btu upon being reduced to dust. In other words, the release of heat would have been 870 Btu/0.1197 lb, or about 7300 Btu per pound of metal, "and this merely in consequence of a change in its specific heat." This could have well seemed "improbable" to Rumford, in view of his knowledge of the quantities of heat that are released under other somewhat comparable circumstances. For instance, compare this figure of 7300 Btu per pound with the 144 Btu of heat released by a pound of water when it freezes, or even with the 970 Btu released by a pound of steam when it liquefies.

> But without insisting on the improbability of this supposition, we have only to recollect that, from the results of actual and decisive experiments made for the express purpose of ascertaining that fact, the specific heat of the metal of which great guns are cast *is not sensibly changed* by being reduced to the form of metallic chips in the operation of boring cannon; and there does not seem to be any reason to think that it can be much changed, if it be changed at all, in being reduced to much smaller pieces by means of a borer that is less sharp.
>
> If the heat, or any considerable part of it, were produced in consequence of a change in the specific heat of a part of the metal of the cylinder, as such change could only be *superficial*, the cylinder would by degrees be *exhausted*; or the quantities of heat produced in any given short interval of time would be found to diminish gradually in successive experiments. To find out if this really happened or not, I repeated the last-mentioned experiment several times with the utmost care; but I did not discover the smallest sign of exhaustion in the metal, notwithstanding the large quantities of heat actually given off.
>
> Finding so much reason to conclude that the heat generated — *or excited*, as I would rather choose to express it — in these experiments was not furnished *at the expense of the latent heat or combined caloric* of the metal, I pushed my inquiries a step farther and endeavored to find out whether or not the air contributed anything in the generation of it.
>
> *Experiment No. 2*
>
> As the bore of the cylinder was cylindrical, and as the iron bar *m*, to the end of which the blunt steel borer was fixed, was square, the air had free access to the inside of the bore, and even to the bottom of it, where the friction took place by which the heat was excited.

As neither the metallic chips produced in the ordinary course of the operation of boring brass cannon, nor the finer scaly particles produced in the last-mentioned experiments by the friction of the blunt borer, showed any signs of calcination [oxidation], I did not see how the air could possibly have been the cause of the heat that was produced; but, in an investigation of this kind, I thought that no pains should be spared to clear away the rubbish, and leave the subject as naked and open to inspection as possible.

In order, by one decisive experiment, to determine whether or not the air of the atmosphere had any part in the generation of the heat, I contrived to repeat the experiment under circumstances in which *it was evidently impossible for it to produce any effect whatever.* A piston was exactly fitted to the mouth of the bore of the cylinder, and through the middle of this piston the square iron bar *m*, to the end of which the blunt steel borer was fixed, passed in a square hole made perfectly airtight. Thus the access of the external air to the inside of the bore of the cylinder was effectually prevented. (In Fig. 3, this piston *p* is seen in its place; it is likewise shown in Figs. 7 and 8.)

I did not find, however, by this experiment that the exclusion of the air diminished, in the smallest degree, the quantity of heat excited by the friction.

There still remained one doubt, which, though it appeared to me to be so slight as hardly to deserve any attention, I was however desirous to remove. The piston *p*, in order that it might be airtight, was fitted into the mouth of the bore of the cylinder with so much nicety, by means of collars of leather, and pressed against it with so much force, that, notwithstanding its being oiled, it occasioned a considerable amount of friction when the hollow cylinder was turned round its axis. Was not the heat, or at least some part of it, occasioned by this friction of the piston? And, as the external air had free access to the extremity of the bore, where it came in contact with the piston, is it not possible that this air may have had some share in the generation of the heat produced?

Experiment No. 3

A quadrangular oblong deal box (Fig. 4), watertight, 11½ English inches long, 9⅖₀ inches wide, and 9⁶⁄₁₀ inches deep (measured in the clear), was provided with holes or slits in the middle of each of its ends, just large enough to receive, the one the square iron rod *m* to the end of which the blunt steel borer was fastened, the other the small cylindrical neck which joined the hollow cylinder to the cannon. This box could be closed above by a wooden cover or lid moving on hinges. By means of the two vertical openings or slits in its two ends (the upper parts of which openings could be closed by means of narrow pieces of wood sliding in vertical grooves), the box (*ghik*, Fig. 3) was fixed to the machinery in such a manner that its bottom *ik* was horizontal and its axis coincided with the axis of the hollow metallic cylinder. It is evident from the description that the hollow metallic cylinder occupied the middle of the box, without touching it on either side (see Fig. 3); and that, on pouring water into the box, and filling it to the brim, the cylinder was completely covered and surrounded on every side by that fluid. And further, as the box was held fast by the strong square iron rod *m* which passed through the *square hole* in the center of its left-hand end (Fig. 4), while the round or cylindrical neck, which joined the hollow cylinder to the end of the cannon, could turn round freely on its axis in the *round hole* in the center of the right-hand end, it is evident that the machinery could be put in motion without the least danger of forcing the box out of its place, throwing the water out of it, or deranging any part of the apparatus.

The hollow cylinder having been previously cleaned out, and the inside of its bore wiped with a clean towel till it was quite dry, the square iron bar *m*, with the blunt steel borer *n* fixed to the end of it, was put into place; the mouth of the bore of the cylinder was closed at the same time by means of the circular piston *p* through the center of which the iron bar *m* passed. The box was now put in place, and the joinings of the iron rod and of the neck of the cylinder with the two ends of the box were made watertight by means of collars of oiled leather. The box was then filled with cold water of temperature 60°F, and the machinery was put in motion.

The result of this beautiful experiment was very striking, and the pleasure it afforded me amply repaid me for all the trouble I had had in contriving and arranging the complicated machinery used in making it.

The cylinder, revolving at the rate of about 32 times in a minute, had been in motion but a short time when I perceived, by putting my hand into the water and touching the outside of the cylinder, that heat was being generated; and it was not long before the water which surrounded the cylinder began to be sensibly warm.

At the end of 1 hour I found, by plunging a thermometer into the water in the box (the weight of this water was 18.77 lb avoirdupois, or 2¼ wine gallons), that its temperature had been raised no less than 47 degrees, being now 107°F. When 30 minutes more had elapsed, or 1½ hours after the machinery had been put in motion, the temperature of the water in the box was 142°F. At the end of 2 hours, reckoning from the beginning of the experiment, the temperature of the water was found to be 178°F. At 2 hours and 20 minutes it was 200°F. At 2½ hours it ACTUALLY BOILED!

It would be difficult to describe the surprise and astonishment expressed in the countenances of the bystanders on seeing so large a quantity of cold water heated, and actually made to boil, without any fire. Though there was, in fact, nothing that could justly be considered as surprising in this event, yet I acknowledged fairly that it afforded me a degree of childish pleasure, which, were I ambitious of the reputation of a *grave philosopher*, I ought most certainly rather to hide than to discover.

> The quantity of heat excited and accumulated in this experiment was very considerable; for, not only the water in the box, but also the box itself (which weighed 15¼ lb), and the hollow metallic cylinder, and that part of the iron bar which, being situated within the cavity of the box, was immersed in the water, were heated through 150 degrees—that is, from 60°F (which was the temperature of the water and of the machinery at the beginning of the experiment) to 210°F, the temperature of boiling water at Munich.
>
> The total quantity of heat generated may be estimated with some considerable degree of precision as follows.

We here replace Rumford's description of his calculation by a somewhat more concise statement utilizing modern thermal units.

Employing the formula $H = sw\Delta t$, which is our Eq. (4), one finds that the quantities of heat needed to raise the temperature of the various parts of the apparatus from 60° to 210°F were:

(1) for 18¾ lb of water in the wooden box,

$$H_1 = 1.0 \frac{\text{Btu}}{\text{lb }^\circ\text{F}} \times 18\tfrac{3}{4}\text{ lb} \times (210 - 60)^\circ\text{F} = 2810\text{ Btu};$$

(2) for 113 lb of gun metal, of specific heat 0.11 Btu/lb °F, comprising the hollow cylinder,

$$H_2 = 0.11 \frac{\text{Btu}}{\text{lb }^\circ\text{F}} \times 113\text{ lb} \times (210 - 60)^\circ\text{F} = 1870\text{ Btu};$$

(3) for 36.75 in.^{3} of iron, comprising that part of the iron bar *m* that entered the box,

$$H_3 \text{ (as reckoned by Rumford)} = 182\text{ Btu}.$$

Rumford does not say how he arrived at this value of 182 Btu, but one can easily show that it is the quantity of heat that would be needed to produce a temperature rise of 150 Fahrenheit degrees in the bar *m* if the specific heat and density of the iron comprising it are taken to be 0.115 Btu/lb °F and 496 lb/ft^3, respectively; these are approximately equal to the modern values for these two quantities.

The *total* quantity of heat produced by friction (not taking into account the heat absorbed by the wooden box and that lost to the atmosphere during the experiment) was therefore

$$H = H_1 + H_2 + H_3 = (2810 + 1870 + 182)\text{ Btu} = 4900\text{ Btu}.$$

This final value has been rounded off to two significant figures, thus indicating the degree of accuracy that appears to be warranted by the data.

> From the knowledge of the *quantity* of heat actually produced in the foregoing experiment, and of the *time* in which it was generated (150 minutes), we are able to ascertain *how fast it was produced* and to determine how much fuel would have to be consumed in order to produce, in burning equably, the same quantity of heat in the same time. . . .

The next three paragraphs are omitted. In them Rumford cites an experiment of Dr. Crawford's, the results of which indicate that 2.1 Btu of heat are generated in the combustion of 1 grain (1/7000 lb) of candle wax. Recalling that the heat generated by friction in experiment No. 3 was computed to be 4900 Btu, Rumford shows that 4900/2.1, or 2300 grains, of candle wax would have to be burned to produce this quantity of heat.

This attempt of Rumford's to compare the heat evolved by burning candles with that evolved by friction is reminiscent of experiments carried out several years earlier by Lavoisier and Laplace, in which they noted that the heat evolved by burning candles was approximately equal to the animal heat evolved by a guinea pig after eating food containing the same weights of carbon and hydrogen. The significance of such experiments is that they represent attempts to find quantitative relations between phenomena that later were to be more clearly recognized as representing conversions of energy from one form to another — chemical energy into heat, mechanical energy into heat, and so on. The idea of correlating these phenomena was in the air.

> Now I found, by an experiment made on purpose to finish these computations, that when a good wax candle, of a moderate size, ¾ inch in diameter, burns with a clear flame, just 49 grains of wax are consumed in 30 minutes. Hence it appears that 245 grains of wax would be consumed by such a candle in 150 minutes; and that to burn the 2300 grains necessary to produce the quantity of heat actually obtained by friction in the experiment in question, and in the given time (150 minutes), nine candles, burning at once, would not be sufficient; for 9 multiplied by 245 (the number of grains consumed by each candle in 150 minutes) amounts to no more than 2205 grains; whereas the weight of wax necessary to be burnt, in order to produce the given quantity of heat, was found to be 2300 grains.
>
> From the result of these computations it appears that the quantity of heat produced equably, or in a continuous stream (if I may use that expression), by the friction of the blunt steel borer against the bottom of the hollow metallic cylinder, in the experiment under consideration, was *larger* than that produced equably in the combustion of *nine wax candles*, each ¾ of an inch in diameter, all burning at the same time with clear bright flames.
>
> As the machinery used in this experiment could easily be driven by

the force of one horse (though, to render the work lighter, two horses actually were employed), these computations show further how large a quantity of heat might be produced, by proper mechanical contrivance, merely by the strength of a horse, without either fire, light, combustion, or chemical decomposition; and, in a case of necessity, the heat thus produced might be used in cooking victuals.

But no circumstances can be imagined in which this method of procuring heat would be advantageous; for more heat might be obtained by using the fodder necessary for the support of a horse as fuel. . . .

In experiment No. 1, which lasted only *half an hour*, the quantity of heat generated was found to be equal to that which would be required to heat 5 lb of ice-cold water through 180 degrees, or up to boiling [that is, 900 Btu were evolved]. In experiment No. 3, the heat generated in *half an hour* would have brought 5.31 lb of ice-cold water to the boiling temperature [that is, about 960 Btu were evolved]. But, in this last-mentioned experiment, the heat generated was more effectually confined, and so less of it was lost; this accounts for the difference in the results of the two experiments.

It remains for me to give an account of one more experiment that was made with this apparatus. I found, by experiment No. 1, how much heat was generated when the air had free access to the metallic surfaces which were rubbed together. By experiment No. 2, I found that the quantity of heat generated was not sensibly diminished when the air did not have free access. Experiment No. 3 indicated that the generation of the heat was not prevented or retarded by keeping the apparatus immersed in water. But, in this last-mentioned experiment, the water, though it surrounded the hollow metallic cylinder on every side, externally, was not suffered to enter the cavity of its bore (being prevented by the piston) and consequently did not come into contact with the metallic surfaces where the heat was generated. To see what effects would be produced by giving the water free access to these surfaces, I now made the next experiment.

Experiment No. 4

The piston which closed the end of the bore of the cylinder being removed, the blunt borer and the cylinder were once more put together; and the box being fixed in its place and filled with water, the machinery was again put in motion.

There was nothing in the result of this experiment that renders it necessary for me to be very particular in my account of it. Heat was generated as in the former experiments, and, to all appearance, quite as rapidly; and I have no doubt but the water in the box would have been brought to boil had the experiment been continued as long as the last. The only circumstances that surprised me was to find how little difference was occasioned in the noise made by the borer in rubbing against the bottom of the bore of the cylinder, by filling the bore with water.

This noise, which was very grating to the ear, and sometimes almost insupportable, was, as nearly as I could judge of it, quite as loud and as disagreeable when the surfaces rubbed together were wet with water as when they were in contact with air.

By meditating on the results of all these experiments, we are naturally brought to that great question which has so often been the subject of speculation among philosophers, namely, what is heat? Is there any such thing as an *igneous fluid*? Is there anything that can with propriety be called *caloric*?

We have seen that a very considerable quantity of heat may be excited in the friction of two metallic surfaces, and given off in a constant stream or flux *in all directions* without interruption or intermission, and without any signs of diminution or exhaustion. From whence came this heat?

Was it furnished by the small particles of metal, detached from the larger solid masses, on their being rubbed together? This, as we have already seen, could not possibly have been the case.

Was it furnished by the air? This could not have been the case; for, in three of the experiments, the machinery was kept immersed in water and access to the air of the atmosphere was completely prevented.

Was it furnished by the water that surrounded the machinery? That this could not have been the case is evident: *first*, because this water was continually *receiving* heat from the machinery, and could not at the same time be *giving* heat to it; and, *second*, because there was no chemical decomposition of any part of this water. Had any such decomposition taken place (which, indeed, could not reasonably have been expected), one of its component elastic fluids — most probably inflammable air [hydrogen] — must at the same time have been set at liberty, and, in making its escape into the atmosphere, would have been detected. But though I frequently examined the water to see if any air bubbles rose up through it, and had even made preparations for catching them, in order to examine them, if any should appear, I could perceive none; nor was there any sign of decomposition of any kind whatever, or other chemical process, going on in the water.

Is it possible that the heat could have been supplied by means of the iron bar *m* to the end of which the blunt steel borer was fixed? Or by the small neck of gun metal by which the hollow cylinder was united to the cannon? These suppositions appear more improbable even than either of those before mentioned; for heat was continually going off, or *out of the machinery*, by both these passages, during the whole time the experiment lasted.

And, in reasoning on this subject, we must not forget to consider that most remarkable circumstance, that the source of the heat generated by friction in these experiments appeared to be *inexhaustible.*

It is hardly necessary to add that anything which any *insulated* body,

> or system of bodies, can continue to furnish *without limitation*, cannot possibly be *a material substance*; and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner in which heat was excited and communicated in these experiments, except it be MOTION.

Here Rumford emphasizes what he considers to be the chief result of these experiments, namely, that the source of the heat generated in friction experiments is inexhaustible. If heat were rubbed out of an object by friction, as the calorists claimed, a stage should eventually be reached in which all the heat in the object would be exhausted. But no such stage was ever observed. It was possibly because of the convincing character of this chief result that Rumford did not trouble to carry out the additional experiments on the heat of fusion of the chips and bulk metal mentioned in our note on page 175.

Rumford points out that, if an insulated object can continue to furnish heat *without limitation*, then heat cannot possibly be a material substance. His argument here could have been set forth as follows: if heat is a material substance, then it must be indestructible and uncreatable (this is the so-called "principle of conservation of caloric," the most basic principle of the caloric theory); but the present experiments show that heat *can* be created (generated) by friction; therefore, heat is not a material substance. Instead, he says, it must be motion which, in the present experiments, was communicated to the particles of metal by the moving cannon in contact with the fixed borer.

One supporter of the caloric theory — J. B. Emmett (1820) — challenged the idea that the source of heat in these friction experiments was inexhaustible in the sense implied by Rumford. Granting that considerable heat is evolved when a metal is rubbed or hammered, Emmett contended that this quantity most probably was a small fraction of the total quantity of heat in the metal. Moreover, the gun metal was subject to a large force during the boring and, as the metal wore off, a fresh surface was continually being exposed to it. Thus, said Emmett, with heat being squeezed out of each fresh layer in succession, one should not expect the evolution of heat to cease until *all* the metal was worn away. Rumford continues:

> I am very far from pretending to know how, or by what means or mechanical contrivance, that particular kind of motion in bodies which has been supposed to constitute heat is excited, continued, and propagated; and I shall not presume to trouble the Society with mere conjectures, particularly on a subject which, during so many thousand

years, the most enlightened philosophers have endeavored, but in vain, to comprehend.

But, even though the mechanism of heat should, in fact, turn out to be one of those mysteries of nature that are beyond the reach of human intelligence, this ought by no means to discourage us, or even lessen our ardor, in our attempts to investigate the laws of its operations. How far can we advance in any of the paths that science has opened to us before we find ourselves enveloped in those thick mists which on every side bound the horizon of the human intellect? But how ample and how interesting is the field that is given us to explore!

Nobody, surely, in his sober senses, has ever pretended to understand the mechanism of gravitation; and yet what sublime discoveries was our immortal Newton enabled to make, merely by the investigation of the laws of its action! The effects produced in the world by the agency of heat are probably *just as extensive*, and quite as important, as those which are due to the tendency of the particles of matter toward one another; and there is no doubt but that its operations are, in all cases, determined by laws equally immutable.

Before I finish this essay, I would beg leave to observe that, although, in treating the subject I have endeavored to investigate, I have made no mention of the names of those who have gone over the same ground before me, nor of the success of their labors, this omission has not been due to any want of respect for my predecessors, but was merely to avoid prolixity, and to be more at liberty to pursue, without interruption, the natural train of my own ideas.

5. HUMPHRY DAVY'S EARLY WORK ON THE PRODUCTION OF HEAT BY FRICTION

In the year following the appearance of Rumford's paper on heat produced by friction, Humphry Davy (1778–1829) published "An Essay on Heat, Light, and the Combinations of Light." It first appeared in a book entitled *Contributions to Physical and Medical Knowledge, Principally from the West of England,* Collected by Thomas Beddoes, M.D. (1799). Beddoes was a physician and had been professor of chemistry in Oxford University.

This essay was concerned in part with the question of heat produced by friction and was directed against the caloric theory. Davy appears to have become interested in this question several years before he began to study physical science systematically, for it is related that in his seventeenth year he went with a friend to the river, to show him that two pieces of ice could be melted by rubbing them together, the melting apparently being due to the heat produced by friction. In this same year — 1795 — Davy was apprenticed to a surgeon-apothecary, and it was during this apprenticeship that he began the study of physical science. Learning of the experiments of Black and Crawford, he soon began to form original views about heat and, four months after beginning his studies, started the research upon which the present essay was based.

Soon after the essay was published, Davy began to see that it contained fallacies, and he came to refer to it as his "infant chemical speculations." Nevertheless, his arguments about heat produced by friction, and the type of experiments that he employed, are in some respects more cogent than those of Rumford's. Consequently, in later years, when the energy theory of heat was becoming established, various writers began to cite Davy's work as a good example of a convincing attack on the caloric theory. For instance, J. P. Joule, in his famous memoir on the mechanical equivalent of heat [*Philosophical Transactions,* vol. 140 (1850), p. 61], said:

> By rubbing two pieces of ice against one another in the vacuum of an air pump, part of them was melted, although the temperature of the receiver was kept below the freezing point. This experiment was the more decisively in favor of the doctrine of the immateriality of heat, inasmuch as the capacity of ice for heat is much less than that of water. It was therefore with good reason that Davy drew the inference that "the immediate cause of the phenomena of heat is motion, and the laws of its communication are precisely the same as the laws of communication of motion."

It should be pointed out that these comments of Joule's, excepting the last sentence, refer to the experiments described in Davy's essay of 1799, here presented. The quotation in the final sentence is taken from a later book of Davy's, his *Elements of Chemical Philosophy* (1812), p. 94. We shall see that Joule's description of Davy's experiment with ice is not accurate; moreover, that similar mistakes occur even in some present-day accounts of his work. Apparently they have been copied from one book to another over a period of more than a century.

The portion of Davy's essay presented here represents less than one-tenth of the entire work, but is the part that deals with heat produced by friction. It is a modified and annotated version, based on the essay as it is reprinted in *The Collected Works of Sir Humphry Davy,* Bart., LL.D., F.R.S., edited by his brother, John Davy, M.D., F.R.S. (London, 1839), vol. II, pp. 9–86.

On the Production of Heat by Friction

by

Humphry Davy

Matter is possessed of the power of attraction. Owing to this attraction the particles of bodies tend to approach one another and to exist in a

> state of contiguity. The particles of all bodies with which we are acquainted can be made to approach nearer to one another by peculiar means; that is, the specific gravity of any body can be increased by diminishing its temperature. Consequently (on the supposition of the impenetrability of matter), the particles of bodies are not in actual contact. There must therefore act on these particles some other power that prevents their actual contact; this may be called repulsion.
>
> The phenomena of repulsion have been supposed, by most chemical philosophers, to depend on a peculiar elastic fluid to which the names "latent heat" and "caloric" have been given. The peculiar modes of existence of bodies — solidity, liquidity, and gaseousness — depend (according to the calorists) on the quantity of caloric entering into their composition; this substance, insinuating itself between their particles, and thus separating the particles from one another and preventing their actual contact, is, by the calorists, supposed to be the cause of repulsion.
>
> Other philosophers, dissatisfied with the evidences produced in favor of the existence of this elastic fluid, and perceiving the generation of heat by friction and percussion, have supposed heat to be a motion. . . .

Davy probably was familiar with Newton's great generalization, arrived at more than a century earlier, that there exist gravitational forces of attraction between all particles of matter. In 1806, Davy made the important but then novel suggestion, which was later confirmed, that there are also electrical forces between atoms, these being much stronger than the gravitational forces.

Davy's statement that the specific gravity of a body can be increased by diminishing its temperature is another way of saying that the body shrinks in volume when cooled; the *specific gravity* of a substance may be defined, accurately enough for present purposes, as the ratio of the weight of any volume of the substance to the weight of a like volume of water.

Incidentally, there are several substances that *expand* when cooled within certain temperature ranges. For instance, water continuously expands while being cooled from 39° down to 32°F. This so-called *anomalous* expansion of water attracted the attention of Count Rumford, who investigated it experimentally and described the results in a paper entitled "Account of Some New Experiments on the Temperature of Water at its Maximum Density" (1805). Here again Rumford's primary object seemingly was to obtain additional evidence for his attack on the caloric theory, for he concluded: "These experiments ought not to be regarded as suitable for determining with great exactness the temperature at which the density of water is at a maximum, but rather as proving that this temperature is really several degrees of the thermometric scale above that of melting ice." Rumford knew that the calorists could satisfactorily explain the *contraction* of an object upon cooling as due to the removal of the caloric from it. But how could they explain the fact that, below a certain temperature, water *expands* when caloric is removed from it? Rumford apparently felt that this phenomenon of anomalous expansion provided strong evidence against the caloric theory. However, it should be noted that the rival view, that "heat is motion" (in the state of its development in Rumford's day) also failed to provide a satisfactory explanation of anomalous expansion.

Davy's phrase, "the impenetrability of matter," evidently refers to the impenetrability of the particles themselves. In his day these particles (atoms or molecules) were thought to be hard — impenetrable — pellets. So the fact that a body can be reduced in volume by cooling or by compressing it indicated that the particles are not in actual contact but have space between them. But how can there be space between the particles if there is an attractive force that tends to pull them together? Apparently, as Davy indicates, there must be some other force acting on the particles that tends to push them apart, thus balancing the effect of the attractive force.

> Considering the discovery of the true cause of the repulsive power as highly important to philosophy, I have endeavored to investigate this part of chemical science by experiments: from these experiments (which I am now about to describe), I conclude that heat, or the power of repulsion, is not matter.
>
> Without considering the effects of the repulsive power on bodies, or endeavoring to prove from these effects that it is motion, I shall attempt to demonstrate by experiments that it is not matter; and in doing this, I shall use the method called by mathematicians, *reductio ad absurdum.*
>
> Let heat be considered [for the sake of argument] to be matter, and let it be granted that the temperature of a body cannot be increased unless its specific heat is diminished from some cause or unless heat is added to it from some bodies in contact.
>
> Now the temperatures of all bodies are raised by friction [by rubbing the surface of one body against that of another]. Consequently, this increase of temperature must be produced in one of three ways: *first,* either by a diminution of the specific heats of the rubbing bodies owing to some change induced in them by friction, a change producing in them an increase of temperature; or, *second,* by heat communicated, as a result of a decomposition of the oxygen gas in contact with one or both of the rubbing bodies; that is, friction must effect some change in these bodies — similar to an increase of temperature — that enables them to decompose oxygen gas, in which case they will afterwards be found to be partially or wholly oxidized; or, *third,* by caloric communicated to the rubbing

> bodies by the other bodies in contact with them; that is, friction induces a change in the bodies which enables them to attract caloric from the surrounding bodies.
>
> Now first let us suppose that the increase of temperature produced by friction arises from a diminution of the specific heats of the rubbing bodies. In this case it is evident that some change must be induced in the bodies by the rubbing action, which lessens their specific heats and thus increases their temperatures.

Davy's comments about oxygen, in connection with the second of his three working hypotheses, indicate that he was familiar with the work of Priestley and Lavoisier; but his reference to "the decomposition of oxygen gas" suggests that he regarded oxygen as a compound, not an element. This makes his ideas here seem muddled, especially in view of his subsequent reference to the oxidation of bodies. Probably he means that friction conceivably could produce some change in a body enabling it to combine readily with oxygen from the air, in which case the heat evolved during this oxidation process might account for the observed rise in temperature of the rubbed body.

Experiment II, which follows, is Davy's first experiment on heat produced by friction. Experiment I, which appears in an earlier section not reproduced here, was an attempt "to demonstrate directly that light is not a modification or an effect of heat."

> *Experiment II*
>
> I procured two parallelepipeds of ice (the result of the experiment is the same if wax, tallow, resin, or any substance fusible at a low temperature be used . . .) of temperature 29°F, and 6 inches long, 2 inches wide, and ⅔ inch thick: they were fastened by wires to two bars of iron. By a special mechanism, their surfaces were placed in contact and were kept in continuous and violent friction for some minutes. They were almost entirely converted into water, which water was collected and its temperature ascertained to be 35°F, after remaining in an atmosphere of a lower temperature for some minutes. The fusion took place only at the plane of contact of the two pieces of ice, and no bodies were in friction but ice.
>
> From this experiment it is evident that ice by friction is converted into water, and according to the supposition of the calorists, its specific heat is diminished. But it is a well-known fact that the specific heat of ice [which is 0.5 Btu/lb °F] is much smaller than that of water; moreover, that a definite quantity of heat [namely, 144 Btu/lb] must be added to ice to convert it into water. Friction consequently does not diminish the specific heats of bodies.
>
> From this experiment it is likewise evident that the increase of temperature consequent on friction cannot be due to the decomposition of the

> oxygen gas in contact, for ice has no [chemical] attraction for oxygen. Since the increase of temperature consequent on friction cannot be due to the diminution of specific heat, or to oxidation of the rubbing bodies, the only remaining supposition is that it arises from a quantity of heat added to them, which heat must be attracted from the bodies in contact. On this supposition friction must induce some change in bodies that enables them to attract heat from the bodies in contact.

In other words, Davy chose for this experiment a material — ice — that he knew would not oxidize, thus automatically disposing of the possibility that the heat produced by rubbing pieces of ice together was due to oxidation.

Davy's argument about melting ice by friction is perhaps even more convincing than was one of Rumford's in the cannon-boring experiment (Sec. 4). Rumford, it will be recalled, showed experimentally that the specific heat of the metallic chips abraded during the boring of the cannon was not sensibly different from that of the solid metal; thus he refuted one of the claims of the calorists, namely, that the heat evolved is the result of a diminution in the specific heat of the abraded material. In Davy's experiment we can think of the melted ice (water) as playing a role similar to that of Rumford's chips; and not only is heat absorbed, rather than released, during the melting, but the specific heat of this melted ice, instead of being less than that of ice, or even equal to it, is twice as large. So Davy was right in thinking it important to determine whether heat is evolved when ice is subjected to friction. The calorists would have found it hard to explain how an *increased* specific heat could result in the evolution of heat.

Although we know today that heat *is* produced, with consequent melting, when two pieces of ice are rubbed together, Davy's experiment II actually was incapable of yielding convincing evidence on this question. As the British physicist E. N. da C. Andrade has pointed out, in the periodical *Nature,* vol. 135 (1935), p. 359, if the rubbing surfaces of the ice contain a film of water, the frictional force is small and little heat is produced; therefore, since the heat of fusion of ice is large (144 Btu/lb), hardly any ice would melt as a result of the rubbing. On the other hand, if the ice is dry, it tends to stick together, thus slowing down or even stopping the rubbing process. Another complication is that force necessarily must be employed to hold the two blocks of ice together, and this lowers slightly the melting temperature of the ice, causing it to melt at the surfaces of contact even when these surfaces are not being rubbed together. Moreover, some of the resulting water flows to the edges, where the pressure is lower, and there it freezes again, thus causing the two blocks to cohere; this phenomenon, which is called *regelation,* may have been unknown or, at least, not well understood in Davy's day.

Davy says that the two blocks of ice were "after some minutes . . . almost entirely converted into water, . . . and its temperature [was] ascertained to be 35°F." To melt this much ice and raise the temperature of the resulting water several degrees requires a much larger quantity of heat than was likely to have been produced by the friction. Therefore, as Andrade says, the effect observed by Davy was doubtless due almost entirely to *conduction* of heat from the surroundings. Andrade adds: "It does not detract from the greatness of Davy to point out that his first experiments, carried out in 1799 while he was still a country lad, were uncritical and lacked all quantitative basis."

In experiment III, which follows, Davy tries to determine whether the heat "collected by friction" is coming from other objects in contact with the rubbing bodies.

> *Experiment III*
>
> I procured a piece of clockwork so constructed as to be set to work in an evacuated vessel; one of the external wheels of this machinery came in contact with a thin metallic plate. A considerable degree of sensible heat [as indicated by a rise in temperature] was produced by friction between the wheel and plate when the machine worked uninsulated from bodies capable of communicating heat.
>
> I next procured a small piece of ice and round its upper edges made a small canal which I filled with water. The machinery was placed on the ice, but not in contact with the water. Thus disposed, the whole was placed in the vessel attached to the vacuum pump. This vessel had been previously filled with carbonic acid gas [carbon dioxide], a quantity of potash (that is, caustic vegetable alkali) [potassium hydroxide] being at the same time introduced.
>
> The vessel was now evacuated. This evacuation, together with the attraction of the carbonic acid gas by the potash, produced a nearly perfect vacuum, I believe.

Carbon dioxide gas (CO_2) was put in the vessel so as to expel the air. Then potassium hydroxide (KOH) was introduced; it combined chemically with the carbon dioxide to produce potassium acid carbonate ($KHCO_3$), which is a nonvolatile solid substance and thus helped to evacuate the vessel. Even with modern high-vacuum pumps, which are immensely superior to the pumps available to Davy, refrigerants and materials called "getters" are often used to remove water vapor and other gases that cannot easily be removed by a pump.

As the next two paragraphs indicate, Davy used wax, not ice, as the substance to be melted in this experiment, a fact that he has not previously mentioned. Apparently the wax was attached to the "thin metallic plate" (it may have been a metallic dish or tray) against which one of the clockwork-driven wheels rubbed. The purpose of the block of ice was to insulate the machinery from surrounding objects.

> The machinery was now set to work. The wax rapidly melted, showing that there was an increase of temperature.
>
> *Note.* The temperature of the ice, machinery and surrounding atmosphere at the commencement of the experiment was 32°F. At the end of the experiment the temperature of the coldest part of the machinery was nearly 33°F, and that of the ice and surrounding atmosphere was the same as at the commencement of the experiment; so the heat produced by the friction of the different parts of the machinery was sufficient to raise the temperature of almost half a pound of metal at least 1°F and to melt 18 grains of wax (the quantity employed).
>
> Caloric therefore was collected by friction; and this caloric, on the afore-mentioned supposition, was communicated to the machinery by the bodies in contact with it. But in this experiment, ice was the only body in contact with the machinery. Had this ice given out caloric, the water in the canal on the top of it would have frozen. But this water was not frozen; consequently, the ice did not give out caloric. Nor could the caloric have come from the other bodies in contact with the ice; for it would have had to pass through the ice to reach the machinery, and an addition of caloric to the ice would have converted it into water.

Davy says that enough heat was furnished in experiment III to increase the temperature of half a pound of metal at least 1°F and to melt 18 grains of wax. Assuming that the "metal" was iron and that the "wax" was beeswax, one can easily show that the quantity of heat evolved was only about 0.06 Btu. If it were the water in the channel that had furnished this heat, (0.06/144) lb of it would have frozen—about 3 *grains*! As Andrade says (*loc. cit.*), the production of so small a weight of ice "actually could not have been observed by the eye in this experiment. The experiment proves nothing at all." In fact, so far as this particular experiment is concerned, one could just as easily arrive at the contrary conclusion, namely, that the heat "collected by friction" did come from the ice. To do this, one need only assume that 3 grains of water *did* freeze, but could not be seen with the eye. It seems evident that Davy did not carry out the foregoing computation, or he would have seen for himself that the experiment lacked *quantitative* significance.

> Thus heat, when produced by friction, cannot be collected from the bodies in contact. Moreover, it was proved by experiment II that the increase of temperature consequent on friction cannot arise from a

> diminution of specific heat or from oxidation. But if heat be considered as matter, it must be produced in one of these three ways. Since (as is demonstrated by these experiments) it is produced in none of these ways, it cannot be considered as matter. It has thus been experimentally demonstrated that caloric, or the matter of heat, does not exist.
>
> Solids expand when subjected to prolonged and violent friction (expansion by friction is common to almost all bodies; and as the exceptions are very few, it may be admitted as a principle . . .) and, if they are of a higher temperature than the human body, affect the sense organs with the peculiar sensation known by the common name of heat [warmth, or hotness]. Since bodies become expanded by friction, it is evident that their particles must move away, or separate, from one another. Now, a motion or vibration of the particles of bodies must be necessarily generated by friction and percussion. Therefore we may reasonably conclude that this motion or vibration is heat, or the repulsive agent.
>
> Heat, then, or that power which prevents the actual contact of the particles of bodies, and which is the cause of our peculiar sensations of heat and cold, is to be regarded as a peculiar motion, probably a vibration, of the particles of bodies, tending to separate them. It may with propriety be called the repulsive motion.

Despite the fact that experiments I and II lack quantitative significance, Davy's main conclusion is now known to be correct: heat *is* due to "a peculiar motion . . . of the particles of bodies." Possibly he felt so sure of the correctness of this view that he was careless or even prejudiced in his observations, and hasty in his generalizations. In his youthful enthusiasm he had tried to perform experiments that would tax the ingenuity of a trained experimental physicist using much more modern equipment.

Davy later realized that he had shown poor judgment in rushing into print at a time when he lacked experience and critical judgment in experimentation. Yet there is another side to this question, which is well illustrated by something said by Benjamin Franklin in a letter to Peter Collinson, reproduced in I. B. Cohen's *Benjamin Franklin's Experiments* (Harvard University Press, 1941), p. 279:

> These thoughts, my dear friend, are many of them crude and hasty; and if I were merely ambitious of acquiring some reputation in philosophy, I ought to keep them by me till corrected and improved by time, and farther experience. But since even short hints and imperfect experiments in any new branch of science, being communicated, have oftentimes a good effect, in exciting the attention of the ingenious to the subject, and so become the occasion of more exact disquisition, and more compleat discoveries, you are at liberty to communicate this paper to whom you please; it being of more importance that knowledge should increase, than that your friend should be thought an accurate philosopher.

It was not until some 40 years after the experiments of Rumford and Davy that the subject of heat produced by friction was reinvestigated in a new and quantitative way by J. R. Mayer, in Germany, J. P. Joule, in England, and others; and by 1850 these investigators had established beyond much doubt that heat is not a separate substance, or fluid, but is kinetic energy associated with the motions of the small particles of ordinary matter. However, many scientists continued to favor the caloric theory and, as late as 1856, it received preference over the energy theory in the article "Heat" in the *Encyclopædia Britannica* (ed. 8).

Even today we sometimes find it useful and convenient to think of heat as a fluid, as when we speak of heat "flowing" from one object to another, or of an object "soaking up" heat. Many modern calorimetric determinations, for example, can be carried out just as well by thinking of heat as an indestructible fluid as by thinking of it as energy. An analysis of such experiments will show that the procedures employed in them do not depend on any assumption concerning the ultimate nature of heat except that heat is conserved. Such procedures are possible when there is no appreciable transformation of heat from, or into, any other form of energy.

Rumford's conclusion, stated in his paper of 1798, that heat is *motion* acquired additional significance a half-century later, when it became clear that heat is a form of energy — the kinetic energy associated with the random motions of the atoms and molecules comprising all matter. Some such notion of the nature of heat must have occurred to the earlier advocates of the mode-of-motion theory, especially those who were familiar with seventeenth- and eighteenth-century developments in mechanics. As early as 1695, G. W. Leibniz, the German mathematician and philosopher, had suggested that the diminution of *vis viva* (essentially what we now call kinetic energy) observed when two inelastic bodies collide "happens only in appearance." It is "not destroyed, but dissipated among the parts. That is not to lose it, but to do like those who change large money into small." Certainly by 1780 this notion had been rendered explicit, for Lavoisier and Laplace, in their *Mémoire sur la Chaleur* (1780), called attention to the opinion that "heat is the *vis viva* resulting from the insensible movements of the particles of a body. It is the sum of the products of the mass of each particle by the square of its velocity."

But these early speculations were not based on quantitative experimentation. Thermal science and mechanics still were almost completely separate disciplines, and seemingly it had not occurred to anyone to try to correlate them by seeking quantitative relations between thermal and mechanical quantities, such as quantity of heat (expressed in British thermal units) and mechanical energy (expressed in foot pounds). Indeed, it was experiments like those of Rumford's that were needed to establish this relation, although their significance in this respect apparently escaped his notice.

Rumford says (p. 185) that his machinery "could be driven by the force of one horse." Whether he had in mind here the mechanical work done by the horse is not clear; for in his day the word "force" had a troublesome double meaning, sometimes being used to denote force in the present-day sense of the term, but more frequently, to denote the concept that we now call *mechanical work*. He does point out that heat was evolved as long as the horse continued to act, and he obtained data (p. 183) which show roughly that *the quantity of heat evolved was directly proportional to the time during which the horse acted*. But he does not state or discuss this relation in his conclusions, or say anything to indicate that he realized its significance.

Some physiologists and medical men of the period saw significance in Rumford's results in connection with their studies of the sources of animal heat. The physical scientists, on the other hand, were undergoing a reaction to a highly speculative philosophy of nature which had strongly influenced them for the past several decades; so they were currently more interested in conscientious factual research than in what appeared to them to be mere speculation about the ultimate nature of heat. Recognition of the importance of the latter problem therefore came only in a later stage of the industrial revolution, when steam engines of improved efficiency were coming into wide use for driving machines. Then the need for correlating the heat and the mechanical work involved in such devices became more obvious and pressing.

The cannon-boring apparatus clearly was not designed for the purpose of establishing a precise quantitative relation between heat and work. Certainly Rumford was aware that the apparatus had shortcomings, but he evidently felt that it served his main purpose, which was — both here and in many other of his experiments performed during a 30-year period — to attack the currently accepted caloric theory from as many different points of view as seemed possible. A few years later he designed a simpler and more compact device for showing the production of heat by friction, which he described in his *Mémoire sur la Chaleur* (Paris, 1804). He felt that the large-scale experiments made in the arsenal might not be convincing unless they could be repeated by other investigators. This new apparatus, which was cleverly designed and easily could have been adapted to quantitative measurements, was very similar to one of a number of devices developed more than half a century later for the express purpose of checking and rechecking the relation between the British thermal unit and the mechanical unit of energy called the foot pound. This relation, which must be determined experimentally, came to be called the *mechanical equivalent of heat.*

To illustrate how Rumford's cannon-boring data could have been used to make a rough but explicit determination of the mechanical equivalent of heat, consider experiment No. 3. There the quantity of heat produced by friction in 2.5 hr, or 9000 sec, was 4900 Btu. Thus the average quantity of heat produced during each second of operation was 4900 Btu/9000 sec, or 0.540 Btu/sec. Now earlier than the time of the present experiments, in about 1783, James Watt had made some estimates which indicated that a "mill horse" could exert a steady pull of 150 lb in the direction in which it was moving while walking with a velocity of 2.5 mi/hr; in other words, it could do mechanical work at the rate of 550 foot pounds per second. Assuming that Rumford used a "mill horse," we can equate the rate of evolution of heat to the rate at which the horse worked. Thus, 0.540 Btu/sec = 550 ft lb/sec, or 1 Btu = (550/0.540) ft lb $\cong$ 1000 ft lb. In Rumford's day this result probably would have been expressed in words similar to the following: the quantity of heat capable of increasing the temperature of a pound of water by one degree of Fahrenheit's scale is equivalent to the work done in raising a 1000-lb object through a vertical distance of one foot.

Rumford did not make the foregoing calculation, or even suggest the possibility of making it. Very likely he was not aware of Watt's estimate of 550 ft lb/sec for the power of a horse, for the latter had recorded it in longhand in one of a series of notebooks in which he was in the habit of making notes and calculations from time to time. A printed reference to Watt's estimate appeared in a book review in the *Edinburgh Review* in 1809, more than a decade after Rumford wrote the present paper; but Watt's own account of his estimate was not published until 1818, several years after Rumford's death.

The first determinations of the mechanical equivalent of heat of which there are published records were made by J. R. Mayer (1842) and J. P. Joule (1843). The presently accepted value is 777.9 ft lb/Btu. Once an exact and unvarying relation between mechanical work and the quantity of heat into which it may be converted was established, the further step of introducing the hypothesis that heat itself is a form of energy was not difficult.

1. *Evolution of the thermometer*

1. Prepare a chronologic epitome of thermometry, with the entries arranged and worded somewhat as follows: *ca.* 1595. Air-expansion barothermoscope invented by Galileo.

2. Fahrenheit devised a fever thermometer that was known as a "pyranthropometer." Is this name suggestive of the purpose for which the instrument was intended?

3. Why was Fahrenheit's substitution of a cylindrical for a spherical bulb an improvement?

4. Cite evidence from the foregoing brief history of the thermometer or from your other readings that appears either to substantiate or to refute each of the following statements taken from recent books or periodical articles: (i) "Boyle devised a thermometer utilizing aniseed oil as the thermometric substance"; (ii) "Boyle's experience in other parts of physical science were of such nature as to make him well qualified for thermometric studies"; (iii) "Two fixed points are an absolute necessity if the degrees of temperature are to be definitely defined"; (iv) "It may well be that, from Galileo's air-expansion instrument, one could trace two historical threads of development, one leading to thermometers, the other to barometers"; (v) "In studying the origin of certain discoveries, one is often perplexed by encountering several claimants for priority. This may be because two or more persons independently reach the same result at about the same time; or because of the effort of each nation to secure credit and renown for its own people; or because of the failure of the discoverer to claim priority owing to the fact that he himself failed to appreciate its importance and utility"; (vi) "A centesimal thermometric system was first suggested by Anders Celsius, in 1642, but it differed from the modern centigrade system in that the values 0° and 100° were assigned to the steam and ice points, respectively, instead of the other way around"; (vii) "For weather reports and many everyday purposes, the Fahrenheit system has the advantages over other systems that the observer seldom has to record negative readings and also can make closer readings without having to *estimate* fractions of a degree."

5. (*a*) Show that $F = \dfrac{9}{5}C + 32$, where F is any temperature expressed in the Fahrenheit system and C is the same temperature expressed in the centigrade system. (*b*) Use the foregoing equation to find the values of F equivalent to the following values of C: $-40°C$, $0°C$, $50°C$, $100°$ C. (*c*) On a sheet of graph paper plot these four values of F as ordinates, and the corresponding values of C as abscissas; for both the horizontal and vertical scales of the graph, let 1 mm, say, represent 1 deg of temperature. (*d*) Use your graph to find the temperature in degrees Fahrenheit that corresponds to 31°C.

6. In the thermometric system devised in 1731 by R. A. F. Réaumur, and still used to some extent in Germany, the ice point and steam point have the values 0°R and 80°R, respectively. (*a*) Show that 68°F is equivalent to 16°R. (*b*) Derive the conversion formula $C = \frac{5}{4}R$, where the symbols C and R represent the same temperature expressed in the centigrade and Réaumur systems, respectively.

7A. J. N. Delisle, a French astronomer, employed a thermometric system in about 1735 in which the ice and steam points were called 150° and 0°, respectively. (*a*) Show that a reading of 140° in this system is equivalent to 44°F. (*b*) Derive the conversion formula $D = 150^\circ - \frac{3}{2}C$, where D and C represent the same temperature expressed in the Delisle and centigrade systems, respectively.

8A. In 1731, R. A. F. Réaumur set up a thermometric scale and system by using an alcohol-in-glass expansion thermometer having the ice point (marked 0°R) as a single fixed point and having successive degrees, each of which represented an expansion of 1/1000 the volume of the alcohol at the ice point. He found that the alcohol expanded from 1000 to 1080 volumes between the ice point and the steam point, thus giving 80°R for the latter temperature. (*a*) Would the degree marks on such a thermometer be equal distances apart? (*b*) Devise a method for determining whether the bore of a glass tube to be used in making a thermometer is of uniform cross-sectional area.

9A. It is often pointed out that the expansion of mercury with increase in temperature is exceedingly regular. (*a*) Suggest an experiment that would serve to test the correctness of this statement. (*b*) If, in this experiment, you wished to use a mercury-in-glass thermometer to measure the temperature, how would you calibrate it?

2. *Joseph Black's discoveries of specific and latent heat*

10. How does Black's conception of "equilibrium of heat" differ from the earlier idea of "equal heat"?

11. (*a*) Using Black's correct formula — our Eq. (4) — show that the quantity of heat required to warm 10 lb of water from 32° to 212°F is 1800 Btu. (*b*) Why it is better to express this result as 18×10^2 Btu?

12. Which of these two definitions is the more acceptable, and why? (i) Given that two objects, A and B, are in contact, and that A is observed to be at a higher temperature than B, we define the direction of flow of heat as being from A to B. (ii) Given that heat is observed to flow from object A to object B, we define A as being at a higher temperature than B.

13. Is there any way to make a *direct* experimental test of the principle of conservation of heat, or can it be verified only by making deductions from it and subjecting the latter to experimental tests?

14. Referring to Martine's experiment with water and mercury (p. 134), state: (*a*) the hypothesis and deductions that led him to make this experiment; (*b*) the factors that he considered relevant in planning it; (*c*) other factors that he might have considered relevant, and why he may have ignored them; (*d*) the factors that he tried to keep constant, and the variables that he measured; (*e*) the main conclusions.

15. Fahrenheit found that the mixing of equal volumes of mercury initially at 150°F and of water initially at 100°F resulted in a mixture temperature of 120°F. (*a*) Use Black's correct formula — our Eq. (4) — to compute the value for the specific heat of mercury given by this experiment. (*b*) What is the percentage difference between this value and the modern one?

16. In an experiment not described in the present excerpts, Black put a lump of ice into an equal weight of water of initial temperature 176°F and found that, after the ice had melted, the mixture "was no hotter than water just ready to freeze." (*a*) Show that the value for the heat of fusion of ice yielded by these data is 144 Btu/lb. (*b*) Would this value be made larger or smaller if account could be taken of the heat lost to the mixture by the hot vessel?

17. In the method-of-mixtures experiment on the melting of ice (p.144), suppose that Black, like his predecessors, had failed to take into account the 4.8 Btu of heat lost by the hot glass. What value would he then have obtained for the heat of fusion of ice?

18. Show that, after Black made his several discoveries, it was no longer acceptable to define *heat* qualitatively as that which always increases the temperature of a body to which it is added.

19. (a) Make a list of the main working hypotheses that are mentioned in connection with Black's work on specific and latent heats. (*b*) Which of these turned out to be incorrect? (*c*) Which of them are broad enough to be regarded as conceptual schemes?

20. What evidence, if any, can you find in Black's work in support of each of the following generalizations: (i) the development of a new instrument of measurement may lead to many new discoveries; (ii) the mere amassing of observational and experimental data does not constitute advance in a science; (iii) a new experimental technique may arise from, or be improved on, from a consideration of a practical art; (iv) new concepts may result from experiments or observations; (v) it is important to distinguish between a new concept and the explanation of this concept; (vi) a working hypothesis often is formulated as the result of relatively few observations, all of which may be no more than semiquantitative in character.

21. Although Black clearly understood the distinction between the concepts of *temperature* and *heat*, he often used various *exact* synonyms for temperature, such as "degree of hotness," "strength of heat," "heat of a body," and "intensity of heat." (*a*) Which of these synonyms probably first came into use before his time, when *temperature* and *heat* were badly confused? (*b*) Do you know of other synonyms for temperature that are still in everyday use? (*c*) Do you know of any nonscientific words in ordinary

language that are *exact* synonyms? (*d*) Why do exact synonyms occur so frequently in the sciences, especially the physical sciences? (*e*) What is your opinion of the tendency in modern scientific literature to avoid using synonyms for scientific concepts — for example, always to use the term *temperature* in referring to this concept? (*f*) Are there any kinds of extrascientific literature for which adoption of this practice by authors should be encouraged? discouraged?

22. Some writers have asserted that Black developed the theory and experimental procedures of heat measurements in response to a practical demand for such knowledge in the further development of steam engines. What evidence can you find for or against this assertion?

23. How do you account for the fact that Black was able to make his important discoveries of specific and latent heats while favoring a theory of heat — the material, or caloric, theory — that is now known to be incorrect?

24. Black warned Robison, as a student, "to suspect all theories whatever . . . and to reject, even without examination, every hypothetical explanation as a mere waste of time and ingenuity." (*a*) How can this advice of Black's be reconciled with the fact that he developed a theory of heat measurements involving concepts, working hypotheses and axioms? (*b*) In what sense was he probably using the phrase "hypothetical explanation"?

25. How much heat is transferred to surrounding, colder objects: (*a*) when 20 lb of liquid in (p. 146) at 450°F freezes to solid tin of the same temperature? (*b*) when 10 lb of steam at 212°F condenses to water of temperature 60°F?

26A. Fahrenheit found that the mixing of 3 volumes of mercury at 150°F with 2 volumes of water at 100°F resulted in a mixture temperature of 125°F. (*a*) Compute the specific heat of mercury from these data. (*b*) What is the percentage difference between this value and the modern one?

27A. (*a*) Prove that it follows from the erroneous weight hypothesis — our Eq. (1) — that the quantity of heat required to produce a temperature rise Δt in any body of weight w is given by the equation $H = cw\Delta t$, where c is a proportionality factor supposedly having the same value for all substances. (*b*) Prove that it follows from Boerhaave's erroneous volume hypothesis — our Eq. (3) — that $H = c'V\Delta t$, where c' supposedly is the same for all substances. (*c*) Show that if the first of the foregoing equations is applied to the mixing of equal volumes of water at 100°F and mercury at 150°F, the predicted mixture temperature will be 140°F, instead of the 120°F actually observed by Fahrenheit. (*d*) What mixture temperature is predicted by the second equation?

28A. When a certain liquid of specific heat s_1 and weight w_1 is placed in a vessel and exposed to a steady source of heat, the temperature of the liquid is observed to rise through 10 Fahrenheit degrees in a time T_1. When the experiment is now repeated with the same vessel, but with another liquid of specific heat s_2 and weight w_2, the temperature is observed to rise through 10 Fahrenheit degrees in a time T_2. Assuming that heat is supplied at the same constant rate in both experiments, show that

$$\frac{T_1}{T_2} = \frac{s_1w_1 + S}{s_2w_2 + S},$$

where S is the quantity of heat required to raise the temperature of the vessel through 1 Fahrenheit degree. (*b*) On the supposition that S for each of the glass vessels used by Martine (p.134) was 0.012 Btu/°F, compute the ratio T_1/T_2 for the equal volumes of mercury and water which he warmed through the same temperature interval. (*c*) How does this value compare with Martine's and also with the value 2.5 obtained in question 29A?

29A. In an experiment similar to that of Martine's, equal volumes of mercury and water are exposed to the same steady fire. Given that the specific heat of mercury is 0.033 Btu/lb °F and that mercury is 13.6 times as dense as water, show that: (*a*) to produce the same temperature rise in both liquids, only 0.4 as much heat must be added to the mercury as to the water, and (*b*) the mercury warms 2.5 times as fast as the water. (*c*) Martine, a careful experimenter who had good thermometers, *observed* that the mercury warmed a little less than twice as fast as the water. Can you account for the discrepancy between this observed value and the computed value of 2.5?

30A. In one experiment on vaporization that is omitted from these excerpts, Black found that 0.55 lb of water warmed from 50° to 212°F in 3.5 min, and all boiled away in 18 min more. Show that: (*a*) heat entered the water from the "red-hot kitchen table" at an average rate of 25.4 Btu/min and (*b*) the value for the heat of fusion of water given by this experiment was 830 Btu/lb.

31A. Which postulate, or postulates, of the caloric theory (p.155) can be used to "explain" each of the following phenomena: (*a*) a body generally expands when warmed; (*b*) a hot object tends to lose heat to the cooler surroundings; (*c*) all bodies conduct heat, but some better than others; (*d*) specific heats differ for different substances and different states of aggregation; (*e*) heats of fusion and vaporization differ for different substances; (*f*) bodies of different initial temperatures tend to acquire a common temperature when mixed; (*g*) heat can be produced by friction or percussion; (*h*) water expands when it freezes; (*i*) some substances contract upon freezing?

32A. Aside from his orally delivered lectures to students and two papers read at club meetings in Glasgow, which were not preserved, Black seemingly never gave any public account of his discoveries in heat. How is his failure to publish explained by historians, and what consequences do they attribute to it? (See, especially, references 23, 28, and 29 in our Bibliography.)

3. *Count Rumford's investigation of the weight ascribed to heat*

33. What does Rumford mean by "philosophical investigation" (p. 160)?

34. On page 160 Rumford refers to weights that were "exactly equal" and to balance arms having lengths "of the most perfect equality." How nearly

equal do two weights or two lengths have to be in order to be "exactly" or "perfectly" equal?

35. (*a*) What observations eventually led Rumford to suspect that his first experiments with water and alcohol (pp. 159 ff) were not dependable? (*b*) Does he ever satisfactorily explain why the water appeared to increase in weight upon freezing?

36. How does Rumford's value for the specific heat of mercury (p. 163) compare with the modern value of 0.033 Btu/lb °F?

37. In one experiment (p. 162), 0.57 lb of water and an equal weight of mercury were cooled from 61° to 34°F. (*a*) Compute the quantity of heat given off by each liquid. (*b*) In what ways was this experiment superior to those of earlier experimenters in which a single metal was heated?

38. In view of Rumford's remarks about the accuracy of his balance (p. 163, would he have been able to *measure* a difference in weight if it had been as small as 0.0002 percent? If it had been 0.0001 percent?

39. (*a*) List all the possible sources of error that Rumford took into account in his final experiment with water, alcohol and mercury (pp. 164 ff). (*b*) In what respects was this experiment superior to his earlier ones? (*c*) Why did he think it unnecessary to place a thermometer in the bottle containing the mercury?

40. What reasons did Rumford have for thinking that changes in atmospheric pressure and density could not affect the apparent weights in his experiments?

41. For each of Rumford's experiments, state: (*a*) the hypotheses and deductions that led him to make the experiment; (*b*) the factors that he considered relevant in planning it; (*c*) other factors that he might have considered relevant, and why he may have ignored them; (*d*) the factors that he tried to keep constant, and the variables that he measured or observed; (*e*) the conclusions.

42. In Fordyce's experiment and Rumford's first experiment, suppose that the increase in weight of the water upon freezing had actually turned out to be due to "the weight of heat" instead of to some "accidental cause." How might the calorists have explained an *increase* in the weight of an object when heat is *removed* from it?

43. What criticisms can be made of Tilloch's argument (p. 167)?

44A. (*a*) In the first experiment (pp. 159 ff), 0.59 lb of water and an equal weight of alcohol were cooled from 61° to 29°F. Assuming that the specific heat of the alcohol was 0.6 Btu/lb °F, compute the quantities of heat lost by the water and by the alcohol. (*b*) If the observed change in weight actually had been due to the "weight of heat," what value would the data for this experiment have yielded for the weight of 1 Btu?

45A. In testing the balance (pp. 160 ff), if the beam were in equilibrium when no weights were attached to its ends, would this have sufficed to show that the two arms of the balance were of equal length?

46A. On p. 161 Rumford says that he could have determined whether or not the arms of his balance were equal in length by "causing the two bottles *A* and *B* to exchange places upon the arms of the balance." This way of testing a balance was later used by Karl Friedrich Gauss (1777–1855) as the basis for his *method of double weighing*, which serves to eliminate errors caused by inequality in the lengths of the balance arms. Suppose that, when an object is put in one pan of a balance, a known weight W must be put in the other pan to balance it; but, when the object is transferred to this second pan, a different known weight W' is needed in the first pan to produce balance. (*a*) Show, with the help of Archimedes' principle of the lever, that the weight of the object is given by the expression $\sqrt{WW'}$. (*b*) Show that, if W and W' have nearly the same value, the foregoing expression reduces to $\frac{1}{2}(W + W')$, which is simpler to use in computations.

47A. P. W. Bridgman, in his book, *The Logic of Modern Physics* (Macmillan, 1927), says: "One of the problems of the future is the self-conscious development of a more powerful technique for the discovery of new relations without the necessity for preconceived opinions on the part of the observer." (*a*) Why might such a technique be advantageous? (*b*) Why might it be impossible?

48A. Show that the quantities of heat lost by the water, alcohol, and mercury in the final experiment (pp. 164 ff) were approximately in the ratios of 170 to 20 to 1.

49A. An open beaker containing hot water is placed on a sensitive balance in a room of temperature 25°F. (*a*) What various factors could conceivably affect the apparent weight of the vessel and contents while they gradually cooled to 25°F? (*b*) Would your answer be different if the water were enclosed in a hermetically sealed flask?

50A. A piece of metal has an apparent weight of 3.0 lb when immersed in water of weight-density 62.4 lb/ft^3. A piece of wood has a true weight of 1.8 lb and an average weight-density of 31.2 lb/ft^3. Show that the metal and wood, when fastened together and immersed in the water, will have an apparent weight of only 1.2 lb.

51A. An empty bottle is hermetically sealed and weighed when immersed in water. The bottle is then opened and, after a piece of cork has been enclosed in it, is resealed and weighed when immersed. (*a*) How does the combined apparent weight of the bottle and cork compare with the apparent weight of the empty bottle? (*b*) Can you apply this example in a critical examination of Tilloch's argument?

4. *Count Rumford's experiments on the source of heat that is excited by friction*

52. What light, if any, does this paper throw on the role of *accident* in discovery and experimentation?

53. (*a*) Is there any indication that Rumford carried out these experiments primarily to solve a technological problem? (*b*) Has this paper served in any way to enlarge your conceptions of how science and technology are related, and of the ways in which each may contribute to the progress of the other?

54. (*a*) What are the meanings and implications of the words "beautiful" and "elegant" when used in such expressions as "beautiful experiment" (p. 183), "beautiful theory," and "elegant mathematical proof"? (*b*) Is Rumford's acknowledgment of "childish pleasure" (p. 183) suggestive of any significant characteristic of the man or, for that matter, of many people who are highly creative and productive in their work?

55. (*a*) Referring to the final paragraph of the paper (p. 189), comment on the advantages and disadvantages of including documentary evidence and bibliographic references in a paper intended for oral delivery; in one intended for publication. (*b*) Comment on the possible value of Rumford's practice (p. 177, and elsewhere) of carefully specifying the dimensions of the apparatus.

56. (*a*) Using the data on page 182, carry out the computation needed to show that the specific heat of the gun metal was 0.11 Btu/lb °F. (*b*) Was Rumford justified in expressing this result to four significant figures? (*c*) Do the data and experimental method employed warrant the retention of two significant figures?

57. In referring to experiment No. 1, Rumford says that the quantity of heat evolved during the first 30 min was equivalent to that needed to warm 5 lb of water from 32° to 212°F. Show that: (*a*) the quantity evolved was 900 Btu; (b) its rate of production was 0.5 Btu/sec.

58. For one or more of Rumford's four experiments — the one on specific heats and Nos. 1, 2, and 3 — state: (*a*) the hypotheses and deductions that led Rumford to make the experiment; (*b*) the factors that he considered relevant in planning it; (*c*) other factors that he might have considered relevant, and why he may have ignored them; (*d*) the factors that he tried to keep constant, and the variables that he measured or observed; (*c*) the conclusions.

59. What prevision, or lack of it, did Rumford appear to have of the important discoveries about energy made near the middle of the nineteenth century? In answering, consider, among other things, his comment (p. 186) that heat for cooking food might be produced by employing a horse coupled with a suitable mechanical contrivance, but that it might better be obtained by using the horse's fodder as fuel.

60. Would the value for the mechanical equivalent of heat computed on page 92 have been larger or smaller if Rumford's data for experiment No. 3 had included estimates of: (*a*) the heat absorbed by the wooden box; (*b*) the heat lost to the atmosphere; (*c*) the mechanical work done against frictional forces in the mechanism connecting the horse to the cannon?

61. In so far as you can judge from the present paper, do you agree or disagree with the assertion that Rumford was unaware of the significance and importance of the quantity that in later years came to be called the mechanical equivalent of heat? Cite evidence for your conclusions.

62. It has been asserted that Rumford was able to conclude from these experiments that the quantity of heat developed was (i) directly proportional to the work done and (ii) had no relation to the weight of the chips or dust.

(*a*) Examine the accuracy of these assertions; include in your examination an analysis of the data of experiment No. 3. (*b*) Discuss the significance and relative importance of conclusions (i) and (ii) in the light of subsequent developments in thermal science.

63. In 1871 a prominent scientist expressed the opinion that Rumford's cannon-boring experiment annihilated the material, or caloric, theory of heat. Do you agree or disagree, and why?

64. Cite evidence to show whether or not Rumford, in his present work on heat, should be characterized as (*a*) a good strategist; (*b*) a good tactician. (*c*) How do Rumford and Black compare in these respects?

65A.. In the specific-heat experiments (p. 172), why was it advantageous to use "thin slips separated from the . . . block of metal by means of a fine saw"?

66A. On page 173, Rumford says that the "4590 grains of water" included an allowance for the heat capacity of the "tin vessel." Supposing that he actually used 4380 grains of water and that the vessel weighed 0.30 lb, show that the specific heat of the "tin" must have been 0.10 Btu/lb °F.

67A. By using the cooling data given in Table 1, estimate what the temperature of the cylinder probably would have been at the end of 30 min of operation if the quantity of heat lost from cylinder to surroundings could have been reduced to a negligibly small amount.

68A. On page 184, it is asserted that the quantity of heat needed to raise the temperature of 36.75 in.^3 of iron from 60° to 210°F was 182 Btu. Show that one can obtain this value by assuming that the specific heat and density of the iron were 0.115 Btu/lb °F and 496 lb/ft^3, respectively, these being approximately the modern values for these two quantities.

69A. John Robison's *Steam and Steam Engines* (1818), vol. II, p. 145, quotes James Watt as saying, in part, that "A horse going at the rate of $2\frac{1}{2}$ miles an hour raises a weight of 150 pounds by a rope passing over a pulley." Show that these figures yield the value 33,000 ft lb/min, or 550 ft lb/sec, for the power of a horse.

70A. (*a*) Show that the value for the mechanical equivalent of heat computed on page 200 from Rumford's data differs by 28 percent from the value accepted today. (*b*) J. P. Joule, from the results of a series of experiments of various types, concluded in 1850 that 772 ft lb/Btu was the best value for the mechanical equivalent of heat that he had obtained up to that time. How much does this value differ from the accepted value?

71A. In what ways might Rumford have improved his apparatus and methods if he had recognized the importance of trying to find an accurate and unvarying quantitative relation between heat and mechanical work?

72A. Sadi Carnot, a brilliant scientist of tremendously great promise who died of cholera during an epidemic in 1832, when he was only 36 years old, made a surprisingly accurate determination of the mechanical equivalent of heat, but this fact remained unknown until 1872, when some of his notes were published posthumously. If you had to help decide the question whether Carnot should be acclaimed as the "real discoverer of the mechanical equivalent of heat," what factors or kinds of information would you try to take into account in reaching a decision?

5. *Humphry Davy's early work on the production of heat by friction*

73. In modern science the term *power* denotes the physical quantity "mechanical work done per unit time." In what sense does Davy use "power" on pages 190 and 192?

74. What was the temperature of the atmosphere during experiment II?

75. From the data on page 193 one can show that 0.5 lb of ice was used in experiment II. (*a*) Show that 74 Btu of heat would be needed to change this ice, which was initially at 29°F, into water at 35°F. (*b*) If it had been true, as Davy thought, that no appreciable part of this heat was supplied by thermal conduction from the surroundings, how much mechanical work would he have done on the ice to produce the heat? (Recall that 1 Btu is equivalent to 777.9 ft lb.)

76. For each of Davy's two experiments, state: (*a*) the hypotheses and deductions that led him to make the experiment; (*b*) the factors that he considered relevant in planning it; (*c*) other factors that he might have considered relevant, and why he may have ignored them; (*d*) the factors that he tried to keep constant and the variables that he observed or measured; (*e*) the conclusions.

77. In experiment III, suppose that Davy — possibly by continuing the operation for a longer time — had succeeded in producing a much larger quantity of heat, so that, if it were freezing water in the channel that was furnishing this heat, the new ice thus produced would have been clearly visible. If, under these circumstances, he had not observed new ice, would he have had an ironclad case for his contentions that the heat evolved did not come from either the water, the ice, or the outside bodies in contact with the ice, and therefore that caloric does not exist? (Before trying to answer this question, it might be well to make a brief outline of Davy's whole argument.)

78. Comment critically on the following statements, which appear in various books published since 1930: (i) "Davy's ingenious experimental procedure was to rub two pieces of ice together in the absence of air." (ii) "Davy rubbed pieces of ice together in air, and then in a vacuum." (iii) "Davy found that the rate of melting of the ice was proportional to the mechanical work done in rubbing the ice." (iv) "The idea of trying to produce heat by means of ice was novel, and has naturally elicited admiration; some historians consequently may have been tempted to give young Davy more credit in this connection than is due him." (v) "Rumford's conclusion in his paper on the boring of cannon was vigorously attacked by the calorists, but it was thoroughly confirmed in 1799 by Davy."

79. In referring to this essay of Davy's, a recent writer says that nine-tenths of it are ingenuous and fallacious speculation, but one-tenth shows the high genius of this young man of 19 years who was soon to enter on a

brilliant career in physical science. Do you find any evidence in the present excerpts to substantiate either of these assertions?

80. Why is it that most people — even those who are familiar with the modern, energy theory of heat — still find it useful to employ the ideas and terminology of the material theory in describing or thinking about thermal processes in which the heat is conserved — that is, not transformed into other forms of energy during the process?

81. It has been said that a certain degree of healthy ignorance is an asset to a research worker. Suggest reasons why this may be true.

82. Michelangelo, the most famous of the Florentine artists of the Renaissance, once said: "I criticize not by finding fault but by a new creation." Referring to the realm of the sciences, J. B. Conant, in "The Overthrow of the Phlogiston Theory" (Case 2, *Harvard Case Histories in Experimental Science*), says: "The overthrow of the phlogiston theory involved the development of a superior conceptual scheme." (*a*) Discuss the implications of these two comments, with special reference to the effectiveness of the methods of attack on the caloric theory employed by Rumford (Secs. 3 and 4) and Davy. (*b*) Is there much evidence that Rumford and Davy were influenced in their choice of experiments and ways of reasoning about them by the fact that they were working in opposition to current scientific beliefs about the nature of heat?

83. In a paper entitled "Recherches sur le Progrès lent du Mélange spontané de certains Liquides. . ." (1807), Rumford described experiments which indicated that the particles of a liquid are in motion even when all parts of the liquid are at the same temperature. In what essential way does this this mode of attack on the caloric theory differ from those employed by Rumford and Davy in the experiments described in Sections 3, 4, and 5?

84A. Compute the weight of the ice used in experiment II.

85A. In connection with experiment III, show that: (*a*) the total quantity of heat needed to warm 0.5 lb of iron through 1°F and at the same time to melt 18 grains of beeswax (heat of fusion, 2 Btu/lb) is 0.06 Btu; (*b*) the heat evolved when about 3 grains of water at 32°F changes to ice at 32°F is 0.06 Btu.

86A. Compute the volume of 3 grains of ice.

87A. An experiment that Rumford or Davy could have performed, if it had occurred to them, is to stir, or churn, a liquid such as water and observe whether it rises in temperature. As a way to attack the caloric theory, how does this experiment compare with those involving either abrasion or melting?

88A. It has been said that we tend to characterize a phenomenon as "anomalous" as long as we are unable to fit it into the conceptual scheme that we employ for describing other related phenomena. (*a*) Can you cite examples from your own experiences that seem to substantiate this assertion? (*b*) Do these examples furnish any indication that you may need to enlarge or revise certain of your conceptual schemes? (*c*) Does the way in which water expands and contracts with changes in temperature (p. 83) appear to be anomalous when viewed in the light of the caloric theory?

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CASE 4

The Atomic-Molecular Theory

BY

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CASE 4

The Atomic-Molecular Theory

PROLOGUE

Some of the earliest writings that have come down to us from ancient civilizations display a recurrent speculation about the ultimate character of matter. Are the materials presented to us by nature, and those produced by art, capable of subdivision without limit; or do they consist of certain extremely minute particles (atoms) which cannot be further subdivided without destruction of the identity of the material? Almost 2500 years ago the Greek philosophers Leucippus and Democritus propounded a fairly clear and persuasive formulation of the atomistic point of view. Prescient as it appears to us, their view was primarily a speculative response to certain everyday observations of nature. This response was conditioned by certain apparent logical paradoxes connected with the idea that matter is infinitely subdivisible; and the scientific development of the early Greeks was entirely inadequate for the basic resolution of such a weighty issue on experimental grounds. Such a towering speculative structure erected on so small a base of common observations could be, and was, opposed by other philosophies similarly based, but differently constructed. Thus the atomic hypothesis, together with the relatively materialistic world view with which it was at first associated, was controverted by other philosophers, notably by Aristotle. However, the original question was still entirely unresolved, and discussion of it continued, more or less actively, for some 2000 years. Only toward the close of the eighteenth century had scientific development achieved a sufficient degree of sophistication to permit a fruitful reëxamination of the entire problem.

By the time of the Late Renaissance, with its notable quickening of interest in experimental science, the original writings of Leucippus and Democritus had been lost, and the learned world was acquainted with their opinions only through the animadversions of other philosophers and, somewhat more directly, through the didactic poem "De Rerum Natura" in which Lucretius (98–55 B.C.) provided an exposition and an enthusiastic appraisal of some aspects of Greek atomism. However, many of the foremost natural philosophers of this era seriously entertained one or another form of the atomistic viewpoint. Furthermore, with the gradual decay of the alchemistic contention that different kinds of matter could be converted into one another, the permanence and immutability of the atoms characteristic of different materials became more plausible. There resulted a vigorous revival of the atomistic viewpoint — so much so that toward the middle of the eighteenth century we find Voltaire writing: "Atoms are accepted, indivisible, and immutable principles to which is due the changelessness of the different elements and the different kinds of bodies."

The more widespread credence accorded the atomistic hypothesis arose not from any new direct evidence for its "correctness" but, at least in part, because it was found to provide an extraordinarily useful way of thinking about nature, helping to construe natural phenomena in terms of mechanical models and analogies. This usefulness was much extended after the completion of the chemical revolution initiated by Lavoisier (1743–1794), when clarification of the concept of chemical elements helped foster the idea that these elements consisted of certain characteristic kinds of atoms. It is perhaps significant that one of the first statements of a detailed atomic hypothesis, in a form approximating that which still prevails, was made in 1789 in a work on *A Comparative View of the Phlogistic and Antiphlogistic Theories*, written by William Higgins (1766–1835) in support of the new oxygen theory of Lavoisier.

Although, up to this time, the atomistic hypothesis had found an ever-widening usefulness in "explaining" or "understanding" natural phenomena, it still remained a speculative idea. Not only was it most tenuously supported by experimental evidence, but it had not been applied in a single definite form to the correlation of a wide variety of phenomena and, most important of all, it had not yet exercised the highest function of a new conceptual scheme — the suggestion of new experiments. With Higgins's publication we see the beginning of the transmutation of this speculative idea. Indeed, before the passage of another score of years this extremely ancient notion had been placed before the learned world in the character of a well-developed conceptual scheme that was found to "explain" a great many of the previously discovered data of chemistry and physics, and that was fruitful of numerous new ideas and experiments. How this metamorphosis was accomplished is the subject of the present work.

In Section 1 we shall view the deceptively simple proposals advanced by John Dalton (1766–1844), the effective architect of the atomic theory as we know it today. Dalton, the son of a poor Quaker weaver, received little formal education but was himself a teacher in a village school when he was no more that twelve years old. He spent most of his life in Manchester, where he was for a time an instructor in various branches of natural philosophy at the New College, and later a freelance tutor in these subjects. Despite his meager training, Dalton displayed considerable scientific acumen in the development of his atomic theory. He presented a clear and concrete formulation of the fundamental postulates on which a meaningful atomic theory could be founded. With the aid of a bold assumption he achieved a drastic simplification of an extraordinarily complex situation. Finally, lacking the means of securing direct evidence for his conception he showed in a masterly way how indirect evidence for this essentially physical hypothesis could be developed from chemical data that were fairly readily obtainable.

In Section 2 we shall observe the striking and immediate achievements of the atomic theory in relation to the then contemporary chemistry. There were few who were not favorably impressed by those achievements, but there were, then and later, many who admitted that matter behaved *as though* it were composed of Daltonian atoms but who nevertheless maintained a skeptical attitude toward the postulated *real existence* of these atoms. In particular, there were many who felt considerable doubt about the validity of the basic simplifying assumption with the aid of which the atomic theory had originally been brought to bear upon chemical phenomena; indeed, to some slight extent, Dalton shared their doubts. The support of this assumption, or the substitution for it of some more prepossessing alternative, was correctly recognized as one of the pivotal factors that would determine the future usefulness of the atomic theory.

In Section 3 we shall follow the discovery, by Joseph Louis Gay-Lussac (1778–1850), of an empirical relation that ultimately suggested the desired better substitute for Dalton's assumption. Gay-Lussac, a superb experimentalist, was a product of the Ecole Polytechnique. In the course of his distinguished career he made a large number of fundamental contributions to both pure science and industrial technology and, in his later years, to the organization of scientific projects of interest to his government.

In Section 4 we shall examine Dalton's *rejection* of Gay-Lussac's important work. Although this work ultimately led to a vital complement to Dalton's original theory, Dalton's rejection of it was based on reasonable grounds. The new relation appeared to be in fundamental contradiction with certain tenets that seemed to him essential to the atomic theory as such.

In Section 5 we shall see how Amadeo Avogadro di Quaregna (1776–1856) penetrated to the heart of this apparent anomaly and showed the way in which it might be dissipated. Avogadro was born in Turin and educated at its University, where he later occupied the chair of mathematical physics. In the important paper that has made his fame secure

Avogadro succeeded not only in providing a reconciliation of apparently incompatible viewpoints, but, in so doing, he also indicated how the empirical relations established by Gay-Lussac could lead to a much less arbitrary supposition than the rather dubious assumption that Dalton had found it necessary to use. With Avogadro's proposal the framework of the modern atomic-molecular theory was essentially completed — less than five years after the publication of the first outline of Dalton's new conceptual scheme.

A major advance achieved with such rapidity inspires our respect. We cannot distinguish all the factors that contributed to the speed of this development. Surely not the least important of these factors was the possession by Dalton, and several of his contemporaries, of a most penetrating scientific intuition — or, more precisely, a genius for forging ahead by *guessing* right when insufficient criteria were available to support a completely reasoned judgment. However, the speed characterizing the initial growth of the atomic-molecular theory is superficially no more remarkable than the delay of approximately 50 years that intervened before the essential correctness of Avogadro's synthesis was fully recognized by the scientific world. Fascinating as it is, the complete story of this 50-year lag is so involved as to lie beyond the compass of the present work.

In Section 6, then, we shall only indicate some of the unavoidable weaknesses in Avogadro's position that, in one form or another, so long delayed the acceptance of his views. Finally, a sketch of the steps leading up to this eventual acceptance will conclude the present study.

1. DALTON'S ATOMIC THEORY

Dalton's Approach to the Atomic Theory. The tradition of atomism, used as a qualitative way of thinking about natural phenomena, was quite strong in English scientific history, and is well displayed in the many works of Bacon, Boyle, Hooke, and Newton. Dalton, a fervent admirer of Newton, was thus thoroughly imbued with this heritage of atomism. Moreover, Newton's striking success in interpreting a large number of terrestrial and celestial phenomena in terms of the action of finite forces between real bodies naturally encouraged attempts to construe other phenomena in like fashion. Dalton's position was further a privileged one in that he worked at a period when the long, slow development of "pneumatic chemistry," culminating in the work of Cavendish, Priestley, and Lavoisier, finally made it possible to approach the atomic theory by the route through which it was most readily accessible, namely, the study of gases. Evidence that the time was, indeed, ripe is seen in the fact that the fruitful line adopted by Dalton had been missed by William Higgins in 1789 by a margin so narrow that Higgins's claim to priority was for some time maintained by Davy, who, however, subsequently foreswore this contention. Thus it appears that Dalton labored at a time when, and in a milieu from which, the development of a realistic atomic theory could not have been too long postponed.

The sequence of events by which Dalton arrived at his celebrated theory is regrettably obscure, particularly since Dalton himself has given us several different accounts. A judgment on the basis of his published papers is rendered difficult by a curious situation reminiscent of that attending the publications of Lavoisier on combustion. The papers, read in 1802 and 1803, in which Dalton appears to be grappling with the problems of the atomic theory were not published until 1805, when they appeared in the *Memoirs of the Literary and Philosophical Society of Manchester*. A study of Dalton's notebooks has indicated that some of the experiments presumably discussed in the paper read in 1803 were actually not performed until 1804. Thus Dalton apparently brought his paper up to date at the time of its publication in 1805; he had ample opportunity for such revision since he was the secretary of the Society at that time. Consequently, it is very difficult for us to decide what represents his original conception and what is the result of subsequent elaboration. A careful examination of the available indications leads to the conclusion that Dalton's earliest intimations of his atomic theory came to him from studies undertaken in connection with his lifelong interest in meteorology. It seems probable that through his purely physical investigations of the behavior of mixtures of gases and of the solubility of gases in liquids (the phenomena here involved are not, in fact, highly relevant to the atomic theory) he was led from a philosophical Newtonian atomism to a concrete apprehension of the methods whereby an atomic theory might be supported by chemical experiments. The excerpts printed below are particularly valuable in showing how this approach encouraged Dalton to believe that there were significant differences in the sizes of the particles of various gases. This belief had a most important influence on the further development of the atomic theory, in that it disposed Dalton to discount subsequent discoveries that provided a vital supplement to his original theory.

The following excerpt, containing Dalton's first announcement of his atomic theory, is the concluding section of a paper "read before a select audience of nine members and friends in the rooms of the Literary and Philosophical Society of Manchester on 21st October 1803." The subject of this paper is "On the Absorption of Gases by Water and Other Liquids," and the fact that the announcement occurs in this context provides a strong indication that Dalton's original conception of his chemical atomic theory grew out of his studies of phenomena in which chemical reactions are scarcely involved. In the final section, dealing with the "Theory of the Absorption of Gases by Water," Dalton remarks:

> The greatest difficulty attending the mechanical hypothesis, arises from different gases observing different laws. Why does water not admit its bulk of every kind of gas alike? [i.e., why are not all gases equally soluble in water?] This question I have duly considered, and though I am not yet able to satisfy myself completely, I am nearly persuaded that the circumstance depends upon the weight and number of the ultimate particles of the several gases: Those whose particles are lightest and single being least absorbable, and the others more according as they increase in weight and complexity. (Subsequent experience renders this conjecture less probable.) An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new: I have lately been prosecuting this enquiry with remarkable success. The principle cannot be entered upon in this paper; but I shall just subjoin the results, as far as they appear to be ascertained by my experiments.

Dalton here appends a "Table of the relative weights of the ultimate particles of the gaseous and other bodies." This is the first published tabulation of atomic weights, and the figures cited make it plain that Dalton had by this time formulated all the essential parts of his theory.

A fuller account of Dalton's progress toward the atomic theory has been found in his manuscript notes for one of a series of lectures which he delivered early in 1810 at the Royal Institution (founded in 1799 at the instance of Count Rumford). The notes here reproduced were for the seventeenth lecture of the series, and it is interesting to observe that this discussion followed directly after two lectures on heat. Dalton's ideas about heat seem to have played an important role in the development of his theory, and he states that "the doctrine of heat is justly considered as constituting an essential part of chemical science." Although Dalton was familiar with the dynamical theory of heat — which related heat to the motion of submicroscopic particles — the "doctrine of heat" that he adopted in the construction of his atomic theory considers heat as a tangible substance which is weightless, or of negligible weight.

> As the ensuing lectures on the subject of *chemical elements* and their combinations will perhaps be thought by many to possess a good deal of novelty, as well as importance, it may be proper to give a brief historical sketch of the train of thought and experience which led me to the conclusions about to be detailed.
>
> Having been long accustomed to make meteorological observations, and to speculate upon the nature and constitution of the atmosphere, it often struck me with wonder how a *compound* atmosphere, or a mixture

of two or more elastic fluids, should constitute apparently a homogeneous mass, or one in all mechanical relations agreeing with a simple atmosphere. [Dalton had published, in 1793, a book on meteorology in which there is some faint foreshadowing of a concern with the problem to which he directs our attention. "Compound" is used here not in the sense of chemical combination, but merely to distinguish a *mixed* atmosphere from a simple one-component atmosphere.]

Newton has demonstrated clearly, in the 23rd Prop. of Book 2 of the *Principia*, that an elastic fluid is constituted of small particles or atoms of matter, which repel each other by a force increasing in proportion as their distance diminishes.[1] But modern discoveries having ascertained that the atmosphere contains three or more elastic fluids, of different specific gravities, it did not appear to me how this proposition of Newton would apply to a case of which he, of course, could have no idea.

The same difficulty occurred to Dr. Priestley, who discovered this compound nature of the atmosphere. He could not conceive why the oxygen gas, being specifically heaviest, should not form a distinct *stratum* of air at the bottom of the atmosphere, and the azotic gas one at the top of the atmosphere. [In conformity with the usage of his day, Dalton employs "azotic gas" or "azote" to signify nitrogen. The form survives in modern French.] Some chemists upon the Continent, I believe the French, found a solution of this difficulty (as they apprehended). It was *chemical affinity* [an attraction or tendency that was believed to cause substances to combine, react, or form solutions with one another]. One species of gas was held in solution by the other; and this compound in its turn dissolved water; hence *evaporation*, *rain*, etc. This opinion of air dissolving water had long before been the prevailing one, and naturally paved the way for the reception of that which followed, of one kind of air dissolving another. It was objected that there were no decisive *marks* of chemical union, when one kind of air was mixed with another. The answer was, that the affinity was of a very *slight* kind, not of that energetic cast that is observable in most other cases. [That is, since there is no readily observed change of volume or temperature when the separated atmospheric gases are mixed, it is hypothesized that their

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[1] If Dalton merits the title of "father of the atomic theory," we must allow Newton the position of "grandfather" of the theory. This is true not only because of his profound influence on Dalton, as here displayed; but even more important, because thousands of years after the earliest thought of an atomic theory, he was the first to assess the value of this concept by quantitatively measuring it against experience. Thus, in the Proposition to which Dalton refers, Newton demonstrates that:

"A . . . gas which is made up of mutually repulsive particles . . . the forces between which are reciprocally proportional to the distances between their centres, will make up an elastic fluid, the density of which is proportional to the pressure . . . " (i.e., an elastic fluid that obeys Boyle's Law).

It is interesting to observe that Dalton has misrepresented the content of Newton's demonstration, which proved only that if such an hypothesis were accepted, Boyle's Law could be "explained," but which did *not* prove, as Dalton suggests, that such an hypothesis is the *only* possible explanation of Boyle's Law. Indeed, the modern explanation is essentially different from that proposed by Newton.

> tendency to react (i.e., their affinity) is weaker than in the normal chemical processes, where there are usually fairly obvious indications of the progress of the reaction.]
>
> I may add, by-the-bye, that this is now, or has been till lately, I believe, the prevailing doctrine in most of the chemical schools in Europe.
>
> In order to reconcile or rather adapt this chemical theory of the atmosphere to the Newtonian doctrine of repulsive atoms or particles, I set to work to combine my atoms upon paper. I took an atom of water, another of oxygen, and another of azote, brought them together, and threw around them an atmosphere of heat . . . I repeated the operation, but soon found that the watery particles were exhausted (for they make but a small part of the atmosphere). [The weight and volume percentages of nitrogen, oxygen and water vapor in the atmosphere were known in Dalton's time. Dalton speaks here in terms of the relative numbers of the ultimate particles of these components, which he probably calculated from the proportions by volume with the aid of the "confused idea" (see page 267) that equal volumes of different gases contain equal numbers of their respective particles. Such a calculation indicates that for each particle of water vapor there are about 20 particles of oxygen, and some 80 azotic particles.] I next combined my atoms of oxygen and azote, one to one; but I found in time my oxygen failed; I then threw all the remaining particles of azote into the mixture, and began to consider how the general equilibrium was to be obtained. [This combination and manipulation of atoms "upon paper" refers to an entirely hypothetical situation, or "thought experiment," by which Dalton proposed to discover the bearing of the atomic theory on the problem of the homogeneity of a "compound" atmosphere.]
>
> My triple compounds of *water*, *oxygen*, and *azote* were wonderfully inclined, by their superior gravity, to descend and take the lowest place; the double compounds of *oxygen* and *azote* affected to take a middle station; and the azote was inclined to swim at the top. I remedied this defect by lengthening the wings of my heavy particles, that is, by throwing more heat around them, by means of which I could make them float in any part of the vessel; but this change unfortunately made the whole mixture of the same specific gravity as azotic gas — this circumstance could not for a moment be tolerated. In short, I was obliged to abandon the hypothesis of the chemical constitution of the atmosphere altogether, as irreconcilable to the phenomena.

A better grasp of Dalton's conception of the heat "atmosphere" around his ultimate particles can be secured from the following excerpt from his short manuscript article "On Heat," dated May 23, 1806: "According to this view of the subject, every atom has an atmosphere of heat around it, in the same manner as the earth or any other planet has its atmosphere of air surrounding it, which cannot certainly be said to be held by chemical affinity, but by a species of attraction of a very different kind. Every species of atoms or ultimate particles of bodies will be found to have their peculiar powers of attraction for heat, by which a greater or less quantity of that fluid will be conglomerated around them in like circumstances: this gives rise to what has been called the *different capacities* of bodies for heat or their *specific* heat. Any two bodies, the atoms of which have different capacities for heat, being placed in any medium will acquire the same *temperature*. This state consists in the several individual atmospheres of heat acquiring the same density at their *exterior surface*, or where they become contiguous. The virtual diameters of atoms of matter will therefore vary in like circumstances according to their attraction for heat; those with a strong attraction will collect a large and denser atmosphere around them, whilst those possessing a weaker attraction will have a less atmosphere, and consequently the virtual diameter, or that of the atom and its atmosphere together, will be less, though the atmospheres of both have precisely the same disposition to receive or to part with heat upon any change of temperature. . ."

Thus by hypothesizing different attractions for heat, and heat shells of variable diameter, Dalton is able to vary the effective densities of his particles in much the same way that a fisherman adjusts the effective density of a lead sinker by attaching to it various quantities of cork. In attempting to adjust the particles of different weights so that all would have the same specific gravity he could not entirely remove the heat shell from the lightest particles (the nitrogen atoms) since he considered the heat shell to be the essential source of the repulsions by which the elastic (gaseous) state was maintained. Consequently he had no alternative but to extend the heat atmospheres around the heavier particles (i.e., to "lengthen their wings") until their specific gravity, and that of this chemically compounded atmosphere, were the same as for nitrogen — a palpable contradiction of experience.

> There was but one alternative left, namely, to surround every individual particle of *water*, of *oxygen*, and of *azote*, with heat, and to make them respectively centres of repulsion, the same in a *mixed* state as in a *simple* state. This hypothesis was equally pressed with difficulties; for, still my oxygen would take the lowest place, my azote the next, and my steam would swim upon the top.
>
> In 1801 I hit upon an hypothesis which completely obviated these difficulties.
>
> According to this, we were to suppose that the atoms of one kind did *not* repel the atoms of another kind, but only those of their own kind. This hypothesis most effectually provided for the diffusion of any one gas through another, whatever might be their specific gravities, and perfectly reconciled any mixture of gases to the Newtonian theorem.

[According to this ingenious idea, stratification or segregation of particles of the same kind is prevented by strong, specific, mutual repulsions, which render any collection of particles of the same kind an unstable grouping. Consequently gases will mix with one another and will remain uniformly mixed despite differences in the intrinsic specific gravities of the components.] Every atom of both or all the gases in the mixture was the centre of repulsion to the proximate particles of its own kind, disregarding those of the other kind. All the gases united their efforts in counteracting the pressure of the atmosphere, or any other pressure that might be opposed to them.

This hypothesis, however beautiful might be its application, had some improbable features.

We were to suppose as many distinct *kinds* of repulsive powers, as of gases; and, moreover, to suppose that *heat* was not the repulsive power in any one case; positions certainly not very probable. Besides, I found from a train of experiments which have been published in the *Manchester Memoirs*, that the diffusion of gases through each other was a *slow* process, and appeared to be a work of considerable effort.

Upon reconsidering this subject, it occurred to me that I had never contemplated the effect of *difference of size* in the particles of elastic fluids. By *size* I mean the hard particle at the centre and the atmosphere of heat taken together. If, for instance, there be not exactly the same *number* of atoms of oxygen in a given volume of air ["air" is used here, as by Priestley, as a generic term for "gas"] as of azote in the same volume, then the *sizes* of the particles of oxygen must be different from those of azote. And if the *sizes* be different, then on the supposition that the repulsive power is heat, no equilibrium can be established by particles of unequal size pressing against each other . . . [Dalton's conclusion here is based on a rather abstruse (and erroneous) line of mechanical and geometrical reasoning which led him to believe that there would be no stratification of the components — "the particles of one kind being from their size unable to apply properly to the other" at their common surfaces of contact.]

This idea occurred to me in 1805. I soon found that the *sizes* of the particles of elastic fluids *must* be different. For a measure of azotic gas and one of oxygen, if chemically united, would make nearly *two* measures of nitrous gas, and those *two* could not have *more* atoms of nitrous gas than the *one* measure had of azote or oxygen. . .[2] Hence the sug-

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[2] Dalton cites experimental data that appear to support his new viewpoint. Although the measurements of the combining volumes were relatively crude, they sufficed to show that, say, 1 cubic foot of oxygen would react with 1 cubic foot of nitrogen to form approximately 2 cubic feet of nitrous gas. Now if we assume that there are n atoms of oxygen in unit volume of oxygen, and n atoms of nitrogen in unit volume of nitrogen, we can form from them a maximum of n molecules of nitrous gas, each of which is composed of one atom of oxygen and one of nitrogen. But experiment showed that these n molecules of nitrous gas occupied *two* unit volumes, implying that each volume of nitrous gas contained only $\frac{1}{2}n$ molecules, or only half as many gaseous "particles" as were assumed to be present in unit volume of nitrogen or of oxygen. Dalton saw no alternative to

> gestion that all gases of different kinds have a difference in the *size* of their atoms; and thus we arrive at the reason for that diffusion of every gas through every other gas, without calling in any other repulsive power than the well-known one of heat. [The compound gas is maintained in a homogeneous condition through the mechanism referred to at the end of the immediately preceding paragraph.]
>
> This then is the present view which I have of the constitution of a mixture of elastic fluids.
>
> The different *sizes* of the particles of elastic fluids under like circumstances of temperature and pressure being once established, it became an object to determine the relative *sizes* and *weights*, together with the relative *number* of atoms in a given volume. This led the way to the combinations of gases, and to the *number* of atoms entering into such combinations, the particulars of which will be detailed more at large in the sequel. Other bodies besides elastic fluids, namely liquids and solids, were subject to investigation, in consequence of their combining with elastic fluids. Thus a train of investigation was laid for determining the *number* and *weight* of all chemical elementary principles which enter into any sort of combination one with another.

In these lecture notes of Dalton's three significant points should be remarked:

(1) The successive consideration of *ad hoc* hypotheses, to discover one that adequately "explains" the experimental phenomena in terms of simple and plausible assumptions, is well exhibited. Such an approach was and is of the greatest importance in scientific investigation.

(2) Dalton's attention was focused on the *sizes* of his particles as well as on their weights, and he was led to believe that the same volume of different gases contained different numbers of "particles." This factor had a most important influence on the later history of the atomic theory.

(3) But Dalton also calls attention to the importance of the weight relations of the ultimate particles, and it was in this connection that his theory proved most fruitful.

(4) He has also stressed the view that chemical combination represents an atom-to-atom linkage of small numbers of constituent bodies, rather than the physical solution of many particles of one kind in a multitude of particles of another kind.

The Framework of the Atomic Theory. In the following passages are stated the fundamental postulates of the atomic theory. To facilitate comprehension of the content of these passages we may prefix them with an orthodox modern summary of the basic postulates. It is important to observe, however, that Dalton did not proceed in a clear-cut

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the conclusion that there were different numbers of particles in equal volumes of different gases. We shall soon see the unhappy consequences of this conclusion.

fashion from postulates to argument but that, rather, he followed a reverse course. The modern summary of his postulates might run:

All matter is composed of atoms which are indivisible.

All the atoms of a given element are alike in weight and in all other respects.

The atoms of different elements are of different weights.

Atoms are indestructible and preserve their identities in all chemical reactions.

The following passage is an excerpt from Dalton's notes for the eighteenth of the lectures that he gave at the Royal Institution, in 1810.

> We endeavoured to show that matter, though divisible in an *extreme degree*, is nevertheless not *infinitely* divisible. That there must be some point beyond which we cannot go in the division of matter. The existence of these ultimate particles of matter can scarcely be doubted, though they are probably much too small ever to be exhibited by microscopic improvements.
>
> I have chosen the word *atom* to signify these ultimate particles, in preference to *particle*, *molecule*, or any other diminutive term, because I conceive it is much more expressive; it includes in itself the notion of *indivisible*, which the other terms do not. It may perhaps be said that I extend the application of it too far, when I speak of *compound atoms*; for instance, I call an ultimate particle of *carbonic acid* a *compound atom*. Now, though this atom may be divided, yet it ceases to be carbonic acid, being resolved by such division into charcoal and oxygen. Hence I conceive there is no inconsistency in speaking of compound atoms, and that my meaning cannot be misunderstood. [The word "atom" derives from the Greek "atomos," signifying uncut or indivisible.]
>
> It has been imagined by some philosophers that all matter, however unlike, is probably the same thing; and that the great variety of its appearances arises from certain powers communicated to it, and from the variety of combinations and arrangements of which it is susceptible. From the notes I borrowed from Newton in the last lecture, this does not appear to have been his idea. Neither is it mine. I should apprehend there are a considerable number of what may be properly called *elementary* principles, which never can be metamorphosed, one into another, by any power we can control. We ought, however, to avail ourselves of every means to reduce the number of bodies or principles of this appearance as much as possible; and after all we may not know what elements are absolutely indecomposable, and what are refractory, because we do not apply the proper means for their reduction.

The next passages are taken from Dalton's *A New System of Chemical Philosophy*, the first part of which was published in 1808.

> Whether the ultimate particles of a body, such as water, are all alike,

that is, of the same figure, weight, etc. is a question of some importance. From what is known, we have no reason to apprehend a diversity in these respects: if it does exist in water, it must equally exist in the elements constituting water, namely, hydrogen and oxygen. Now it is scarcely possible to conceive how the aggregates of dissimilar particles should be so uniformly the same. If some of the particles of water were heavier than others, if a parcel of the liquid on any occasion were constituted principally of these heavier particles, it must be supposed to affect the specific gravity of the mass, a circumstance not known. Similar observations may be made on other substances. Therefore we may conclude that *the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, &c.* In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen. . .

When any body exists in the elastic state, its ultimate particles are separated from each other to a much greater distance than in any other state; each particle occupies the centre of a comparatively large sphere, and supports its dignity by keeping all the rest, which by their gravity, or otherwise are disposed to encroach upon it, at a respectful distance. When we attempt to conceive the *number* of particles in an atmosphere, it is somewhat like attempting to conceive the number of stars in the universe; we are confounded with the thought. But if we limit the subject, by taking a given volume of any gas, we seem persuaded that, let the divisions be ever so minute, the number of particles must be finite; just as in a given space of the universe, the number of stars and planets cannot be infinite.

Chemical analysis and synthesis go no farther than to the separation of particles one from another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce, consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance.

In all chemical investigations, it has justly been considered an important object to ascertain the relative *weights* of the simples which constitute a compound. But unfortunately the enquiry has terminated here; whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms of the bodies might have been inferred, from which their number and weight in various other compounds would appear, in order to assist and to guide future investigations, and to correct their results. Now it is one great object of this work, to show the importance and advantage of ascertaining *the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle.*

The Determination of the Relative Atomic Weights. The decks have now been cleared for action, and the calculation of the weights (relative to hydrogen taken as 1) of the ultimate particles defined above has been set as the goal. But, unfortunately, while the postulates already considered are essentially satisfactory and correct, they are not in themselves sufficient to make possible a calculation of the atomic weights. A simple example will illustrate this point.

The crude analyses used by Dalton indicated that about 6 grams of oxygen united with 1 gram of hydrogen to form 7 grams of water. Letting n represent the number of water molecules (or "compound atoms") so formed, then if the molecular formula of water is HO it is plain that n atoms of hydrogen weigh 1 gram while n atoms of oxygen weigh 6 grams; or one oxygen atom weighs six times as much as one hydrogen atom; or the atomic weight of oxygen, relative to hydrogen, is 6. However, if the formula of water is taken as HO_2, n atoms of hydrogen will have reacted with $2n$ atoms of oxygen. Consequently, n atoms of oxygen weigh only 3 grams, and the weight of one oxygen atom relative to one hydrogen atom is then 3. In the same way, if the formula of water is assumed to be H_2O, the atomic weight of oxygen is calculated to be 12.

It is thus made evident that no valid calculation of relative atomic weights can be undertaken until molecular formulas can be determined. Lacking the essential criteria for such a determination, Dalton forges ahead with the bold assumption of an arbitrary set of maxims — the "rule of greatest simplicity" — with which the following passage is concerned. Today those postulates of Dalton that have already been examined are retained essentially intact; the rule of greatest simplicity is rejected. Yet it appears that one of Dalton's greatest single contributions to the formulation of an atomic theory was made through this rule, and that his theory was most valuable in just that aspect in which it was most in error. Before examining the basis of this apparent paradox, let us first consider the rule of greatest simplicity as it is outlined by Dalton in a continuation of the last excerpt.

> If there are two bodies, *A* and *B*, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple: namely,
>
> 1 atom of *A* + 1 atom of *B* = 1 [compound] atom of *C*, binary.
> 1 atom of *A* + 2 atoms of *B* = 1 [compound] atom of *D*, ternary.
> 2 atoms of *A* + 1 atom of *B* = 1 [compound] atom of E, ternary.
> 1 atom of *A* + 3 atoms of *B* = 1 [compound] atom of *F*, quaternary.
> 3 atoms of *A* + 1 atom of *B* = 1 [compound] atom of *G*, quaternary.
> &c. &c.
>
> The following general rules may be adopted as guides in all our investigations respecting chemical synthesis.

> 1st. When only one combination of two bodies can be obtained, it must be assumed to be a *binary* one, unless some cause appear to the contrary.
>
> 2d. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.
>
> 3d. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.
>
> 4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, &c . . .
>
> 7th. The above rules and observations equally apply, when two bodies, such as *C* and *D*, *D* and *E*, &c. are combined.

Dalton now proceeds to show how, with these additional postulates, the calculation of atomic weights can be carried out. However, we possess a clearer, if more elementary, presentation of this material in the words of one of Dalton's contemporaries and admirers, Thomas Thomson. In 1807, a year before the appearance of Dalton's own book, Thomson published in the third edition of his *System of Chemistry* the first printed exposition of Dalton's ideas, and it was through this account that most of the scientific world first became familiar with Dalton's views. Throughout this account Thomson uses the terms "density of the atom" and "relative density of the atom" to signify "weight of the atom" and "relative weight of the atom" or "atomic weight," respectively. He says:

> We have no direct means of ascertaining the density of the atoms of bodies; but Mr. Dalton, to whose uncommon ingenuity and sagacity the philosophic world is no stranger, has lately contrived an hypothesis which, if it prove correct, will furnish us with a very simple method of ascertaining that density with great precision. Though the author has not yet thought fit to publish his hypothesis, yet as the notions of which it consists are original and extremely interesting, and as they are intimately connected with some of the most intricate parts of the doctrine of affinity, I have ventured, with Mr. Dalton's permission, to enrich this work with a short sketch of it.
>
> In justice to Mr. Dalton, I must warn the reader not to decide upon the notions of that philosopher from the sketch which I have given, derived from a few minutes' conversation, and from a short written memorandum. The mistakes, if any occur, are to be laid to my account, and not to his; as it is extremely probable that I may have misconceived his meaning in some points. [This gracious disclaimer was not entirely necessary; in so far as the present excerpt is concerned, Thomson seems to have given a surprisingly accurate account of the ideas entertained by Dalton in 1804.]
>
> The hypothesis upon which the whole of Mr. Dalton's notions respecting chemical elements is founded, is this. [It is interesting to observe

that Thomson here calls attention to the "rule of greatest simplicity" (a more detailed expression of the key idea of atom-to-atom combination) as the cornerstone of Dalton's theory. That is, to Thomson at least, there was nothing strikingly new or improbable about Dalton's other postulates, but the rule of greatest simplicity is recognized as an advance of pivotal importance.] When two elements unite to form a third substance, it is to be presumed that *one* atom of one joins to *one* atom of the other, unless when some reason can be assigned for supposing the contrary. Thus oxygen and hydrogen unite together and form water. We are to presume that an [a compound] atom of water is formed by the combination of *one* atom of oxygen with *one* atom of hydrogen. In like manner *one* [compound] atom of ammonia is formed by the combination of *one* atom of azote [nitrogen] with *one* atom of hydrogen. If we represent an atom of oxygen, hydrogen, and azote, by the following symbols,

Oxygen	○
Hydrogen	⊙
Azote	⦶

Then an [a compound] atom of water and of ammonia will be represented respectively by the following symbols:

Water	○⊙
Ammonia	⊙⦶

[These symbols represent a real departure. Although the alchemists had been accustomed to the use of symbols to represent indeterminate amounts of their "elements," Dalton's new symbols definitely refer to a single atom of the element symbolized; and instead of using new symbols for more complex substances, the composition of the compound is systematically represented as a combination of the symbols for the atoms of which it is supposed to be composed. This representation also emphasizes Dalton's concept of compound formation as the direct application or addition of an atom of one element to one or a few atoms of another element, rather than as a vague aggregate of indeterminate numbers of the particles of different elements.] But if this hypothesis be allowed, it furnishes us with a ready method of ascertaining the relative density of those atoms that enter into such combinations; for it has been proved by analysis, that water is composed of 85⅔ of oxygen and 14⅓ of hydrogen. An [a compound] atom of water of course is composed of 85⅔ parts by weight of oxygen and 14⅓ parts of hydrogen. Now if it consist of one atom of oxygen united to one atom of hydrogen, it follows, that the weight of one atom of hydrogen is to that of one atom of oxygen as 14⅓ to 85⅔, or as 1 to 6 very nearly. In like manner an [a compound] atom of ammonia has been shown to consist of 80 parts of azote and 20 of hydrogen. Hence an atom of hydrogen is to an atom of azote as 20 to 80, or 1 to 4. Thus we have obtained the following relative densities of these three elementary bodies.

Hydrogen	1
Azote	4
Oxygen	6

> . . . Azote and oxygen unite in various proportions, forming nitrous oxide, nitrous gas, and nitric acid,[3] besides some other compounds which need not be enumerated. The preceding hypothesis will not apply to all these compounds; Mr. Dalton, therefore, extends it farther. Whenever more than one compound is formed by the combination of two elements, then the next simple combination must, he supposes, arise from the union of *one* atom of the one with *two* atoms of the other. If we suppose *nitrous gas*, for example, to be composed of *one* atom of azote, and *one* of oxygen, we shall have two new compounds, by uniting an [a compound] atom of nitrous gas to an atom of azote, and to an atom of oxygen, respectively. If we suppose farther, that nitrous oxide is composed oxide contains two atoms of azote united to one of oxygen, while nitric acid consists of nitrous gas and oxygen, united [compound] atom to atom, then the following will be the symbols and constituents of these three bodies:
>
> Nitrous gas . . . . 
> Nitrous oxide . . . . 
> Nitric acid . . . . 
>
> The first gas consists only of two atoms, or is a binary compound, but the two others consist of three atoms, or are ternary compounds; nitrous oxide contains two atoms of azote united to one of oxygen, while nitric acid consists of two atoms of oxygen united to one of azote. [The compositions given for these compounds are entirely correct. This is one of the relatively few instances in which the rule of greatest simplicity yields a satisfactory formulation. However, in this case the interpretation of the rule could be guided by the approximately known values of the gaseous densities.]

Thomson now proceeds to compare the analyses predicted by these formulas with those obtained empirically, and concludes that, within the limits of the rather large experimental errors, a satisfactory agreement obtains.

Dalton's Contributions to the Atomic Theory. Dalton is usually denominated the "father of the atomic theory." Though the theory is venerable almost beyond measure, Dalton's deceptively simple but vital contributions to the atomic theory, as set forth in the passages reproduced above, were indeed instrumental in the formulation of the highly developed conceptual scheme we know today. Let us consider the nature and value of Dalton's essential work.

(1) Dalton contributed a notably plausible, precise, and unambiguous statement of the basic postulates of the atomic theory. The clarity

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[3] "Nitrous oxide" signifies N_2O. "Nitrous gas" signifies "nitric oxide," NO. "Nitric acid" signifies "nitrogen dioxide," NO_2, the "red fumes" obtained when oxygen is added o "nitrous gas." This simple alphabetical symbolism for the elements and compounds was suggested by Berzelius (whom we shall meet later in our story) as a convenient substitute for the much more cumbersome ideographic notation used by Dalton.

of the statement is, indeed, much more noteworthy than its content. We can see, by reference to the following famous passage from Newton's *Opticks* (1706), that in so far as content is concerned there is little in Dalton's preliminary statements (excluding the "rule of greatest simplicity") that is definitely new. Even the content of Newton's statement is little more than a paraphrase of a much older work — Lucretius' *De Rerum Natura* (57 B.C.) — which is in turn derived through Epicurus from Democritus and perhaps even more ancient scholars.

That Dalton was familiar with, and impressed by, Newton's statement is demonstrated by the fact that the following excerpt from the *Opticks* has been found in Dalton's notebook, transcribed by his own hand:

> It seems probable to me that God in the beginning formed matter in *solid*, *massy*, *hard*, *impenetrable*, *movable* particles, of such *sizes* and *figures*, and with such other *properties*, and in such proportion to space as most conduced to the end for which he formed them; and that these primitive particles being solids, are incomparably harder than any porous bodies compounded of them; even so very hard as never to wear or break in pieces; no ordinary power being able to divide what God Himself made *One*, in the first creation. While the particles continue entire they may compose bodies of one and the same nature and texture in all ages; but should they wear away or break in pieces, the nature of things depending on them would be changed. Water and earth, composed of old worn particles and fragments of particles, would not be of the same nature and texture now, with water and earth composed of *entire* particles in the beginning. And therefore that nature may be lasting, the changes of corporeal things are to be placed only in the various *separations* and new *associations*, and motions of these permanent particles; compound bodies being apt to break, not in the midst of solid particles, but where those particles are laid together, and only touch in a few points . . .
>
> God is able to create particles of matter of several *sizes* and *figures*, and in several proportions to the space they occupy, and perhaps of different *densities* and forces . . . At least I see nothing of contradiction in all this.

To be sure, as an inspirational declaration, Newton's statement is immeasurably superior to Dalton's. Moreover, some of the arguments advanced by Dalton in support of his hypothesis are seen to be almost certainly of derivative origin. But what of inspiration is lacking in Dalton's rather pedestrian prose is more than compensated by the lucidity and definiteness of his statements; by the fashion in which he strips his atoms of their aura of semidivinity, and reveals them as finite bodies many of whose attributes are knowable by man; and by his suggesting, through a clear statement of tentative axioms and rules of procedure, how such knowledge might be secured.

(2) One crucial aspect in which Dalton's theory is a striking advance beyond all previous theories is in its major stress on one atomic property — *weight*. Other theories (Newton's, for example) occasionally recognized weight as one of the properties of "ultimate particles," but it had never been singled out for special attention. Rather, it was considered as one of many other properties, like size, shape ("figure"), color, hardness, wetness, motion, etc. As long as attention was diverted to any or all of this group of properties the theory was incapable of advancing with the then available empirical data. As it happened, a consideration of weight relations proved to be the fruitful line, and to the extent that Dalton made atomic *weights* the keystone of his theory, using them as the chief criterion for the distinction of one atomic species from another, he set his conceptual scheme on the road that led it toward the "validation" [4] denied all previous atomic theories. We may apprehend the narrowness of this privileged path when we observe that, to the extent that Dalton laid a subsidiary but by no means minor emphasis on the property of atomic *size*, he was led into a series of errors and contradictions that made it impossible for him to appreciate the significance of the subsequent investigations of Gay-Lussac and Avogadro.

Probably we shall never completely understand how Dalton came to attach so much importance to *weight*, nor can we deny the possible intervention of chance. However, at least two factors that may have conditioned his response to the problems of his theory can be discerned. For one thing, recent experiments had shown that no appreciable weight was associated with the hypothetical "matter of heat" ("caloric"), so that the weight of an ordinary body — or of its components — acquired new significance, in so far as it was now more a *characteristic* constant, and no longer complexly variable with temperature. Even more important, in all probability, was the influence of Lavoisier's notable triumph over the phlogiston theory, largely achieved through the careful study of weight relations. But however Dalton may have been led to his new emphasis on atomic weights, there can be no question but that this stress was rapidly fruitful of a new usefulness for, and a new faith in, the atomic theory.

(3) The rule of greatest simplicity is recognized by Thomson as the

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[4] Words like "explain," "validate," "prove," "real," "correct," etc. will usually be enclosed in quotation marks, to suggest their association with the qualifying phrase: "what is meant in science when we say . . ." Some such qualification appears desirable because there are still unsettled philosophic issues that pertain to the precise significance of these words when they are used in connection with scientific conceptualization and its attendant processes.

heart of Dalton's new theory, and it was indeed an invaluable contribution to the development of the atomic theory. As already observed, this rule, of all Dalton's basic postulates, is the most arbitrary and the least "correct." Yet, for the time at which it was stated, the rule represented a bold and intelligent choice of a simplifying assumption.

The rule is in no way an essential part of an atomic theory as such, but it exercised the vital function of providing the molecular formulas, however mistaken, which were absolutely essential for the operations of an atomic theory that lacked any more rational method for the evaluation of such formulas. Using the formulas provided by his rule Dalton was able to bring the simple abstract concept of atoms to bear upon the difficult concrete problem of determining atomic weights. We shall soon see that it was also this rule which led the atomic theory to its decisive test and greatest triumph — the prediction of the law of multiple proportions.

The use of an arbitrary simplifying assumption like the rule of greatest simplicity is a tactical device not infrequently applied in the earlier stages of a difficult scientific enterprise. When the complexity of the data confronting the investigator appears to exceed the bounds of human comprehension, one of the few courses open to him is to consider the situation in a grossly oversimplified way, using arbitrary working rules as a mechanism for the organization, assessment, and comprehension of his data. The creation of such rules may come as an emotional response to a naïve faith in the simplicity of nature, or as a conscious attempt to sift certain regular relations from a disorganized mass of data. With Dalton, the framing of the simplifying assumption was almost certainly due to a belief in the "regularity and simplicity generally observable in the laws of nature" (*New System*), and some of the most sophisticated conceptual advances of recent years have first appeared in an oversimplified form.

To the extent that Dalton's arbitrary "rule" was the simplest assumption permitting further progress, it was the best possible assumption. It was not in itself implausible; and, in commenting on an analogous situation in modern science, T. W. Richards, the first American Nobel Prize winner in chemistry, has very justly remarked:

"Whether or not it [a provisional hypothesis] may be a nearer approach to a definite picture of reality is a question of less importance than that concerning its ability to suggest new experimental work, and thus to lead to new generalization based upon fact. Hypotheses are temporary in their very nature; it has been said that science is being built up of stones taken from their ruins. Perhaps it might rather be said that hypotheses are the scaffolding which the scientific man erects around the growing solid structure, enabling him to build more swiftly and freely. Danger can arise from the use of such temporary assistance only when the builder confounds the temporary with the permanent, and builds one into the other in such a way that the collapse of one injures the other; or when the scaffolding is so badly constructed as not to bear a reasonable weight for a reasonable time."

When the theory becomes capable of supporting itself the provisional working rules and hypotheses may be incorporated, amended, or discarded entirely — in the light of the fuller understanding which they have made possible. The inadequacy of Dalton's "rule" ultimately became apparent, but only after it had served the purpose for which it was created.

(4) One last contribution of Dalton's, the importance of which should not be underestimated, was his development of a simple symbolism for the representation of *atoms* and their combinations. Dalton's symbols have since been replaced by more serviceable ones; but, in the early days of his atomic theory, his symbols made it possible for scientists to manipulate atoms, on paper, in a simple, economical and meaningful fashion. As already remarked (page 232), these symbols also serve to represent compounds as direct atom-to-atom combinations.

Students of semantics have called attention to the dangers arising from the mistaken feeling that, in handling symbols, we are in effect dealing with the realities they are intended to represent. The danger is undeniable; but it also seems plain that by providing atomic symbols and rules for their manipulation, Dalton encouraged his contemporaries to acquire a faith in the reality, significance, and usefulness of atoms.

2. THE APPLICATION OF THE ATOMIC THEORY TO CHEMISTRY

The Impact of the Atomic Theory. So far we have considered the origin of what is generally called Dalton's atomic theory, the content of that theory, the means by which it was applied to the determination of atomic weights, and the extent of Dalton's own contributions to the theory. We may now examine the services that the new atomic theory was able to perform in the scientific world in which it appeared, and the way in which it was received by that world.

Considering the long delays and hard struggles that occurred before the general adoption of Lavoisier's antiphlogistic hypothesis, the comparative rapidity with which the atomic theory won more or less general assent is somewhat surprising. However, there are several major differences in the two stories. Lavoisier sought to displace a strongly entrenched and generally accepted theory; Dalton's theory replaced nothing but, rather, grew by leaps and bounds in a scientific environment that had long nourished an implicit qualitative atomism. Furthermore, while the phlogiston theory could "explain" the facts almost as well as the antiphlogiston theory, albeit in a somewhat more complicated fashion, Dalton's hypothesis accounted for two broad empirical generalizations that were already in unexplained existence, and suggested yet a third. In this respect the atomic theory was indeed the creation of the "skilful observer" mentioned in Dalton's curiously modern appraisal of the dynamic nature of a scientific advance:

> Facts and experiments, however, relating to any subject, are never duly appreciated till, in the hand of some skilful observer, they are made the foundation of a theory by which we are able to predict the results and foresee the consequences of certain other operations which were never before undertaken.

One other striking difference between the situations of Lavoisier and of Dalton lies in the former's great ability as an experimentalist — a skill that allowed him to buttress his theory with his own brilliant experiments. Dalton, on the other hand, did not begin the serious study of chemistry until 1795, and never became a very able laboratory worker. Fortunately, Dalton's shortcomings in this respect were not of major importance because, as explained by his biographer, William Henry,

> his experiments, though wanting the exactitude of modern research, were not unskilfully devised and were most sagaciously interpreted.
>
> They were, perhaps, such as were most needed at the close of the last century, when so many fields of experimental research were untilled, that bold tentative incursions into new domains of thought, large groupings, and happy generalizations of approximate results were more effective instruments of advance than scrupulous precision in details.

Thus Dalton secured his position not so much through his own experiments but, rather, by showing prospective doubters how their *own* experimental results could be most readily interpreted with the aid of certain "large groupings and happy generalizations." Although, owing to the inaccuracy of the analyses and faultiness of the assumptions on which they were based, Dalton's atomic weights were well wide of the mark, his theory possessed a fundamental soundness that made it extraordinarily useful and attractive as the first rationalization of three of the major generalizations of experience that form the basis of modern chemistry. To these let us now turn.

The Law of Definite Proportions. It has long been an implicit article of faith among chemists that a given compound always contained its components in fixed proportion by weight — for example, that the weights of hydrogen and oxygen present in 1 gram of water would not vary with the source of the water. This assumption underlies the careful analytic work of Lavoisier and his contemporaries, but its general applicability had never been established. At the turn of the nineteenth century this implicit assumption became the subject of a famous dispute between two French chemists — Berthollet and Proust. Berthollet based his arguments on his theory of "chemical affinity" and on the obvious experimental fact that a metal heated in air undergoes oxidation gradually, yielding products in which the oxygen-to-metal ratio appears to be continuously variable up to a fixed maximum value. He contended that there was an infinite series of, for example, copper oxides — with progressively variable colors and progressively variable weight proportions. This point of view was disputed by Proust, who demonstrated experimentally that all of these apparently distinct copper oxides actually contained just two oxides of copper, each of invariant composition. Proust maintained that the "compounds" of continuously variable oxygen-to-copper ratio reported by Berthollet were actually nothing but variable *mixtures* of just two compounds in which the oxygen-to-copper ratio had two discrete but invariant values. He also asserted that the other cases of this class to which Berthollet had called attention could be similarly explained, and he buttressed his position by demonstrating the identity of composition of certain materials of synthetic (laboratory) origin and the same materials derived from natural (mineral) sources. Proust defines his position in the following trenchant declaration.

> According to our principles a compound . . . is a privileged product to which nature assigns fixed ratios; it is, in short, a being which Nature never creates even when through the agency of man, otherwise than with her balance in hand, *pondere et mesura*. Let us recognize, therefore, that the properties of true compounds are invariable as is the ratio of their constituents. Between pole and pole, they are found identical in these two respects; their appearance may vary owing to the manner of aggregation, but their [chemical] properties never. No differences have yet been observed between the oxides of iron from the South and those from the North. The cinnabar of Japan is constituted according to the same ratio as that of Spain. Silver is not differently oxidized or muriated in the muriate of Peru than in that of Siberia. . . .
>
> We shall . . . concur in the belief that if the combinations which we make every day in our laboratories have a perfect resemblance to those of nature, this is due to the fact that the powers of nature hold invisible sway over all the operations of our arts. If we find it impossible to make an ounce of nitric acid, an oxide, a sulfide, a drop of water, in ratios other than those which nature had assigned to them from all eternity, we must again recognize that *there is a balance which, subject to the decrees of nature, regulates even in our laboratories the ratios of compounds*. And even if some day we should succeed in clearly recognizing

> the causes which retard or accelerate the action of substances tending to combine, we could only flatter ourselves with knowing one more thing, namely, the means which nature uses to restrict compounds to the ratios in which we find them combined. But such knowledge, would it invalidate the principle I have proved? I think not, because the principle is only the corollary of the facts which we discover every day; there is nothing hypothetical about it; facts have led to it, facts alone could overthrow it.

To another group of materials cited by Berthollet — the alloys, amalgams, and glasses — Proust quite correctly denied the status of "compound." These substances showed no evidence of bearing their components in fixed proportions, nor did they appear to be mixtures of compounds of fixed compositions. Such materials are now known to be solutions of one solid in another, and just as the amount of salt dissolved in water can be varied continuously up to a limit fixed by the solubility of salt in water, the composition of an alloy, amalgam, or glass can be similarly varied. Proust very wisely refrained from saying why there resulted in some cases chemical compounds of fixed composition, inseparable except by chemical means, and in others physical mixtures of variable composition and separable by physical means. However, while adroitly side-stepping this speculative issue, he stressed the importance of the distinction between mixtures and compounds.

> But what difference, it will be asked, do you recognize between your chemical *combinations* [compounds] and the *unions of combinations* [mixtures of compounds] which latter you tell us nature restricts to no fixed ratios?
>
> Is the power which makes a metal dissolve in [react with] sulfur different from that which makes one metallic sulfide dissolve in another? I shall be in no hurry to answer this question, legitimate though it be, for fear of losing myself in a region not yet sufficiently lighted up by the facts of science; but my distinctions will, I hope, be appreciated when I say: The attraction which causes sugar to dissolve in water may or may not be the same as that which makes a fixed quantity of carbon and of hydrogen dissolve in [react with] another quantity of oxygen to form the sugar of our plants, but what we do see clearly is that these two kinds of attractions are so different in their results that it is impossible to confound them.

What bearing does this controversy, leading to the conclusion that there are chemical "compounds" with definite, invariant weight proportions, have on the atomic theory?

(1) A clear definition of a chemical compound, as distinct from a mixture, was created. The application of the atomic theory to com-

pounds was fruitful; its immediate application to mixtures would probably have been futile and confusing.

(2) As a result of the enormous labors of Proust and others, undertaken to maintain their respective positions in the controversy, there was secured a vast body of analytical information which later served as grist for the mill of the atomic theory.

(3) The controversy called the attention of the learned world to the existence of a large number of cases in which two elements were capable of combining in more than one proportion. Some instances of the formation of multiple compounds had been known previously; but now such multiplicity of compounds of the same elements was shown to be a quite general phenomenon, and one that fairly clamored for an explanation. Such an "explanation" was, as we shall see, furnished by the atomic theory.

(4) Last, and probably most important, is the consideration that Dalton's theory had the advantage that the law of definite or invariant proportions was a logical deduction from his postulates: the weight of the atoms of a given element is invariant; and the rule of greatest simplicity suggests that compounds are formed by the combination of fixed numbers of different atoms. By the time (1807) when Dalton's theory reached the scientific world, opinion on the Berthollet-Proust controversy had begun to run quite definitely in the latter's favor—and it was thus an item of credit to the atomic theory that it was in harmony with Proust's findings. It would, of course, be incorrect to say that the law of definite proportions "proved" the correctness of the atomic theory, since, as we have seen, the theory contained the law among its axioms. But, contrariwise, it is difficult to see how any theory that denied the existence of atoms could have accommodated the law of definite proportions in a more elegant and convincing manner.

The Law of Equivalent Proportions. Another major generalization of analytic experience, which also antedated the development of Dalton's atomic theory, was progressively disclosed by Richter in a series of papers published between 1792 and 1802. This generalization represented the culmination of a prolonged and widespread study of a special class of chemical reactions (acid-base neutralizations). In the latter half of the eighteenth century the quantitative data on these reactions, collected by Cavendish and others, prompted several workers to give various partial statements of the law of equivalent proportions. However, it remained for Richter, an obscure German chemist, to recognize the full generality and importance of the mathematical relations between the quantities of various substances that reacted with one another.

The type of experimental data that formed the basis for Richter's generalization is best suggested by a hypothetical instance. Suppose that experiments are performed with two substances, *A* and *B*, each of which is capable of reacting chemically with either of two other substances, *C* and *D*. There are then four reactions to be studied: *A* with *C*, *B* with *C*; *A* with *D*, and *B* with *D*. In each case a measurement is made of the weight of one of the materials which reacts completely with a given weight of the other substance. By "reacts completely" we mean that both of the starting materials are completely expended, so that no residue of either is present at the conclusion of the experiment. From four such determinations, the following results might be obtained.

50 grams of *A* react completely with 33 grams of *C*,
75 grams of *B* react completely with 33 grams of *C*,
64 grams of *A* react completely with 26 grams of *D*,
96 grams of *B* react completely with 26 grams of *D*.

It is apparent that there is a striking relationship among these figures, since

$$\frac{50}{75} = \frac{64}{96}.$$

From the unorganized mass of empirical data available to him, Richter successfully separated a number of such coördinated sets of values. In most instances the ratios were not as simple as the 2:3 ratio involved in the illustrative example; but, in general, the internal consistency of the experimental data was most impressive. The existence of these regularities suggested, and served to justify, a statement of a law of equivalent proportions, which may be paraphrased as follows: *If, for any two substances, there are certain weights that are equivalent in their capacity for reaction with some third substance, the ratio of such weights is the same regardless of what the third substance may be.*

Whether Dalton was aware of Richter's work at the time when the atomic theory was being developed is uncertain. Until 1802 Richter's results were apparently either almost completely unknown or ignored even in Germany, where they had been published; and the balance of the available evidence indicates that Dalton first learned of Richter's work after the atomic theory was essentially completed. When considered in the light of this theory, however, it was apparent that Richter's generalization, like that of Proust, was in essential harmony with the concepts of the atomic theory.

Thus, on Dalton's atomic theory, it is only necessary to hypothesize that, when quantities of two substances display equivalent capacities for reaction, there are present equal numbers of molecules of the two species. It is easy to see how this works out in the illustrative example cited above. It is plain that the equivalent quantities of *A* and *B*, defined by the reaction of these substances with equal weights of *C*, stand in the ratio 50 : 75, or 1 : 1½. If these quantities of *A* and *B* contain equal numbers of their respective molecules, then each molecule of *B* must be 1½ times as heavy as one molecule of *A*. This suggests that *any* time we have equivalent quantities of *A* and *B*—i.e., equal numbers of the two kinds of molecule—the weight of *A* will stand to that of *B* as 1 : 1½. But this constancy of the ratio of the weights of equivalent amounts of the two substances is the very import of the law of equivalent proportions. Once again, therefore, the atomic theory is found to accord well with experience.

The Law of Multiple Proportions. Unlike the two laws considered above, the law of multiple proportions was not fully apprehended until after Dalton's atomic theory had indicated its probable existence. The experimental confirmation of this prediction resulted in an immeasurable strengthening of the position of the atomic theory.

The prediction of this law is a logical outgrowth of the rule of greatest simplicity, in which Dalton recognizes the possibility that the atoms of two elements may combine in more than one numerical proportion, giving rise to two or more compounds of the same two elements. As we have already seen, the fairly frequent occurrence of such families of compounds was revealed by the work of Proust and others. However, while Proust had observed that two elements might combine in more than one weight proportion, Dalton now showed that the different fixed proportions were not independent entities, but, rather, that they were related to each other in a simple way that was readily understood in terms of the atomic theory.

A modern statement of the law of multiple proportions might run: "When two elements unite to form more than one compound, the weights of one element that combine with a fixed weight of the other element in the different compounds are in the ratio of small whole numbers." Now, Dalton had hypothesized that compounds were formed by the combination of definite small numbers of atoms of characteristic fixed weights. Thus, let us imagine that the elements *A* and *B* form two compounds, AB and A_2B. In compound AB one atom of *A* is united with each atom of *B*, but in compound A_2B *two* atoms of *A* are combined with one of *B*. If, now, we consider the number of atoms of *A* that react with a fixed number of atoms of *B* (i.e., with some fixed weight of *B*), it is plain that in the formation of compound A_2B there will be required twice as many atoms of *A* as are needed to form compound AB. Consequently, in combining with a fixed weight of element *B*, the weight of *A* expended in forming compound A_2B

will stand to that required in the formation of compound *AB* in the very simple ratio 2 : 1. Consideration of other such cases indicates that the law of multiple proportions is a necessary consequence of the basic postulates of Dalton's atomic theory. Somewhat more complicated ratios, like 2 : 3 or 3 : 4, are also to be expected on occasion; but the rule of greatest simplicity definitely suggests that the ratios will always be *simple* ones, involving only *small* numbers. Had the predicted ratios been something like 24 : 25 or 87 : 88 it would have been quite hopeless to search for them in the relatively crude analyses of Dalton and his contemporaries. However, in its prediction of simple, readily perceived ratios, the rule of greatest simplicity more than justified its existence by stimulating the quest for such ratios. This quest rapidly proved to be very fruitful.

Curiously enough, when, some fifteeen years earlier, the existence of a law of multiple proportions was intimated by William Higgins, his suggestion attracted no attention whatever. Part of this neglect can be attributed to the fact that Higgins's reference was purely incidental to a discussion of Lavoisier's oxygen theory, which was then the cynosure of all scientific eyes. Furthermore, it appears that Higgins contented himself with the bare assertion of this relation, and made no attempt to provide it with an experimental "validation." An interesting appraisal of the contributions of Higgins and of Dalton is available in a paper by W. H. Wollaston that appeared in the *Philosophical Transactions* of the Royal Society, in 1814—some years after the events referred to.

> The first instance in which the same body was supposed to unite with different doses of another, in such proportions that one of these doses is a simple multiple of the other, was noticed by Mr. Higgins, who conceived, rather than actually observed to occur, certain successive degrees of oxidation of azote, and represented the series of its combinations with oxygen to be
>
> Azote 1 with 2 oxygen making nitrous gas.
> Azote 1 with 3 oxygen making red nitrous vapour.
> Azote 1 with 4 oxygen making yellow nitrous acid.
> Azote 1 with 5 oxygen making white nitric acid.
>
> He at the same time added his opinion, that such are the proportions in which these gases unite to each other by *bulk* [i.e., by volume], having before observed one instance of union by exactly double bulk in the formation of water by the combustion of hydrogen and oxygen, and expressed his persuasion that the number of particles in a given bulk of the different gases is the same, and that the number of particles in the compounds of azote and oxygen, are successively in the proportions above stated.
>
> But though Mr. Higgins, in the instance of the union of hydrogen

> with oxygen, anticipated the law of bulks observed by M. Gay-Lussac [see Section 3], with respect to the union of gases, and in his conception of union by ultimate particles clearly preceded Mr. Dalton in his atomic views of chemical combination, he appears not to have taken much pains to ascertain the actual prevalence of that law of multiple proportions by which the atomic theory is best supported, and it is in fact to Mr. Dalton that we are indebted for the first correct observation of such an instance of a simple multiple in the union of nitrous gas with oxygen. In his endeavours to determine the composition of the atmosphere, he found that the quantity of oxygen contained in 100 measures of common air would combine with either 36 or 72 measures of nitrous gas, according to certain variations in the mode of conducting the experiment.

Dalton's studies of the reaction of nitrous gas with oxygen were carried out in the years 1801–1804, during the very time when his atomic theory was being formulated. Shortly afterward Dalton discovered another pertinent case of such simple proportions. In his study of two gases, methane and ethylene, he found that the weight of hydrogen that combined with a fixed weight of carbon to form methane was just twice as great as the weight of hydrogen that combined with the same weight of carbon in ethylene. It was the great strength of Dalton's position, however, that his demonstration of the application of his theory was not limited to the results of his own rather imperfect experiments. He was soon able to show that the working of the law of multiple proportions might be detected in analyses previously reported by other investigators. Such an instance was presented by the carbon oxides. The analysis of carbon dioxide ("carbonic acid," "fixed air") by Lavoisier had yielded results of 28 percent by weight of carbon and 72 percent of oxygen. Carbon monoxide ("carbonic oxide"), the heavy inflammable "air" with which Priestley confounded Lavoisier, had been identified and analyzed in 1801 by Clément and Désormes, who reported its composition as 44 percent of carbon and 56 percent of oxygen. Dalton remarks, in his notes for the nineteenth of his lectures at the Royal Institution:

> Experience confirmed the truth of Lavoisier's conclusion that 28 parts charcoal + 72 oxygen constituted carbonic acid; also that carbonic oxide contained just half the oxygen that carbonic acid does, which indeed had been determined by Clément and Désormes, two French chemists, who had not, however, taken notice of this remarkable result.

From the percentages cited before the last quotation, the foundation of Dalton's confident statement is far from evident, and it is not surprising that the "remarkable result" had long lurked unsuspected in the raw data. Yet the essential relation of the two weights of oxygen is at once apparent when the analyses are reduced to the common basis of a fixed weight of carbon. This simple recalculation is Dalton's suggestion, and is performed, as follows. In carbon dioxide, 72 grams of oxygen are combined with 28 grams of carbon, or 2.57 grams of oxygen with 1 gram of carbon. In carbon monoxide, 56 grams of oxygen unite with 44 grams of carbon, or 1.27 grams of oxygen with 1 gram of carbon. The weights of oxygen reacting with 1 gram of carbon — 2.57 and 1.27 grams, respectively — are then seen to stand in the ratio 2.02 : 1, or very nearly 2 : 1.

Owing to the inaccuracies of the analyses on which the calculations are grounded, the relation here, and elsewhere, is not exactly the simple ratio predicted; but as an increasing number of such sets of data were examined, it was apparent that the results showed an overwhelming tendency toward simple ratios. There is a moral in all this. Though facts may help to pave the road for a conceptual advance, the accumulation of facts does not, in and of itself, constitute or guarantee a conceptual advance. We must allow Santayana's rather cynical appraisal: "The empiricist . . . thinks he believes only what he sees, but he is much better at believing than at seeing." Not knowing what there was to see, diverted by a mode of (percentage) calculation that hid the inner harmony of their data, distracted by results that only approximated the correct values, Proust and his contemporaries held the critical data in their hands and failed to see the significance of what they "knew." With the advent of Dalton's atomic theory, the new beliefs it encouraged brought about a remarkable sharpening of the empiricists' vision. They were told what to look for, and where and how to look for it — and, behold, it was there. Dalton's obvious contribution, a new method of calculating analytical results, seems almost contemptible; but his more fundamental contribution was the powerful stimulus to investigation provided by his conceptual scheme.

Before long there appeared new and better analyses, which helped to solidify the position of the law of multiple proportions. A particularly important series of determinations showed that the law of multiple proportions applied not only to the combinations of gases, but also, to the major class of acid-base reactions. Many of these reactions result in the formation of two kinds of salts, distinguished as "acid" and "normal." The general case is easily understood from an examination of one specific instance. Thus, sodium carbonate (Na_2CO_3, washing soda) is a normal salt; sodium bicarbonate ($NaHCO_3$, baking soda) is an acid salt. If we consider the weights of sodium (Na) combined with a fixed weight of carbonate (CO_3) in these compounds, it is evident that the sodium-to-carbonate ratio is twice as great in sodium carbonate as in sodium bicarbonate. This, then, is another instance of simple multiple proportions, and its extension to the general case presents no difficulty. Thus, letting *M* represent some metal, and *A* some acid group, while H as usual represents hydrogen, then if salts such as M_2A and MHA are formed, the weights of *M* combined with the same weight of *A* in the two compounds are as 2 to 1 respectively; and, conversely, the weights of *A* combined with a fixed weight of *M* are as 1 to 2.

A first report on pairs of salts of this character was made early in 1808 by Thomas Thomson; two weeks later W. H. Wollaston reported a very considerable series of similar experiments which yielded results in excellent agreement with the law of multiple proportions. The beginning of Wollaston's communication to the Royal Society is of particular interest, and is here reproduced.

> In the paper which has just been read to the Society Dr. Thomson, has remarked, that oxalic acid unites to strontian as well as to potash in two different proportions, and that the quantity of acid combined with each of these bases in their super-oxalates, is just double of that which is saturated by the same quantity of base in their neutral compounds.
>
> As I had observed the same law to prevail in various other instances of super-acid and sub-acid salts [acid and normal salts respectively], I thought it not unlikely that this law might obtain generally in such compounds, and it was my design to have pursued the subject with the hope of discovering the cause to which so regular a relation might be ascribed.
>
> But since the publication of Mr. Dalton's theory of chemical combination, as explained and illustrated by Dr. Thomson (Thomson's *Chemistry* . . .) the inquiry which I had designed appears to be superfluous, as all the facts that I had observed are but particular instances of the more general observation of Mr. Dalton, that in all cases the simple elements of bodies are disposed to unite atom to atom singly, or, if either is in excess, it exceeds by a ratio to be expressed by some simple multiple of the number of its atoms.

It appears from this passage that Wollaston was an independent discoverer of at least part of the law of multiple proportions. His statement is also of particular interest because it suggests the way in which a successful theory makes it possible to (in Dalton's words, quoted on page 32) "predict the results and foresee the consequences of certain other operations which were never before undertaken." Thus Wollaston, having found his preliminary experiments in complete accord with Dalton's theory, abandons his projected investigation as an act of supererogation. In this respect a successful conceptual scheme both encourages and discourages experimental work: on the one hand, it stimulates and directs the experiments by which it may be tested;

but once having sustained these tests, it stands in lieu of a host of further experiments that can be omitted in favor of others more apt to be productive of *unpredictable* facts and *new* ideas.

In one last episode in the early history of the modern atomic theory we may observe the profound initial impact of the theory on a keen mind previously unaware of it. This is the mind of the Swede Berzelius, the titan among theoretical and experimental chemists of the early nineteenth century. Berzelius, writing in 1811, says:

> Berthollet, who is one of the most celebrated chemists of our age, in the course of his ingenious investigations into the laws of affinity, has attempted to demonstrate that substances could combine in an infinite number of continuous ratios. But Proust, another authority in chemical science, has proved on the contrary, that no such infinite variations occur in Nature, but that all complex definite substances [compounds] contain their fundamental constituents in a fixed ratio. . . . The truth of Proust's view cannot have failed to strike the experienced chemist; but what so far had not been known was, whether these sudden changes in composition occurred according to one and the same law for all substances, or in some indeterminate manner peculiar to each substance. . . .
>
> I have been attracted to these investigations . . . through finding that in the basic chloride of lead and in the basic chloride of copper the acid is saturated by four times as much of the base as in the neutral salts. [The neutral and basic salts with which Berzelius worked bear to each other a relationship which is entirely analogous to that of the normal and acid salts already discussed. Berzelius here reports another independent discovery of a case of multiple proportions. However, it appears that neither he nor Wollaston realized the general prevalence of such relationships prior to their respective introductions to Dalton's atomic theory.]
>
> I had hoped to discover the cause of so remarkable a relation by accurately investigating the result of mixing different substances of this sort. Whilst engaged in this work I came across Nicholson's Journal for 1808 and found in it the experiments of Wollaston on acid salts which had been suggested by Dalton's hypothesis. [This is not quite correct; Wollaston apparently began his work before hearing of Dalton's atomic theory.] This hypothesis affirms that if substances can be made to combine in different ratios, these ratios are always produced by simple multiplication of the weight of the one substance by 1, 2, 3, 4, etc. [Berzelius here gives an oversimplified account of the law of multiple proportions, which did not exclude somewhat more complicated ratios, like 2:3, 3:4, etc.] Wollaston's experiments seem to support this hypothesis. But such a doctrine of the composition of compounds would so illuminate the province of affinity, that supposing Dalton's hypothesis be found correct, we should have to look upon it as the greatest advance that chemistry has ever yet made in its development into a science. I

> have no knowledge whatever of how Dalton developed his theory and on what experiments he has based it, and hence I cannot judge whether my own experiments confirm his hypothesis in its full extent, or whether they modify it in a greater or less degree.

Berzelius took effective steps to put an end to his ignorance, obtaining a copy of the *New System* directly from its author. In 1812, a year later, we find him writing to Dalton: "The theory of multiple proportions is a mystery but for the Atomic Hypothesis, and as far as I have been able to judge, all the results so far obtained have contributed to justify this hypothesis."

Berzelius' growing knowledge of Dalton's atomic theory is of interest because of the light it throws on the state of scientific communications in the epoch of the birth of the atomic theory. Berzelius, in Sweden, learns of Wollaston's work only some two or three years after the publication of the latter's results. This delay is not inconsiderable, though it should be remembered that this was the period of the Napoleonic Wars. It appears, however, that the liaison between scientific workers on the two sides of the Channel was maintained with some success. Thus in 1809 we find Thomson writing to Dalton: "I write you at present to give you some information respecting your *atomic* theory . . . Berthollet has written a long attack upon it in the introduction to the French translation of my "System of Chemistry," a book which I have not yet seen and cannot therefore give you any account of his arguments . . . " That is, the first published account of Dalton's atomic theory, appearing in England in 1807, has been brought to the attention of Continental chemists in a translation completed by 1809. It appears that this translation did not reach Berzelius in Sweden, but he was able to secure further information about the atomic theory directly from Dalton.

In general, Dalton's "explanation" of the laws of definite, equivalent, and multiple proportions was welcomed by a generation of chemists hard pressed by too great an abundance of "facts" and with all too few generalizations in terms of which the "facts" might be construed. To be sure, there were protests such as that of Berthollet, who saw in Dalton's work the vindication of Proust's position. Such protests were soon heard no more; but there were other, more persistent voices that objected with good reason, and could not be stilled. Thus Davy, Gay-Lussac, Wollaston, and others, though impressed by the achievements of the atomic theory, objected to its general conjectural character, and particularly expressed their doubts about that part of Dalton's atomic theory which, in its youth, had been one of its great sources of strength, but which, in its maturity, was seen to be its greatest weakness—the "rule of greatest simplicity." While the experimental data from which the atomic weights were computed might be refined, the meaningfulness of these weights would remain doubtful as long as the interpretation of the analytic data rested upon molecular formulas furnished by an arbitrary, highly speculative, working rule. Dalton, in the second part of his *New System*, published in 1810, recognizes this shortcoming. After remarking that

> As only *one* compound of oxygen and hydrogen is certainly known, it is agreeable to the 1st rule [see page 25] that water should be concluded a *binary* compound; or, one atom of oxygen unites with one of hydrogen to form one of water. Hence the relative weights of the atoms of oxygen and hydrogen are 7 to 1 . . . [observe that Dalton is using as the combining weights 1 of hydrogen to 7 of oxygen, rather than the cruder proportion of 1 to 6 that he had employed earlier],

he goes on to say:

> After all, it must be allowed to be possible that water may be a ternary compound. In this case, if two atoms of hydrogen unite to one of oxygen, then an atom of oxygen must weigh 14 times as much as one of hydrogen; if two atoms of oxygen unite to one of hydrogen, then an atom of oxygen must weigh 3½ times one of hydrogen.

Further extension of the usefulness of the atomic theory was inseparably connected with the possibility of placing its molecular formulas and atomic weights on a more strictly rational foundation. Dalton himself was unable to suggest such a basis. The discovery, by another investigator, of the cornerstone of a more permanent foundation is the subject of the next section. The scene shifts to France, where the great pneumatic chemist Gay-Lussac holds the center of the stage.

3. GAY-LUSSAC'S LAW OF COMBINING VOLUMES

In 1808 Gay-Lussac announced his discovery of a simple regularity in the combining proportions of gases. It was this observation that, when correctly interpreted, led to a sounder criterion for the establishment of molecular formulas (and, thence, of atomic weights) than was provided by Dalton's "rule of greatest simplicity."

Gay-Lussac asserts that he was led to a general study of combining volumes in gas reactions by the result of an investigation of the combining proportions of hydrogen and oxygen which he and Alexander von Humboldt had completed three years before. This earlier work was carried out in order to ascertain the accuracy of a promising method for determining the oxygen content of "airs." Cavendish and others (including Dalton) had shown that the analyses derived from Priestley's "nitrous air test" were subject to large uncertainties, since the results were strongly influenced by small changes in the experimental conditions. Volta had proposed an alternative approach, based on a measurement of the volume contraction produced when a measured quantity of the gas under analysis was exploded with excess hydrogen. Such determinations could be conducted conveniently and accurately with the Volta eudiometer — a graduated tube like Priestley's nitrous air eudiometer, but with the addition of sparking terminals sealed through the glass.

The excellence of this method and technique was amply demonstrated by Gay-Lussac and von Humboldt in a research conducted with exemplary skill and thoroughness. Taking care to maintain constant temperature and pressure throughout each experiment, they found that the more carefully their experiments were performed, the closer was the approach to the very simple combining proportion of just two volumes of hydrogen per volume of oxygen — their best figure being 1.9989 volumes of hydrogen per 1.0000 volume of oxygen. With this datum, and with the knowledge that several other gas reactions involved volume proportions that roughly approximated simple ratios, Gay-Lussac apparently came to hope that with more exact measurements it would be found that volumetric combining proportions of great simplicity prevailed in the generality of gas reactions.

His hope was founded on sound theoretical arguments. It was believed, quite correctly, that there were forces of attraction, or *cohesion* between the ultimate particles of substances. An argument, at once ingenious and ingenuous, for the existence of such forces is put forward by Lavoisier in a passage in his *Elements of Chemistry* which is also of interest for its display of the real cognitive usefulness of pre-Daltonian atomism. To Lavoisier the primitive atomic theory was a qualitative concept, in terms of which certain natural phenomena were more readily "understood" or construed. However, the theory lacked the definiteness, the quantitative usefulness, and the more direct "evidence" with which Dalton subsequently endowed it. Lavoisier says:

> That every body, whether solid or fluid, is augumented in all its dimensions by any increase of its sensible heat [i.e., temperature] was long ago fully established as a physical axiom. . . . It is easy to perceive that the separation of particles by heat is a constant and general law of nature.
>
> When we have heated a solid body to a certain degree, and have thereby caused its particles to separate from each other, if we allow the body to cool, its particles again approach each other . . . and, if brought back to the same temperature which it possessed at the commencement

> of the experiment, it recovers exactly the same dimensions which it formerly occupied. We are still very far from being able to produce the degree of absolute cold, or total deprivation of heat, being unacquainted with any degree of coldness which we cannot suppose capable of still further augmentation; hence it follows, that we are incapable of causing the ultimate particles of bodies to approach each other as near as possible, and that these particles of bodies do not touch each other in any state hitherto known. Though this be a very singular conclusion, it is impossible to be denied.
>
> It may be supposed that, since the particles of bodies are thus continually impelled by heat to separate from each other, they would have no connection between themselves; and that, of consequence, there could be no solidity in nature, unless these particles were held together by some other power which tended to unite them and, so to speak, to chain them together. This power, whatever be its cause or manner of operation, is named Attraction.
>
> Thus the particles of all bodies may be considered as subject to the action of two opposite powers, Repulsion and Attraction, between which they remain in equilibrium. So long as the attractive force remains stronger, the body must continue in a state of solidity; but if, on the contrary, heat has so far removed these particles from each other as to place them beyond the sphere of attraction, they lose the cohesion they before had with each other, and the body ceases to be solid.

Thus, when a substance boiled, the liquid being changed to a gas, this was taken to signify that so much heat had been conveyed into the system as to overcome the cohesive forces that had previously held the liquid together. The striking differences in the specific heats, heats of vaporization, and boiling temperatures of different substances could be taken to indicate that different amounts of caloric fluid were required to overcome the cohesive forces in the various cases. Conversely, it might be inferred that there must be considerable differences in the cohesive forces of different substances. From this point of view, it would be expected that many aspects of the behavior of solids and liquids should show wide variations from one material to another, according to the magnitude of the cohesive forces in each instance.

In gases, on the other hand, the effects of these forces should be much less marked, owing to the vastly greater separation of the ultimate particles of gases — a circumstance that profoundly reduces the interaction between neighboring ultimate particles. Thus Watt's demonstration that 1 cubic inch of water gives rise to approximately 1 cubic foot of steam indicates that, in this case, the aqueous particles are distributed through a volume about 1700 times as great as they occupy in the liquid state. Gay-Lussac was thus led to expect that the behavior of all gases might be expressed in terms of relatively simple laws, while in the solid and liquid states the simple regularities would be partially or wholly masked by the great unsystematic variations of the cohesive forces in different substances. And, indeed, although the compressibilities of solids and liquids show great differences, the elastic behavior of *all* gases is closely approximated by Boyle's law; and, although the thermal expansions of solids and liquids are notably different from substance to substance, *all* gases follow Charles's law fairly closely. Therefore, although the relative combining volumes of liquids and solids showed no such simple regularity, there was still room for hope that, in view of the generally simpler deportment of gases, all gaseous reactions might display simple combining proportions analogous to that found in the hydrogen-oxygen reaction.

Such is the line of reasoning displayed in the opening paragraph of Gay-Lussac's paper, and it suggests that his study of gas reactions was undertaken by no "happy accident," but at least in part as the consequence of a fairly sophisticated line of theoretical reasoning. Let us now examine Gay-Lussac's classic paper, published in 1809 in the *Mémoires de la Société d'Arcueil*, in which he demonstrates economically yet convincingly that there are, indeed, conspicuously simple and regular relationships between the combining volumes of gases.

Memoir on the Combination of Gaseous Substances with Each Other

> Substances, whether in the solid, liquid, or gaseous state, possess properties that are independent of the force of cohesion; but they also possess others that appear to be modified by this force (so variable in its intensity), and that no longer follow any regular law. The same pressure applied to all solid or liquid substances would produce a diminution of volume differing in each case, while it would be equal for all elastic fluids. Similarly, heat expands all substances; but the dilations of liquids and solids have hitherto presented no regularity, and it is only those of elastic fluids that are equal and independent of the nature of each gas. The attraction of the molecules in solids and liquids is, therefore, the cause that modifies their special properties; and it appears that it is only when the attraction is entirely destroyed, as in gases, that bodies under similar conditions obey simple and regular laws. At least, it is my intention to make known some new properties in gases, the effects of which are regular, by showing that these substances combine amongst themselves in very simple proportions, and that the contraction of volume which they experience on combination also follows a regular law. I hope by this means to give a proof of an idea advanced by several very distinguished chemists—that we are perhaps not far removed from the time when we shall be able to submit the bulk of chemical phenomena to calculation.

This statement mirrors the enormous impact of the Newtonian synthesis on scientific thinking. As a result of Newton's studies of terrestrial and celestial mechanics, a large number of physical and astronomical phenomena could be understood in terms of a single set of laws, which could be expressed in a simple mathematical form. Newton's work thus unified and rationalized two broad and highly important domains of knowledge. It was only natural, then, that Gay-Lussac and many of his contemporaries should hope that chemistry too might soon achieve a state of similarly perfected development. Unfortunately this hope was not soon fulfilled; and although we can now construe in mathematical terms the bulk of the chemical phenomena with which Gay-Lussac was concerned, the progressively widening field of chemistry now comprehends vast new areas in which mathematical methods do not provide an adequate correlation of the observed phenomena.

However, although the "time when we shall be able to submit the bulk of chemical phenomena to calculation" was remote, the stimulus provided by the belief in the possibility and desirability of reaching such a state was a most beneficent one. It not only quickened interest in scientific research at large, but it particularly encouraged painstaking *quantitative* investigations in which accurate numerical data were secured, as well as the careful scrutiny of these data to discover any mathematically simple relations that they might contain. It was through such investigations that Richter, who was almost obsessed by the idea that chemistry could at once be made a branch of applied mathematics, discovered the law of reciprocal proportions; and here in Gay-Lussac's work we see another important and successful effort to trace a distinct strand of mathematically regular behavior in the tangled skein of reality that nature presents to the physical scientist.

> It is a very important question in itself, and one much discussed amongst chemists, to ascertain if compounds are formed in all sorts of proportions. M. Proust, who appears first to have fixed his attention on this subject, is of opinion that the metals are susceptible of only two degrees of oxidation, a *minimum* and a *maximum*; but led away by this seductive theory, he has seen himself forced to entertain principles contrary to physics in order to reduce to two oxides all those which the same metal sometimes presents. M. Berthollet thinks, on the other hand — reasoning from general considerations and his own experiments — that compounds are always formed in very variable proportions, unless they are determined by special causes, such as crystallization, insolubility, or elasticity. Lastly, Dalton has advanced the idea that compounds of two bodies are formed in such a way that one atom of the one unites with one, two, three, or more atoms of the other. (Dalton has been led to this idea by systematic considerations; and one may see from his work, *A*

> *New System of Chemical Philosophy*, p. 213, and from that of Thomson, Vol. 6, that his researches have no connection with mine.) It would follow from this mode of looking at compounds that they are formed in constant proportions, the existence of intermediate bodies being excluded, and in this respect Dalton's theory would resemble that of M. Proust; but M. Berthollet has already strongly opposed it in the Introduction he has written to Thomson's Chemistry, and we shall see that in reality it is not entirely exact. Such is the state of the question now under discussion; it is still very far from receiving its solution, but I hope that the facts that I now proceed to set forth, facts which had entirely escaped the notice of chemists, will contribute to its elucidation.

Gay-Lussac's rather neutral attitude, as here expressed, was probably the product of personal as well as scientific considerations. The fact that the present paper was published in the *Mémoires de la Société d'Arcueil* is in itself suggestive, since the *Mémoires* was in the literal sense Berthollet's "house" organ. At this period, in his country house at Arcueil, Berthollet held frequent meetings with his friends, pupils, and protégés (of whom Gay-Lussac was one), and the results of these discussions were published in the *Mémoires*. Under such circumstances it is little wonder that Gay-Lussac was disposed to view Berthollet's position sympathetically, especially as Berthollet's theory of affinity had much to recommend it.

But it is curious that Gay-Lussac does not tell us in what sense Proust's contentions contravene the laws of physics nor does he indicate in the balance of the present paper how "we shall see that in reality it [i.e., Dalton's theory] is not entirely exact." On the contrary, he later states that he finds his own results "very favorable" to the atomic theory.

When, in the text that follows, Gay-Lussac uses the unqualified expression "100 of oxygen," for example, he means 100 *parts by volume* of oxygen. It is an important indication of the different lines of approach adopted by the two investigators that whenever Dalton uses the word "parts" without qualification he refers to *parts by weight*, whereas under similar circumstances in this paper Gay-Lussac always signifies *parts by volume*. Indeed, this difference may be symptomatic of a major difference in philosophic outlook. The British physicist James Clerk Maxwell suggested that there are "two modes of thinking, which have had their adherents in ancient and in modern times. They correspond to the two methods of regarding quantity — the arithmetical and the geometrical. To the atomist the true method of estimating the quantity of matter in a body is to count the atoms in it. The void spaces between the atoms count for nothing. To those who identify matter with extension, the volume of space occupied by a body is the only measure of the quantity of matter in it."

Gay-Lussac continues:

> Suspecting, from the exact ratio of 100 of oxygen to 200 of hydrogen, which M. Humboldt and I had determined for the proportions of water, that other gases might also combine in simple ratios, I have made the following experiments. I prepared fluoboric, muriatic, and carbonic gases, and made them combine successively with ammonia gas. 100 parts of muriatic gas saturate precisely 100 parts of ammonia gas, and the salt which is formed from them is perfectly neutral, whether one or other of the gases is in excess.

That is, if 100 volumes of ammonia gas are added to 100 volumes of muriatic gas (hydrogen chloride), the gases disappear completely, with the formation of a solid salt, ammonium chloride: HCl (gas) $+ NH_3$ (gas) $\rightarrow NH_4Cl$ (solid). If there is an excess of one or the other gas, the surplus is simply left over. Thus if 100 volumes of muriatic gas are added to 150 volumes of ammonia, the product will be solid ammonium chloride formed from 100 volumes each of ammonia and muriatic gas, and 50 volumes of unreacted ammonia gas.

It is interesting to observe how much these experiments of Gay-Lussac's owe to the technical advances made in the course of 150 years' study of pneumatic chemistry. Such experiments, had they been conceived, could not have been performed adequately by Boyle and his contemporaries. The convenient collection and measurement of gases became possible only after Hales's deceptively simple invention of the pneumatic trough, first described in 1727. Much later Cavendish's suggestion that gases be stored over mercury led to Priestley's use of a pneumatic trough filled with mercury, with which he was able to collect and characterize several new gases, like ammonia and muriatic gases, which are very soluble in water. Furthermore, eudiometric (i.e., gas-analyzing) techniques were greatly improved by the work of Priestley, Cavendish, Volta, and others, so that the reactions of both the new and the old gases could be studied quantitatively. Hence when Gay-Lussac's experiments were performed the time was ripe both in the sense that the desirability of making such experiments was indicated, and in the sense that the laboratory tools and techniques required for these experiments had become available.

Gay-Lussac next goes on to consider the combinations of carbonic and fluoboric acids with ammonia. He proceeds in the same way and secures results of comparable simplicity, except that he finds two possible combinations of fluoboric acid with ammonia, and two of carbonic acid with ammonia, experimental conditions determining which one of either pair is actually obtained in a given case. These pairs of compounds correspond to the formation of what Gay-Lussac denominates "normal" and "sub-salts," and are reminiscent of the normal and acid salts discussed (page 40) in connection with Wollaston's work. Furthermore, when two different compounds can be formed from the same reactants, Gay-Lussac finds that, with a fixed volume of one gas, the volumes of the other gas, required to form the two compounds, are in the ratio 1 : 2. This, then, is another instance of simple multiple proportions and a further confirmation of Dalton's atomic theory.

Since the particular reactions mentioned involve some relatively difficult chemistry and yield nothing that is essentially different from a number of other simpler instances that are discussed we will not consider Gay-Lussac's description of these experiments, on the basis of which he continues:

> Thus we may conclude that muriatic, fluoboric, and carbonic acids take exactly their own volume of ammonia gas to form neutral salts, and that the last two take twice as much to form *sub-salts*. It is very remarkable to see acids so different from one another neutralize a volume of ammonia gas equal to their own; and from this we may suspect that if all acids and all alkalis could be obtained in the gaseous state, neutrality would result from the combination of equal volumes of acid and alkali. [This somewhat hasty generalization on the basis of a very few experiments is not, in fact, entirely correct.]
>
> It is not less remarkable that, whether we obtain a neutral salt or a *sub-salt*, their elements combine in simple ratios which may be considered as limits to their proportions. . .
>
> We might even now conclude that gases combine with each other in very simple ratios; but I shall still give some fresh proofs.
>
> According to the experiments of M. Amédée Berthollet, ammonia is composed of
>
> 100 of nitrogen,
> 300 of hydrogen,
>
> by volume. . .

The values given here, and elsewhere, by Gay-Lussac represent rounded figures derived from experimental data. However, here and at several other points in his paper, Gay-Lussac appears to overstate his case. Presumably he means to imply only that *within the limits of experimental error*, the figures stand in the very simple relation shown. In view of the acknowledged existence of experimental inaccuracies, such a claim would be justified; but without its important qualifying phrase, as used by Gay-Lussac and Dalton, it leaves a rather mistaken impression of either the accuracy of the experiments or the judgment of the investigator.

The actual experimental results on which the figures for ammonia are grounded, and a brief description of the determinations by which they were secured, are given in a note to the German translation of Gay-Lussac's paper which appeared in Gilbert's *Annalen* for 1810: "The first decomposition of ammonia was that communicated in 1785 to the Paris Academy by M. Berthollet. He passed electric sparks through ammonia gas until there was no further expansion; thereby the volume increased in the ratio 1 : 1.94117; he then examined the mixed gases in Volta's eudiometer, and found that they were composed of 0.725 hydrogen and 0.275 nitrogen by volume. But Berthollet *junior* found as the mean of six such experiments made by him with absolutely pure ammonia in graduated vessels, that after absorption of the undecomposed gas by muriatic acid, and after the necessary corrections [for variations] in temperature and pressure were made (because even with a good electrical machine the experiment takes 6 to 8 hours at least), the volume had increased in the ratio 1:2.04643 and that the gaseous mixture consisted of 0.755 hydrogen and 0.245 nitrogen by volume (but 0.755 : 0.245 = 3.08163 : 1)." Note the loose use of significant figures in this passage.

Gay-Lussac goes on to say:

> When a mixture of 50 parts of oxygen and 100 of carbonic oxide (formed by the distillation of oxide of zinc with strongly calcined charcoal) is inflamed, these two gases are destroyed and their place taken by 100 parts of carbonic acid gas. Consequently carbonic acid may be considered as being composed of
>
> 100 of carbonic oxide gas,
> 50 of oxygen gas.
>
> [That is, carbonic oxide, prepared by the reaction $ZnO + C \rightarrow Zn + CO$, combines with half its volume of oxygen; and the product is carbonic acid in volume just equal to the original volume of the carbonic oxide alone.]
>
> Davy, from the analysis of various compounds of nitrogen with oxygen, has found the following proportions by weight: —

	Nitrogen	Oxygen
Nitrous oxide	63.30	36.70
Nitrous gas	44.05	55.95
Nitric acid	29.50	70.50

> Reducing these proportions to volumes we find —

	Nitrogen	Oxygen
Nitrous oxide	100	49.5
Nitrous gas	100	108.9
Nitric acid	100	204.7

> The first and the last of these proportions differ only slightly from 100 to 50, and 100 to 200; it is only the second which diverges somewhat from 100 to 100. The difference, however, is not very great, and is such as we might expect in experiments of this sort; and I have assured myself that it is actually nil . . . [This is probably an overstatement.]

We may then admit the following numbers for the proportions by volume of the compounds of nitrogen with oxygen:—

	Nitrogen	Oxygen
Nitrous oxide	100	50
Nitrous gas	100	100
Nitric acid	100	200

By this ingenious manipulation of data available from contemporary scientific literature Gay-Lussac is able to show that these figures contain a previously undetected regularity. Such a demonstration is always peculiarly convincing since, when the data antedate the theory and the experimentalist is someone other than the propounder of the theory, there can be no question about the data's freedom from the influences of conscious or unconscious desires to "validate" the theory. Of the many examples cited by Gay-Lussac in this paper, only a few represent his own experimental work; the balance are culled from previously published data available to everyone.

The mechanism of the calculation in the present instance is a conspicuously simple one—the combining *weights* given by Davy are converted to combining *volumes* by the use of the gas densities (which we will define as weight per unit volume) of nitrogen and oxygen. Thus if, in a given experiment in which one of the nitrogen oxides is formed, w_N represents the weight of nitrogen combining with a weight w_O of oxygen, and if we let d_N represent the weight per unit volume (the density) of nitrogen, then there participates in this reaction a

$$\text{Volume of nitrogen} = \frac{\text{weight of nitrogen participating}}{\text{weight of unit volume of nitrogen}} = \frac{w_N}{d_N}.$$

Furthermore, if the density of oxygen, measured under comparable conditions of temperature and pressure, is represented by d_O, then there participates a

$$\text{Volume of oxygen} = \frac{w_O}{d_O}.$$

Hence, for this reaction,

$$\text{Volume of nitrogen : volume of oxygen} = \frac{w_N}{d_N} : \frac{w_O}{d_O}.$$

The weights w_N and w_O were given by Davy; and the densities d_N and d_O had been measured by Gay-Lussac's colleagues Biot and Arago, among others. Consequently, the ratio of the combining volumes of oxygen and nitrogen were readily calculable in each case, all the data having been available previously.

This type of indirect calculation was a particularly shrewd stroke in the present instance, because it made it possible for Gay-Lussac to draw inferences about the combining volumes in reactions in which the direct measurement of the volume ratios would have been difficult if not impossible, because of various experimental problems. The process of indirect calculation of quantities that are not susceptible to direct measurement lends science the peculiar ability to reach beyond immediately attainable experience to apprehend — not with certainty, but with some degree of probability — the nature and significance of experiments that cannot be performed.

After discussing several other examples, Gay-Lussac continues:

> Thus it appears evident to me that gases always combine in the simplest proportions when they act on one another; and we have seen in reality in all the preceding examples that the ratio of combination is 1 to 1, 1 to 2, or 1 to 3. It is very important to observe that in considering weights there is no simple and finite [integral] relation between the elements of any one compound; it is only when there is a second compound between the same elements that the new proportion of the element that has been added is a multiple of the first quantity. Gases, on the contrary, in whatever proportions they may combine, always give rise to compounds whose elements by volume are multiples of each other.
>
> Not only, however, do gases combine in very simple proportions, as we have just seen, but the apparent contraction of volume which they experience on combination has also a simple relation to the volume of the gases, or at least to that of one of them.
>
> I have said, following M. Berthollet, that 100 parts of carbonic oxide gas, prepared by distilling oxide of zinc and strongly calcined charcoal, produce 100 parts of carbonic gas on combining with 50 of oxygen. It follows from this that the apparent contraction of the two gases is precisely equal to the volume of oxygen gas added. The density of carbonic gas is thus equal to that of carbonic oxide gas plus half the density of oxygen gas; or, conversely, the density of carbonic oxide gas is equal to that of carbonic gas, minus half that of oxygen gas. Accordingly, taking the density of air as unity, we find the density of carbonic oxide gas to be 0.9678, rather than 0.9569, as experimentally determined by Cruikshank. . . .

Here we have another indirect calculation, but in this case the result can be checked against an empirical determination of the same factor, thus providing a valuable check on the data and the theory through which they are correlated. The data indicate that

(unit volume of carbon monoxide) plus (one-half unit volume of oxygen) gives (unit volume of carbon dioxide), and inasmuch as no matter is created or destroyed in the reaction, the weight of the product must be the sum of the weights of the reactants. Therefore:

(weight of unit volume of carbon monoxide) + (weight of one-half unit volume of oxygen) = (weight of unit volume of carbon dioxide) or:

(weight of unit volume of carbon monoxide) + ½ (weight of unit volume of oxygen) = (weight of unit volume of carbon dioxide).

Now, using the definition of density, we may write:

(density of carbon monoxide) + ½ (density of oxygen) = (density of carbon dioxide),

or

(density of carbon monoxide) = (density of carbon dioxide) − ½ (density of oxygen).

Considering the relatively crude equipment and impure gases used, the discrepancy between the calculated value and Cruikshank's experimental value — only slightly greater than 1 percent — is about as small as could be expected.

The "densities" to which Gay-Lussac refers here and elsewhere are actually specific gravities, i.e., ratios of the actual densities of the gases to that of air, which is thus taken as a standard and assigned a "density" of 1.

> We have seen that 100 parts of nitrogen gas take 50 parts of oxygen gas to form nitrous oxide, and 100 of oxygen gas to form nitrous gas. In the first case, the contraction is a little greater than the volume of oxygen added; for the specific gravity of nitrous oxide, calculated on this hypothesis, is 1.52092, while that given by Davy is 1.61414. But it is easy to show, from some of Davy's experiments, that the apparent contraction is precisely equal [again an overstatement] to the volume of oxygen gas added . . . From this circumstance, its [i.e. nitrous oxide's] specific gravity referred to that of air should be 1.52092. [This calculation is based upon the same line of reasoning outlined above. Here, however, a relatively large discrepancy, of about 6 percent, makes its appearance. Nevertheless Gay-Lussac, confident in the correctness of a generalization proved sound in so many other instances, rejects Davy's value as mistaken — and, indeed, Gay-Lussac's figure is much more nearly correct.]
>
> The apparent contraction of the elements of nitrous gas appears, on the other hand, to be nil. If we admit, as I have shown, that it is composed of equal parts of oxygen and nitrogen, we find that its density, calculated on the assumption that there is no contraction, is 1.036, while that determined directly is 1.038. . .
>
> Ammonia gas is composed of three parts by volume of hydrogen and one of nitrogen, and its density compared to air is 0.596. But if we sup-

> pose the apparent contraction to be half of the whole volume, we find 0.594 for the density. Thus it is proved, by this almost perfect concordance, that the apparent contraction of its elements is precisely half the total volume, or rather double the volume of the nitrogen. . .
>
> We see, then, from these various examples, that the contraction experienced by two gases on combination is in almost exact relation with their volume, or rather with the volume of one of them. Only very slight differences exist between the densities of compounds obtained by calculation and those given by experiment, and it is probable that, on undertaking new researches, we shall see them vanish entirely. . .
>
> I shall not discuss more of these determinations, because they are only based on analogies, and it is besides easy to multiply them. I shall conclude this Memoir by examining if compounds are formed in constant or variable proportions, as the experiments of which I have just given an account lead me to the discussion of these two opinions.
>
> According to Dalton's ingenious idea, that combinations are formed from atom to atom, the various compounds which two substances can form would be produced by the union of one molecule of the one with one molecule of the other, or with two, or with a greater number, but always without intermediate compounds. Thomson and Wollaston have indeed described experiments which appear to confirm this theory. Thomson has found that super-oxalate of potash contains twice as much acid as is necessary to saturate the alkali; and Wollaston, that the subcarbonate of potash contains, on the other hand, twice as much alkali as is necessary to saturate the acid.
>
> The numerous results I have brought forward in this Memoir are also very favorable to the theory. But M. Berthollet, who thinks that combinations are made continuously, cites in proof of his opinion the acid sulfates, glass, alloys, mixtures of various liquids,—all of which are compounds with very variable proportions, and he insists principally on the identity of the force which produces chemical compounds and solutions. [See Proust's statement (page 240), in which he admits that the same force may be responsible for both solution phenomena and chemical reactions, but points out very clearly that the action of this force is recognizably different in the two instances.]

Thomson, in a letter to Dalton dated Nov. 13, 1809, writes: "In the second volume of the Mém. d'Arcueil which Mr. Chenevix brought over . . . the most important paper respecting your atomic theory is by Gay-Lussac. It is entirely favorable to it, and it is easy to see that Gay-Lussac admits it, though respect for Berthollet induces him to speak cautiously." Perhaps it was this respect for Berthollet, as well as the real merits of Berthollet's theory, that impelled Gay-Lussac to present the rather strained reconciliation of the views of Berthollet and Dalton that appears in the succeeding text.

> Each of these two opinions has, therefore, a large number of facts in

its favour; but although they are apparently utterly opposed it is easy to reconcile them.

We must first of all admit, with M. Berthollet, that chemical action is exercised indefinitely in a continuous manner between the molecules of substances, whatever their number and ratio may be, and that in general we can obtain compounds with very variable proportions. But then we must admit at the same time that, — apart from insolubility, cohesion, and elasticity, which tend to produce compounds in fixed proportions, — chemical action is exerted more powerfully when the elements are in simple ratios or in multiple proportions among themselves, and that compounds are thus produced that separate out more easily. In this way we reconcile the two opinions, and maintain the great chemical law, that whenever two substances are in presence of each other they act in their sphere of activity according to their masses, and give rise in general to compounds with very variable proportions, unless these proportions are determined by special circumstances. [The "great chemical law" was a mass-action relation by which Berthollet sought to construe chemical combination in terms of the gravitational forces between reacting bodies. That is, it represented an attempt to secure a mathematical description of chemical phenomena by a further extension of the Newtonian synthesis (see page 254).]

Conclusion

I have shown in this Memoir that the compounds of gaseous substances with each other are always formed in very simple ratios, so that representing one of the terms by unity, the other is 1, or 2, or at most 3. These ratios by volume are not observed with solid or liquid substances, nor when we consider weights, and they form a new proof that it is only in the gaseous state that substances are in the same circumstances and obey regular laws. It is remarkable to see that ammonia gas neutralises exactly its own volume of gaseous acids; and it is probable that if all acids and alkalies were in the elastic state, they would all combine in equal volumes to produce neutral salts. The capacity of saturation of acids and alkalies measured by volume would then be the same, and this might perhaps be the true manner of determining it. The apparent contraction of volume suffered by gases on combination is also very simply related to the volume of one of them, and this property likewise is peculiar to gaseous substances.

It will be noted that Gay-Lussac's conclusion is a strictly factual one. As Berzelius observes: "M. Gay-Lussac was satisfied with having determined the ratios in which gaseous substances combine, but he made no wider application of this discovery." It may be that Gay-Lussac's cautious temperament made him disinclined to attempt a speculative flight on the basis of his experimental work. Whatever the reason, however, he did not indicate the important bearing of the law of combining volumes on the apparatus of the atomic theory.

4. THE APPARENT INCONSISTENCY OF THE ATOMIC THEORY AND THE LAW OF COMBINING VOLUMES

Dalton was made aware of Gay-Lussac's work within the year of its publication. His first informant was probably Thomson, whose letter has been cited previously, and soon afterward Dalton was in possession of the complete text. In a letter addressed to his brother and dated December 1809, Dalton states that Berthollet has sent him a copy of the journal containing Gay-Lussac's article. Considering the then current state of Anglo-French relations the speed and courtesy of this communication are noteworthy, though apparently by no means unique. An even more rapid transmission of information appears to have occurred in the case of the work of Wollaston and Thomson which, though not published in England until 1808, is mentioned in Gay-Lussac's paper read late in 1808 (published in 1809). At all events, Dalton was familiar with Gay-Lussac's generalization by late 1809, and was in a position to comment on it in an appendix to the second part of his *New System of Chemical Philosophy*, which was published in 1810.

In view of the new examples of simple multiple proportions and the generally regular behavior presented by Gay-Lussac's work, we might expect that Dalton, like Gay-Lussac, would view the law of combining volumes as "very favorable" to his atomic theory. In fact, he did not. He rejected this work summarily, and maintained his opposition to the end of his life.

Dalton concluded, quite correctly, that Gay-Lussac's results, as interpreted by the atomic theory, strongly suggested that equal volumes of different gases must contain the same (or simply related) numbers of atoms. However, his own point of view was that there were other very strong indications that these numbers could be neither the same nor simply related to one another. Let us examine Dalton's arguments.

The Case Against the Idea that There Are Equal Numbers of Particles in Equal Volumes of Different Gases. As early as 1803 (the year in which he first publicly intimated the existence of his atomic theory) Dalton wrote in his notebook:

> Though it is probable that the specific gravities of different elastic fluids has some relation to that of their ultimate particles, yet it is certain that they are not the same thing; for the ultimate particles of water or steam are certainly of greater specific gravity than those of oxygen, yet the last gas is *heavier* than steam.

Here is an apparent paradox: although something with finite weight (hydrogen) is added to oxygen in the formation of water, the density of water vapor or steam is *less* than that of oxygen by itself. The hypothesis that different gases contain different numbers of particles per unit volume appears to be almost unavoidable. In itself it provides a satisfactory explanation, for if there are fewer particles in unit volume of steam than there are in unit volume of oxygen, then it is quite conceivable that the greater number of lighter particles in unit volume of oxygen will yield a greater density than will the smaller number of heavier particles in unit volume of water vapor. In entirely analogous fashion ammonia, formed by the *addition* of hydrogen to nitrogen, is *less* dense than nitrogen itself. Nor can such cases be "explained" in terms of conjectural buoyancy effects produced by the hydrogen. Thus, for example, carbon monoxide is *less* dense than oxygen gas, although the former is a compound of oxygen *plus* carbon. It is difficult to avoid the conclusion that there are fewer of these heavier carbon monoxide particles in unit volume of this gas than there are particles of oxygen in unit volume of oxygen gas; and in general such density data suggest that there are unequal numbers of particles in unit volumes of the various gases.

This conclusion is powerfully supported by a scrutiny of the combining volumes in many gaseous reactions. In 1808 Dalton wrote (*New System*, page 71):

> It is evident the number of ultimate particles or molecules in a given weight or volume of one gas is not the same as in another; for, if equal measures of azotic and oxygenous gas were mixed, and could be instantly united chemically, they would form nearly two measures of nitrous gas, having the same weight as the two original measures; but the number of ultimate particles could at most be one half of that before the union. No two elastic fluids, probably, therefore, have the same number of particles, either in the same volume or the same weight.

This mode of reasoning is, apparently, impeccable. If a given volume of nitrogen contains n nitrogen atoms, and the same volume of oxygen also contains n oxygen atoms then, when these gases are mixed we have 2 volumes of a mixed gas containing a total of $2n$ atoms. When the oxygen and nitrogen combine there appears to be little volume change, and the product is approximately 2 volumes of nitrous gas. But now, even if the simplest formula is assigned to the molecule of nitrous gas — that is, one atom of nitrogen and one atom of oxygen — it is plain that from the $2n$ atoms originally present only n molecules of nitrous gas can result. Consequently, since the nitrous gas contains only n particles in 2 volumes, while the nitrogen and oxygen were each assumed to contain *n* particles in 1 volume, the nitrous gas can contain no more than half as many particles per unit volume as do nitrogen and oxygen.

Some illustration of this relation may be of value. Suppose we have a (very small) unit volume of nitrogen, containing just 1,000 nitrogen atoms. We will suppose that an equal volume of oxygen contains 1,000 oxygen atoms. When the gases are mixed, and made to react, it appears that no more than 1,000 molecules of nitrous gas could be obtained. But experiment shows that *two* unit volumes of this gas are formed. Therefore it seems that each unit volume of nitrous gas contains but 500 molecules, or only half as many "particles" as were supposed to be present in an equal volume of nitrogen or oxygen.

This is but one of a number of similar cases with which Dalton was familiar. Thus the combining volumes in the following reactions were known to be roughly as stated below even before Gay-Lussac indicated that they were almost *exactly* as shown;

1 volume nitrogen + 3 volumes hydrogen → 2 volumes ammonia,
1 volume oxygen + 2 volumes hydrogen → 2 volumes water vapor.

In the first case it is plain that if *n* atoms of nitrogen are present in unit volume of nitrogen gas, we can secure from it no more than *n* molecules of ammonia, each containing one nitrogen atom. However, since *two* volumes of ammonia are produced, the number of molecules in each of these volumes of this gas must be $n/2$, or only half as great as the number of nitrogen particles in unit volume of that gas. An analogous line of reasoning indicates that the number of molecules of water vapor in unit volume of steam can be only half as great as the number of oxygen atoms in unit volume of oxygen. And in general, in any case in which the volume of a gaseous reaction product exceeds the volume of one of the reacting gases, there is a strong indication that there are fewer particles in unit volume of the product than there are in an equal volume of the reacting gas. Thus the conclusion that there are different numbers of particles in equal volumes of different gases was powerfully supported by experimental data on gaseous densities and combining volumes in gaseous reactions.

Dalton was also able to show that this conclusion was consistent with one of his previous suppositions. Believing as he did (see page 225) that the particles of an elastic fluid were in direct contact with one another, through their heat atmospheres, Dalton had the following conception of the structure of a gas:

> When we contemplate upon the disposition of the globular particles in a volume of pure elastic fluid, we perceive it must be analogous to that of a square pile of shot; the particles must be disposed into horizontal

> strata, each four particles forming a square: in a superior stratum, each particle rests upon four particles below.

However, if the space ocupied by all gases is uniformly and tightly packed with the particles of the various gases, and if, as suggested above, different numbers of particles suffice to fill the same volume of different gases — then there appears to be no alternative to the belief that the different gaseous particles occupy different volumes, and hence have different diameters. This is the view adopted by Dalton (*New System*, page 188):

> At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous; or if not, that we had no data from which the question could be solved. But from a train of reasoning, similar to that exhibited at page 71 [see page 265], I became convinced that different gases have *not* their particles of the same size: and that the following may be adopted as a maxim, till some reason appears to the contrary: namely, —
>
> *That every species of pure elastic fluid has its particles globular and all of a size; but that no two species agree in the size of their particles*, the pressure and temperature being the same.

This conclusion is in the most gratifying agreement with a conclusion previously adopted (page 226) by Dalton: namely, that the homogeneity of a complex atmosphere was maintained by a mechanism depending on the existence of differences in the effective diameters of the various constituent gases.

Not content with the conclusion that the particle diameters were unequal in different gases, Dalton proceeded to derive numerical values for the relative diameters of the particles of the different gaseous species. We need not consider the details of this computation, which was based on the solid geometry of a pile of shot and made use of the measured gas densities and the atomic and molecular weights determined from chemical data. Owing to the errors in the primary experimental data and the misconceptions involved in their interpretation, Dalton found, quite in accord with his expectations, that the particle diameters (and volumes) were usually different in the various elastic fluids for which the calculations were made. To be sure, in a few cases he did find equal diameters for the particles of different gases, but he apparently considered them as no more than accidental approximations to the same diameter, rather than as precisely equal diameters. In any event, he saw in them no essential contradiction of the maxim enunciated in the last-quoted passage; on the contrary, he was much impressed by the striking differences in the calculated diameters of the particles of the large majority of the gaseous species considered.

The further significance of this computation lay in its intimation that in equal volumes of different gases, tightly packed with particles of different sizes, the relative numbers of particles must be unequal. Most important of all, the calculated values of *these relative numbers were not related in any simple way.*

Dalton Rejects the Law of Combining Volumes as an Exact Portrayal of Phenomena, but Inferentially Accepts and Uses It as an Approximation. Although the evidence outlined above appears to be decisive, the conclusion to which it leads is the very antithesis of the import of Gay-Lussac's generalization, as interpreted by the atomic theory. If we admit, with Gay-Lussac, that the combining volumes of different gases are always in the ratio of small whole numbers, and if — as postulated by the atomic theory — a molecule of a compound is always formed from a small number of atoms, then equal volumes of different gases must contain numbers of their respective atoms that are either equal or in the ratio of small whole numbers. Thus, for example, when Gay-Lussac asserted that equal volumes of nitrogen and oxygen combined to form nitrous gas (each molecule of which was rightly believed to contain one atom of oxygen and one atom of nitrogen) the unavoidable implication was that the equal volumes of these two gases contained exactly equal numbers of their respective atoms. But according to Dalton's calculations the relative numbers of atoms of oxygen and nitrogen in equal volumes of the respective gases stood in the ratio 1 : 0.833. Consequently the combining volumes of oxygen and nitrogen should be in the ratio 0.833 : 1, to which the 1 : 1 ratio asserted by Gay-Lussac is only a crude approximation. Examination of the other instances discussed by Gay-Lussac brought to light a multitude of similar anomalies, and Dalton, very naturally, came to believe that Gay-Lussac had grossly oversimplified what were actually nonintegral ratios. And indeed, as we have already observed (page 257), Gay-Lussac never did secure precisely integral volume ratios directly from his empirical data, but only obtained them by rounding off volume ratios that were more or less close approximations to simple integral ratios. Thus Dalton must have felt every confidence in his position when, in 1810, he wrote:

> Some observations on nitric acid, and the other compounds of azote and oxygen, have been made by Gay-Lussac, in the 2d. vol. of the Mémoires d'Arcueil. He contends that one *measure* of oxygenous gas unites to two *measures* of nitrous gas to form nitric acid, and to three measures to form nitrous acid. Now I have shewn that 1 measure of oxygen may be combined with 1.3 of nitrous gas, or with 3.5, or with any

> intermediate quantity whatever, according to circumstances,[5] which he seems to allow; what, then, is the nature of the combinations below 2, and above 3, of nitrous gas? No answer is given to this; but the opinion is founded upon an hypothesis that all elastic fluids combine in equal measures, or in measures that have some simple relation one to another, as 1 to 2, 1 to 3, 2 to 3, etc. In fact, his notion of measures is analogous to mine of atoms; and if it could be proved that all elastic fluids have the same number of atoms in the same volume, or numbers that are as 1, 2, 3, etc. the two hypotheses would be the same, except that mine is universal, and his applies only to elastic fluids. Gay-Lussac could not but see . . . [see page 267] that a similar hypothesis had been entertained by me, and abandoned as untenable; however, as he has revived the notion, I shall make a few observations upon it, though I do not doubt but he will soon see its inadequacy.

After this rather patronizing introduction Dalton goes on to attack the accuracy of Gay-Lussac's data, as well as his interpretations of them. However, while it is quite true that Gay-Lussac's generalization was only *suggested* (rather than "*proved*") by the relatively inaccurate data available to him, Dalton's criticism is not without an element of unconscious humor, since he had himself, on numerous occasions, accepted even less striking approximations as quite satisfactory "verification" of his own atomic theory. In the same book from which the preceding passage is taken we find him writing that in considering the compounds of oxygen with azote:

> Our plan requires a . . . principle of arrangement; namely, to begin with that which is most simple, or which consists of the smallest number of elementary particles, which is commonly a binary compound, and then to proceed to the ternary and other higher compounds. According to this principle, it becomes necessary to ascertain, if possible, whether any of the [compounds], and which of them, is a binary compound. As far as the specific gravities of the two simple gases are indicative of the weights of their atoms, we should conclude that an atom of azote is to one of oxygen as 6 to 7 nearly; the relative weights of ammonia and water also give countenance to such a ratio.

Although Dalton had previously established to his own satisfaction (see the preceding extract) that the numbers of particles in equal

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[5] Dalton is quite right in asserting the wide variability of the combining proportions of nitrous air and oxygen. As already remarked, the nitrous air test is not reliable because the exact course of the reaction is too sensitive to small changes in the experimental conditions. According to whether these conditions favor formation of NO_2 ($NO + O$) or N_2O_3 ($2NO + O$) in greater or smaller proportion, the reacting volumes are continuously variable between fixed extremes. Owing to various experimental aberrations the extremes defined by Gay-Lussac (2 nitrous gas to 1 oxygen, and 3 nitrous gas to 1 oxygen), which readily allow for the possibility of combining proportions between 2 to 1 and 3 to 1, did not agree with the limits determined by Dalton as 1.3 and 3.5 of nitrous air to 1 of oxygen, according to the conditions.

volumes of different gases could not be equal, he here embarks upon a calculation of relative atomic weights which is based on the assumption that the numbers are at least approximately equal. If there is almost the same number n of atoms in unit volumes of azote and oxygen, and if a and o represent the weights of atoms of azote and oxygen, respectively, then the total weights of azote and oxygen in unit volumes of each must be $n \times a$ and $n \times o$, respectively. The ratio of the specific gravities of azote and oxygen, given by Dalton as 6 : 7, must be the same as the ratio of the respective densities. Hence:

$$\frac{\text{Specific gravity of azote}}{\text{Specific gravity of oxygen}} = \frac{6}{7} = \frac{\text{Density of azote}}{\text{Density of oxygen}}$$

But

$$\begin{aligned}\frac{\text{Density of azote}}{\text{Density of oxygen}} &= \frac{\text{Weight of unit volume of azote}}{\text{Weight of unit volume of oxygen}}\\ &= \frac{n \times a}{n \times o}\\ &= \frac{a}{o}.\end{aligned}$$

Consequently the atomic weights stand in the same ratio as, and may be calculated from, the ratio of the specific gravities or densities. That is, the atomic weights stand in the ratio of 6 : 7.

These figures were consistent with the atomic weights calculated from the combining weights of the elements in ammonia and water, when the molecular formulas were taken to be NH and HO respectively, as predicted by the rule of greatest simplicity. Such concordance was reassuring, but was attainable only by the use of an assumption that Dalton had previously rejected — that there are equal numbers of atoms in equal volumes of the gaseous elements. Indeed, Dalton did not hesitate to attack Gay-Lussac's work vigorously when the very same assumption appeared to be justified as a logical deduction from that work. The distinction suggested by Dalton's use of this assumption is that, though he would not regard it as exact, he did accept and use it as a serviceable approximation. Dalton was very explicit in indicating the provisional nature of his calculation — "as far as the specific gravities of the two simple gases are indicative of the weights of their atoms . . ." — thus signifying that the basic assumption was entertained only as a provisional approximation, rather than as a mathematically exact relation. The values he then secured proved to be in good agreement with those obtained from an independent calculation based on the combining weights of the elements in ammonia and water. This concordance served to justify the use of the assumption as a provisional approximation.

> But the best criterion is derived from a comparison of the specific gravities of the compound gases themselves. Nitrous gas has the least specific gravity of any of them; this indicates it to be a binary compound; nitrous oxide and [nitric] acid are both much heavier; this indicates them to be ternary compounds; and the latter being heavier than the former, indicates that oxygen is heavier than azote, as oxygen is known to abound most in the latter.

Dalton again makes use of an assumption like that mentioned in the previous text. He accepts the relative magnitudes of the compounds' specific gravities as "the best criterion" for the assignment of their respective molecular formulas. This implies the risky assumption that there are equal numbers of molecules in equal volumes of the compound gases; but even if these numbers are only roughly the same, the specific gravities provide a sufficiently good indication of the relative magnitudes of the molecular weights to make it possible to distinguish the binary from the ternary compounds, for example.

Now, of all the compounds containing only azote and oxygen, nitrous gas has by far the smallest specific gravity. If the numbers of molecules in equal volumes of the compound gases are even approximately the same, we might then be justified in concluding that the gas with the least specific gravity must be the material with the lightest molecules, i.e., that it is the binary compound, containing one atom of oxygen and one of azote. Hence, the formula of the binary compound, NO, may be provisionally assigned to nitrous gas. The next heavier oxides of azote, nitrous oxide and nitric acid, have much larger specific gravities, that of nitric acid being the greater. This indicates that they are the ternary compounds, N_2O and NO_2. It was known that, of these two substances, nitric acid was the richer in oxygen. Hence the formula NO_2 could be assigned to it, leaving N_2O as the formula of nitrous oxide. The slightly greater specific gravity of the nitric acid (in which one of the azote atoms in nitrous oxide is replaced with an oxygen atom) is in harmony with the previously developed evidence (see page 270) that the atomic weight of oxygen is slightly greater than that of azote.

It should be observed that this assignment of molecular formulas is a conspicuously reasonable one, and that the assumption on which it rests need only be accurate enough to show the *relative orders of magnitude* of the various molecular weights. However, since there is still no assurance that it is sound enough even for that purpose, the molecular formulas derived from it have only a provisional status. Fortunately, Dalton was able to develop strong evidence for the validity of these formulas. He presents this evidence in the form of a table obtained by treating an entirely different set of data by an independent interpretive procedure.

> Let us now see how far the facts already known will corroborate these observations.
>
> According to Cavendish and Davy, who are the best authorities we yet have in regard to these compounds, they are constituted as under. [See Table 1.]
>
> The above table is principally taken from Davy's Researches: where two or more results are given under one article, they are derived from different modes of analysis In the third column are given the ratios of the weights of azote and oxygen in each compound, derived from the preceding column, and reduced to the determined weight of an atom of oxygen 7. This table corroborates the theoretic views above stated most remarkably. The weight of an atom of azote appears to be between 5.4 and 6.1: and it is worthy of notice, that the theory does not differ more from the experiments than they differ from one another; or, in

TABLE 1. Dalton's table of weight ratios of nitrogen oxides

[Compound]	Sp. gr.	Constitution by weight	Ratios *	
Nitrous gas	1.102	46.6 azote + 53.4 oxygen	*6.1* : 7	Cavendish
		44.2 .... + 55.8	*5.5* : 7	
		42.3 .... + 57.7	*5.1* : 7	
Nitrous oxide	1.614	63.5 .... + 36.5	2 × *6.1* : 7	
		62 .... + 38	2 × *5.7* : 7	
		61 .... + 39	2 × *5.4* : 7	
Nitric acid	2.444	29.5 .... + 70.5	*5.8* : 7 × 2	
		29.6 .... + 70.4	*5.9* : 7 × 2	Davy
		28 .... + 72	*5.4* : 7 × 2	
		25.3 .... + 74.7	*4.7* : 7 × 2	

* If we take *a* as the atomic weight of azote and *o* as the atomic weight of oxygen, then, if the provisional formulas are correct, the weight ratios of the elements in the various nitrogen oxides should be:

Compound	Weight of azote : Weight of oxygen
NO	$a : o$
N_2O	$2 \times a : o$
NO_2	$a : o \times 2$

Dalton calculates these weight ratios from the tabulated analytic data of Cavendish and Davy. For *o*, the atomic weight of oxygen, he uses the figure 7 (deduced from the combining weights of the elements in water) and he computes the corresponding value of *a* in each case. If the atomic theory were correct, and if the molecular formulas were correctly assigned, then we would expect to find that *a* is a *constant in the neighborhood of 6*, since it has previously been indicated (see page 270) that the atomic weights of azote and oxygen stand approximately in the ratio 6:7.

> other words, the mean weight of an atom of azote derived from the above experiments would equally accommodate the theory and the experiments . . .
>
> I have been solicitous to exhibit this view of the compounds of azote and oxygen, as derived from the experience of others, rather than from my own; because, not having had any views at all similar to mine, the authors could not have favoured them by deducing the above results, if they had not been conformable to actual observation.

Dalton expresses his satisfaction with the results of his calculation — "this table corroborates the theoretic views above stated most remarkably." Yet, although the (italicized) figures for the atomic weight of azote approximate a constant, as they should, the range is fairly broad, from 4.7 to 6.1 (not 5.4 to 6.1, as stated by Dalton). But Dalton, guided by the precepts of his theory, perceives that these figures are sufficiently close to a constant to serve as "confirmation" of the atomic theory; and he feels, quite correctly, that the observed variability is no greater than is to be anticipated as a result of the inaccuracies of the primary data.

Compare with this Dalton's appraisal of Gay-Lussac's interpretation of the same data. Dalton denies the validity of volume relations that approximate their ideal values as well as do the deductions he had himself drawn *from the same analyses.* Furthermore, while he confidently assumes that improved analyses will lend even stronger support to his own theory, he suggests that if better data were available they would *not* support Gay-Lussac's interpretation. The origin of Dalton's diverse appraisals is fairly apparent: in one case his theory taught him to expect and recognize certain regularities; in the other case it taught him that no regularities could exist, and impelled him to deny any such regularities although they were no less apparent than those that he discerned for himself. A theory or conceptual scheme thus acts as a two-edged weapon, and it appears probable that Dalton's situation at this juncture was much like that which he rather smugly attributes to some of his contemporaries:

> When the mind is ardently engaged in prosecuting experimental enquiries, of a new and extraordinary kind, it is not to be expected that new theoretic views can be examined in all their relations, and formed so as to be consistent with all the well known and established facts of chemistry; nor that the facts themselves can be ascertained with that precision which long experience, an acquaintance with the instruments, and the defects to which they are liable, and a comparison of like observations made by different persons, are calculated to produce. This may appear to be a sufficient apology for the differences observed in the results of . . . celebrated chemists, and for the opposition, and sometimes extravagance, of their views.

The extravagance of Dalton's own view is expressed in his forthright rejection of Gay-Lussac's generalization:

> The truth is, I believe, that gases do not unite in equal or exact measures [integral ratios] in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments. In no case, perhaps, is there a nearer approach to mathematical exactness, than in that of 1 measure of oxygen to 2 of hydrogen; but here, the most exact experiments I have ever made, gave 1.97 hydrogen to 1 oxygen.

It is a little amusing to observe Dalton, whose experiments were generally very crude, quoting his own values as a refutation of those of Gay-Lussac, who was an acknowledged experimental virtuoso. Had this been an instance where Dalton would have expected to find a simple 1 : 2 ratio he would certainly have accepted 1 : 1.97 as a very satisfactory check. Here, however, armed with the staff of his theory, he enjoyed full confidence that Gay-Lussac *could not* be right, and the deficiency of 1.5 percent assumed a very large importance in his eyes.

We possess an interesting exchange of letters between Dalton and Berzelius. Writing in 1812 Dalton reiterates his position:

> The French doctrine of *equal measures* of gases combining, etc., is what I do not admit, understanding it in a mathematical sense. At the same time I acknowledge there is something wonderful in the frequency of the approximation.
>
> The doctrine of [multiple] proportions appears to me *mysterious* unless we adopt the atomic hypothesis. It appears like the *mystical ratios* of Kepler, which Newton so happily elucidated. [Kepler had shown that the movements of the planets could be correlated in terms of several simple mathematical relations. These he derived from purely observational data, in the interpretation of which he was, however, guided by his firm belief in Pythagorean-Platonic number mysticism. The "real" reasons for the existence of the simple relations discovered by Kepler remained entirely obscure until Newton showed that they could be deduced from, and understood in terms of, the action of universal gravitation.] The prosecution of the investigation can terminate, I conceive, in nothing but in the system which I adopt of particle applied to particle.

To this Berzelius responded with full appreciation of Dalton's accomplishments, but without disguising his opinion that Dalton had adopted an unreasonable attitude with regard to Gay-Lussac's work.

> I believe that it is necessary to let experiment mature the theory. If the latter begins to concern itself with constraining nature into certain forms, the theory will stop growing toward perfection and will cease to be useful. [This is a handy stick with which to beat an opposing point of view. However it should be noted that when his own profoundest

> scientific convictions were involved, Berzelius did not hesitate to "force" the facts into conformity with his theories, and in this respect he did no more than a number of other brilliant investigators.] I agree that the theory of multiple proportions is a mystery but for the Atomic Hypothesis, and as far as I have been able to judge, all the results so far obtained have contributed to justify this hypothesis.
>
> I believe, however, that there are parts of the general theory, for which science is indebted to you, which require some slight alteration. That part, for example, which induces you to declare inexact the experiments of Gay-Lussac on the combining volumes of gases. I should have thought that these experiments were the finest proof of the probability of the atomic theory, and, moreover, I cannot so easily believe that Gay-Lussac is mistaken, especially in a matter where it is only a question of measuring well or badly.

Berzelius suggests here that there is nothing conjectural about Gay-Lussac's results; as experimental values derived by a gifted investigator they lay claim to the status of "brute facts." Berzelius' injunction was, however, disregarded by Dalton who, seeing no way of reconciling his theory with the alleged facts, continued to deny the validity of the facts. However, with the passage of time, the evidence for the facts ultimately became conclusive, and the reconciliation of the theory and the facts became a matter of more crucial importance. Possible roads to such a reconciliation will be discussed in succeeding sections.

5. AVOGADRO'S RECONCILIATION

The Italian physicist Avogadro suggested a highly ingenious method for the mutual reconciliation of the atomic theory and Gay-Lussac's law of combining volumes, but before we examine the details of Avogadro's proposal, it will be well to review the contradiction that seemed so irreconcilable to Dalton.

First then, we must allow that Gay-Lussac's law of combining volumes, as interpreted by the atomic theory, strongly suggests that in equal volumes of different gases the numbers of the respective gaseous particles are either equal or simple (integral) multiples of one another. One such derivation has already been suggested (page 268) and might run: if the formula of nitrous gas is NO, the formation of this substance will always require equal numbers of nitrogen and oxygen atoms. Gay-Lussac asserted that under the same conditions of temperature and pressure the volumes of oxygen and nitrogen that reacted with each other to form nitrous gas were precisely equal. Thus it is plain that at equal temperatures and pressures there must be equal numbers of the respective atoms in equal volumes of oxygen and nitrogen.

(1) There are a number of chemical reactions in which the volume of a gaseous product exceeds the volume of at least one of the reacting gases. Among these cases we may note:

1 volume of oxygen + carbon (solid)
→ 2 volumes of carbon monoxide (CO),
1 volume of oxygen + 1 volume of nitrogen
→ 2 volumes of nitrous gas (NO),
1 volume of oxygen + 2 volumes of hydrogen
→ 2 volumes of water vapor (H_2O).

In the first instance, for example, if we allow that each molecule of carbon monoxide must contain at least one oxygen atom, then it is plain that the *two* volumes of carbon monoxide can contain only as many molecules as there are atoms of oxygen in the *one* volume of oxygen. It would appear, then, that there are only half as many particles (molecules) in a given volume of carbon monoxide as there are particles (atoms) in an equal volume of oxygen. There *is* one rather implausible-looking way in which the "equal volumes–equal numbers" idea can be salvaged in such instances. If we were to assume that there occurred something essentially impossible under Dalton's definition of an atom — namely, that the oxygen atom was split into two identical fragments — then we would have twice as many of these oxygenous fragments as there were atoms of oxygen to begin with. If each carbon monoxide molecule contained just one of these fragments, then we could have twice as many molecules of carbon monoxide as we had atoms of oxygen, and the fact that the volume of the carbon monoxide is twice as great as that of the oxygen is made consistent with the "equal volumes–equal numbers" scheme. In the same way, by allowing the splitting of the oxygen atom, that scheme can also be maintained in the other instances cited.

However, this consistency is dearly bought — at the price of postulating an occurrence repugnant to one of the definitions of the atomic theory. (Note, once again, that the Greek "atomos" means uncut, indivisible.) This price seemed inordinately high to Dalton, and he preferred to abandon the speculative "equal volumes-equal numbers" argument that exacted it. He concluded that there simply *were* substantially fewer particles in a given volume of nitrous gas, or of water vapor, or of carbon monoxide, than there were in an equal volume of oxygen.

(2) Several anomalies in the measured gaseous densities seemed to lend color to this view. Thus the densities of water vapor (oxygen *plus* hydrogen) and of carbon monoxide (oxygen *plus* carbon) are *less* than that of oxygen itself, though in each case something has been *added* to the oxygen. That the individual molecules of carbon monoxide

must be heavier than the oxygen particles appears evident, and when this proposition is combined with the observed gaseous densities, we seem to be led inescapably to the conclusion that there are fewer particles in a volume of carbon monoxide or water vapor than there are in an equal volume of oxygen. This conclusion is in good agreement with Dalton's provisional interpretation of item (1).

(3) Dalton's meteorological considerations had led him to believe that the particles of different gases were of different diameters (see page 20). If we accept the Daltonian conception of a gas as solidly packed with particles, like a pile of shot, it is plain that, except in a few fortuitous cases, equal volumes of gases containing particles of different size could not well contain equal numbers of these particles.

(4) If we accept the analogy between a volume of gas and a container full of shot, then we must also admit the pertinence of Dalton's calculation, from gas-density and atomic-weight data, of the relative numbers of particles present in different gases. The results of the calculations indicated that, by and large, these numbers were significantly different, and not simply related to one another.

(5) Dalton asserted, quite correctly, that the experimental figures of Gay-Lussac, and the figures that the latter calculated from the experiments of others, supported the law of combining volumes relatively weakly, because these figures had to be rounded off more or less arbitrarily before the data and the "law" could be brought into agreement. To Gay-Lussac this rounding off was a legitimate operation that simply took cognizance of the existence of substantial experimental errors in the data used; to Dalton it was, as we have seen in the last Section, an unacceptably gross oversimplification of these data.

Not all of these five points are equally crucial. Thus, for example, argument (5) gradually lost its force as subsequent investigations provided more precise confirmation of the very simple combining proportions postulated by Gay-Lussac. Furthermore, the significance attaching to points (3) and (4) is directly dependent on the degree of acceptance accorded to the Daltonian (pile-of-shot) model of a gas. This was, of course, a strictly hypothetical conception, without any direct "proof," and as time went on there was a gradual accumulation of opinion and evidence against it. Thus, if the Daltonian model is not accepted, and a gas is viewed as a space only thinly populated with particles, there ceases to be any direct and compelling connection between the particle diameters and the numbers of these particles present.

We have still to deal with points (1) and (2), and these cannot be dismissed lightly. They do not in themselves exclude the idea that the numbers of particles in equal volumes of different gases are simply related to one another. (Thus, for example, the assumption that there are twice as many particles in unit volume of oxygen as there are in unit volumes of carbon monoxide, or nitrous gas, or water vapor meets with no serious contradiction.) But it does appear that the observations embodied in these points rule out the possibility that there are *equal* numbers of particles in equal volumes of different gases. This is the crux of the matter with which Avogadro concerns himself, and we may now address ourselves to a consideration of his work.

Avogadro's Proposals. Avogadro, an Italian physicist, published his celebrated paper in the French *Journal de Physique*, in 1811. The French text suffers from occasional obscurity, which must have confused Avogadro's contemporaries even as it does us. The situation was further beclouded by the fact that in his text Avogadro does not make a clear distinction between atoms and molecules, though he apparently distinguished them clearly in his thinking. He abjures the use of the word "atom" and, just as we have used the word "particle" (from the Latin for "small part") to denote any minute body, so he uses the word "molecule" (from the Latin for "small mass") with various qualifying adjectives. He is fairly consistent in employing these terms and qualifications in the following senses: *molecule* (unqualified) signifies any small particle, atom or molecule; *integral* (or *composite* or *compound*) *molecule* usually signifies a molecule of a compound, though it is occasionally used in the sense of a molecule of any sort; *constituent molecule* means the molecule of an element; *elementary molecule* means the atom of an element.

Extracts from Avogadro's paper follow.

Essay on a Manner of Determining the Relative Masses of the Elementary Molecules of Bodies, and the Proportions in which They Enter into These Compounds

I.

> M. Gay-Lussac has shown in an interesting Memoir that gases always unite in a very simple proportion by volume, and that when the result of the union is a gas, its volume also is very simply related to those of its components. But the proportions by weight of substances in compounds seem only to depend on the relative number of molecules which combine, and on the number of compound molecules which result. It must then be admitted that very simple relations also exist between the volumes of gaseous substances and the numbers of simple or compound molecules which form them. The first hypothesis to present itself in this connection, and apparently even the only admissible one, is the supposition that the number of integral molecules in any gas is always the same for equal volumes, or always proportional to the volumes.

The reasoning on which Avogadro founded this statement was probably based, at least in part, on an algebraic argument which we need not here consider. This treatment indicates that the numbers of particles in equal volumes of different gases are *simply* (integrally) *related*. This is not at all the same as saying that the numbers are *equal*, which is merely the simplest possible (one-to-one) integral relation. However, lacking any clear criterion for deciding just what the relations actually were, Avogadro wisely declared in favor of the provisional adoption of the simplest possible one. This relation is quite promising. As we have already seen, it goes far toward explaining the existence of the law of combining volumes. Furthermore, as Avogadro points out in his next sentence, it is so simple that any special postulates, about "the law regulating the distances" between the particles, are unnecessary. Presumably by this "law" he means a relation such as that shown by Newton to describe the relative positions of the bodies of the solar system.

His emphasis on the "equal volumes–equal numbers" idea is one of Avogadro's two major contributions. There is, of course, little that is new in this hypothesis; more than fifty years earlier it had been entertained by Bernouilli, and we have seen (page 265) that it was both recognized and rejected by Dalton. However, Avogadro now goes on to display the extraordinary value of this idea; and, at the same time, he is able to show that some of the theoretical difficulties which its acceptance seemed to entail are not nearly as disastrous as they were thought to be by Dalton.

> Indeed, if we were to suppose that the number of molecules contained in a given volume were different for different gases, it would scarcely be possible to conceive that the law regulating the distance of molecules could give in all cases relations as simple as those which the facts just detailed compel us to acknowledge between the volume and the number of molecules. On the other hand, it is very well conceivable that the molecules of gases being at such a distance that their mutual attraction cannot be exercised, their varying attraction for caloric may be limited to condensing a greater or smaller quantity around them, without the atmosphere formed by this fluid having any greater extent in the one case than in the other, and, consequently, without the distance between the molecules varying; or, in other words, without the number of molecules contained in a given volume being different . . . But in our present ignorance of the manner in which this attraction of the molecules for caloric is exerted . . . we should rather be inclined to adopt a neutral hypothesis, which would make the distance between the molecules and the quantities of caloric vary according to unknown laws, were it not that the hypothesis we have just proposed is based on that simplicity of relation between the volumes of gases on combination, which would appear to be otherwise inexplicable.

The argument here invoked by Avogadro is strongly reminiscent of that advanced by Gay-Lussac (see page 253) in explanation of the generally simple behavior of gases, that is, the distances between individual gaseous particles are assumed to be so great in comparison with their diameters that the variable attractive forces between neighboring particles are negligible. Avogadro suggests that under such circumstances the various quantities of caloric fluid held by the particles of different gases do not significantly influence the effective particle diameters, so that this fluid may be present in different amounts "without the distance between the particles varying; or, in other words, without the number of molecules contained in a given volume being different." While Avogadro says explicitly that he knows of no absolute criterion for the estimation of relative particle diameters, interparticle separations, or particle numbers in equal volumes of different gases, he emphasizes that the hypothesis of equal effective diameters squares well with Gay-Lussac's law, while Dalton's assumption of characteristically different diameters does not.

A few years after Avogadro's publication, the French physicist Ampère arrived independently at the same conclusion — that equal volumes of different gases contain the same number of particles. In this case the effect of differences in the various particle diameters was entirely ignored, apparently because Ampère felt that the distances between individual gaseous particles were so great that the unequal diameters of the particles would have no substantial effect on the volumes of different gases that contained equal numbers of these particles. Ampère's statement on this point is so clearly and thoughtfully presented that it is worth while to examine it here.

> When bodies pass into the gaseous state, their several particles are separated by the expansive force of heat to much greater distances from each other than when the forces of cohesion or attraction exercise an appreciable influence; so that these distances depend entirely on the temperature and pressure to which the gas is subjected, and under equal conditions of temperature and pressure the particles of all gases, whether simple or compound, are equidistant from each other. The number of particles is, on this supposition, proportional to the volumes of the gases. Whatever be the theoretical reasons which, in my opinion, support the above conclusion, it cannot be considered as anything but an hypothesis. But if, on comparing the inferences which follow from it as necessary consequences with the phenomena or the properties that we can observe . . . then if the inferences are confirmed by subsequent experiment, the hypothesis will acquire a degree of probability approximating to what in physics is called certainty.

With arguments such as this Avogadro and Ampère sapped the foundation — i.e., the pile-of-shot model of a gas — of arguments (3) and (4) against the "equal volumes–equal numbers" idea. Also, regarding the controversy from the outside, Avogadro was, unlike Dalton, prepared to accept Gay-Lussac's conclusion at its face value, so that argument (5) — to the effect that Gay-Lussac's law represents only a crude approximation to reality — failed to impress him. Consequently, in the sequel, Avogadro had only to dispose of points (1) and (2) which, as already remarked, represent much more difficult considerations.

The special cases discussed by Avogadro in the continuation of his discourse are most readily construed in terms of a general formulation of his argument. If the density of gas A is taken as d_A, and that of gas B as d_B, then d_A and d_B represent the weights of unit volumes of the two gases, measured under the same conditions of temperature and pressure. By Avogadro's hypothesis, the numbers of gas particles present in each case are identical. Calling this number n, it is plain that

$$\frac{n \times \text{Particle weight of } A}{n \times \text{Particle weight of } B} = \frac{d_A}{d_B};$$

hence

$$\frac{\text{Particle weight of } A}{\text{Particle weight of } B} = \frac{d_A}{d_B}.$$

Here we have an expression from which the relative particle weights can be calculated from the measured gas densities. This calculation is most conveniently carried out if the particle weight of one gas is defined as a standard — e.g., the weight of the hydrogen particle may be taken as unity — after which numerical values can be assigned to the particle weights of all the other gases, on the basis of the relative gas densities. Thus, oxygen gas being (according to Avogadro's evaluation) fifteen times as dense as hydrogen, the weight of the gaseous particle of oxygen is 15 relative to the hydrogen particle taken as 1.

With regard to the numbers of particles combining in a given reaction, if V_A unit volumes of gas A react with V_B unit volumes of gas B, then if n is taken as defined above, we must have nV_A particles of A reacting with nV_B particles of B. Consequently, for the relative numbers of particles entering into the reaction we have

$$\frac{\text{Number of particles of } A}{\text{Number of particles of } B} = \frac{nV_A}{nV_B} = \frac{V_A}{V_B}$$

so that from the ratio of the combining volumes we may deduce the relative numbers of particles involved in the reaction. Thus, since two volumes of hydrogen react with one volume of oxygen to give water, there are two particles of hydrogen for every particle of oxygen involved in this reaction.

It should be noted that both of these important calculations were possible only because of Avogadro's basic simplifying assumption, that equal volumes of different gases contain the same number of particles.

Let us now return to Avogadro's text.

> Setting out from this hypothesis [i.e., the "equal volumes–equal numbers" idea] it is apparent that we have the means of determining very easily the relativc masses of the molecules of substances obtainable in the gaseous state, and the relative number of these molecules in compounds; for the ratios of the masses of the molecules are then the same as those of the densities of the different gases at equal temperature and pressure, and the relative number of molecules in a compound is given at once by the ratio of the volumes of the gases that form it. For example, since the numbers 1.10359 and 0.07321 express the densities [i.e., specific gravities] of the two gases oxygen and hydrogen compared to that of atmospheric air as unity, and the ratio of the two numbers consequently represents the ratio between the masses of equal volumes of these two gases, it will also represent on our hypothesis the ratio of the masses of their molecules. Thus the mass of the molecule of oxygen will be about 15 times that of the molecule of hydrogen, or, more exactly, as 15.074 to 1. In the same way the mass of the molecule of nitrogen will be to that of hydrogen as 0.96913 to 0.07321, that is, as 13, or more exactly 13.238, to 1. On the other hand, since we know that the ratio of the volumes of hydrogen and oxygen in the formation of water is 2 to 1, it follows that water results from the union of each molecule of oxygen with two molecules of hydrogen. Similarly, according to the proportions by volume established by M. Gay-Lussac for the elements of ammonia, nitrous oxide, nitrous gas and nitric acid, ammonia will result from the union of one molecule of nitrogen with three of hydrogen, nitrous oxide from one molecule of oxygen with two of nitrogen, nitrous gas from one molecule of nitrogen with one of oxygen, and nitric acid from one of nitrogen with two of oxygen.

II.

> There is a consideration that appears at first sight to be opposed to the admission of our hypothesis with respect to compound substances. It seems that a molecule composed of two or more elementary molecules should have its mass equal to the sum of the masses of these molecules; and that in particular, if in a compound one molecule of one substance unites with two or more molecules of another substance, the number of compound molecules should remain the same as the number of molecules of the first substance. Accordingly, on our hypothesis, when a gas combines with two or more times its volume of another gas, the resulting

> compound, if gaseous, must have a volume equal to that of the first of these gases.

Consider the case in which unit volume of gas *A* reacts with V_B volumes of gas *B*, where V_B is greater than unity. Letting *n* represent the number of particles in unit volume of any gas, it is apparent that we then have *n* particles of *A* reacting with nV_B particles of *B*. If each molecule of the product contains one particle (atom) of *A* then, plainly, we cannot have more than *n* molecules of product; and, consequently, we would expect to find no more than unit volume of this product.

Avogadro continues:

> Now, in general, this does not in fact occur. For instance, the volume of water in the gaseous state is, as M. Gay-Lussac has shown, double that of the oxygen which enters into it, or, what comes to the same thing, equal to that of the hydrogen instead of being equal to that of the oxygen. But a means of explaining facts of this type in conformity with our hypothesis presents itself naturally enough. We suppose that the constituent molecules of any simple gas (i.e., the molecules that are at such a distance from each other that they cannot exert their mutual action) are not formed of only one elementary molecule [atom], but are made up of a certain number of these molecules united by attraction to form a single whole. Further, that when such molecules unite with those of another substance to form a compound molecule, the integral molecule which should result splits up into two or more parts (or integral molecules), each composed of half, quarter, &c., the number of elementary molecules forming the constituent molecule of the first substance, combined with half, quarter, &c., the number of constituent molecules of the second substance that ought to enter into combination with one constituent molecule of the first substance. . . . This is supposed to occur in such a way that the number of integral molecules of the compound becomes double, quadruple, &c., what it would have been if there had been no splitting up, and exactly what is necessary to satisfy the volume of the resulting gas. Thus, for example, the integral molecule of water will be composed of a half-molecule of oxygen with one molecule, or, what is the same thing, two half-molecules of hydrogen.

Here we have the heart of Avogadro's second major and, apparently, entirely original, contribution: the idea of polyatomic molecules of the gaseous elements.

Avogadro had previously convinced himself that, if equal volumes of different gases contained equal numbers of the respective particles, then, whenever unequal volumes of different elementary gases took part in some chemical combination, the volume of any gaseous reaction product should not exceed the volume of that one of the reacting gases which was involved in smaller quantity. However, this prediction was flatly contradicted by well-known experimental facts. For example, Gay-Lussac and von Humboldt had shown (see page 251) that when *one* volume of oxygen combined with two volumes of hydrogen, *two* volumes of water vapor were formed. Now if these volume relations are construed in terms of Avogadro's first assumption — that there is always the same number (*n*) of particles in unit volumes of different gases — they suggest that *n* particles of oxygen react with 2*n* particles of hydrogen to give 2*n* particles of water vapor. As already mentioned, this might imply that in some way each of the oxygen particles is divided into two fragments, one of which is incorporated in each of the water molecules.

Viewed on the basis of the implicit assumption that the "particles" of gaseous oxygen are identical with oxygen *atoms*, the suggested subdivision (of atoms), opposed as it was to the fundamental tenet of the atomic theory, was not entertained as a serious possibility. And indeed, the postulated indivisibility of the chemical atom was strongly buttressed by the very existence of the laws of definite, multiple, and equivalent proportions, which were so well explained in terms of the atomic theory. But Avogadro was sufficiently acute to perceive that, despite the superficial plausibility of the identification of the "particles" of the gaseous elements with the chemical atoms of those elements, this identification was in fact an arbitrary one, unsupported by any experimental evidence. To be sure, this was the simplest possibility, but Avogadro came to regard it as an oversimplification. He suggested, instead, that the "particles" present in the gaseous elements *do not consist of the individual atoms* of the elements *but of groups of atoms of the same element joined in a single molecule* of that element. That is, the particles that, in the gaseous elements, behave as essentially independent entities (i.e., "the molecules that are at such a distance from each other that they cannot exercise their mutual action") are not, as had been generally believed, single atoms, but consist of two or more atoms of the same element.

Now if we were to suppose that the oxygen "particle" contained, say, two oxygen atoms, it would then be possible to divide it into two equal fragments (atoms) without in any way threatening the integrity of the individual oxygen atoms. Thus from the *n* oxygen "particles" (O_2 molecules each containing two oxygen atoms) in one volume of oxygen we could obtain 2*n* oxygen atoms, sufficient to form the 2*n* molecules of water vapor required to fill two volumes of this gas. If we further assume that the "particle" of gaseous hydrogen is a molecule similarly constituted of two atoms (i.e., H_2), we can then formulate the reaction of oxygen with hydrogen, to give water, in the following way:

1 volume oxygen + 2 volumes hydrogen → 2 volumes water vapor,
n particles + $2n$ particles → $2n$ particles,
$n\,O_2 + 2n\,H_2 \rightarrow n[H_4O_2] \rightarrow 2n\,H_2O$;

or, most simply,

$$O_2 + 2\,H_2 \rightarrow [H_4O_2] \rightarrow 2\,H_2O.$$

The bracketed term $[H_4O_2]$ in the chemical equation represents the "integral molecule" which Avogadro imagined was first formed by the combination of one particle of oxygen with two of hydrogen. This "integral molecule" was then supposed to "split up" spontaneously, to form two H_2O molecules as a final product. This transient intermediate was entirely conjectural, since Avogadro had no knowledge save of the initial reactants and the final products. And, indeed, the reaction actually proceeds through a much more complicated "mechanism" which is still only imperfectly understood. Current practice is to omit from the chemical equation all such unstable intermediate compounds, showing only the initial reactants and the final products. However, the intermediates to which Avogadro refers will be shown here, in brackets as above.

It will be seen that in the foregoing case Avogadro, with the aid of his ingenious second assumption, namely, the existence of polyatomic molecules of elements, has succeeded in reconciling the "equal volumes–equal numbers" idea suggested by Gay-Lussac's law of combining volumes with the indivisibility of the chemical atom so strongly championed by Dalton. Now the apparent difficulty in achieving such a reconciliation was one of the points stressed by Dalton in his attack on the validity of Gay-Lussac's law. But all the troublesome instances comprehended under this argument (a few are listed on page 276) can now be dealt with satisfactorily, as is illustrated in the following examples. Note that in every case the number of molecules of each gas is directly proportional to the volume of that gas, and, further, that this harmonization with the "equal volumes–equal numbers" idea can now be secured without "splitting" any atoms, but by merely subdividing polyatomic molecules.

1 volume oxygen + solid carbon → 2 volumes carbon monoxide,
n particles → $2n$ particles,
$O_2 + 2\,C \rightarrow 2\,CO$.

1 volume nitrogen + 1 volume oxygen → 2 volumes nitrous gas,
n particles + n particles → $2n$ particles,
$N_2 + O_2 \rightarrow [N_2O_2] \rightarrow 2\,NO$.

3 volumes hydrogen + 1 volume nitrogen → 2 volumes ammonia,
$3n$ particles + n particles → $2n$ particles,
$3\ H_2 + N_2 \rightarrow [N_2H_6] \rightarrow 2\ NH_3$.

The last two cases are mentioned by Avogadro in the next paragraph of his text, where he also cites the following reaction:

2 volumes nitrogen + 1 volume oxygen → 2 volumes nitrous oxide,
("laughing gas")
$2n$ particles + n particles → $2n$ particles,
$2\ N_2 + O_2 \rightarrow [N_4O_2] \rightarrow 2\ N_2O$.

Thus argument (1) (see page 276) against the "equal volumes—equal numbers" idea can be neatly side-stepped by postulating the existence of polyatomic molecules of the gaseous elements. It will be recalled that arguments (3), (4), and (5) were dismissed previously (see page 75), so we have only to deal with argument (2), which called attention to certain apparent anomalies in the measured gaseous densities. Avogadro does not discuss this point explicitly, but it is easy to see how these difficulties can be dissipated with the aid of formulations such as those that have been given above.

Among the anomalies of this type we may remark: steam, formed from oxygen *plus* hydrogen, is *less* dense than oxygen itself; carbon monoxide, formed from oxygen *plus* carbon, is *less* dense than oxygen; and ammonia, formed from nitrogen *plus* hydrogen, is *less* dense than nitrogen. It at first appears that the product molecules formed by such addition reactions *must* be heavier than the particles of the starting material; so that, if unit volume of each of these gases contains the same number of particles, water vapor and carbon monoxide should both be *more* dense than oxygen, and ammonia *more* dense than nitrogen, contrary to the experimental findings. But Avogadro's new formulation clearly indicates how these contradictions can be obviated. What had been assumed to be *addition* reactions were now seen to be, in effect, *substitution* reactions. Thus in the formation of the molecules of water vapor (H_2O) two hydrogen atoms have been *substituted* for one of the oxygen atoms in the oxygen molecule (O_2). Since two hydrogen atoms together weigh less than one oxygen atom, the water molecule *should* be lighter than the oxygen molecule. Thus if the weights of unit volumes of these gases are compared it is now only to be expected that the water vapor will prove less dense than the oxygen, as is indeed the case. In the same way, carbon monoxide is formed by the substitution of a carbon atom for a heavier oxygen atom in the oxygen molecule, so that the carbon monoxide molecule should weigh less than one of oxygen. Similarly, the substitution of three hydrogen atoms for one of the nitrogen atoms in the nitrogen molecule (N_2) yields a molecule of ammonia (NH_3) weighing less than the nitrogen molecule itself. In this way the last of the major arguments advanced against the "equal volumes–equal numbers" idea can be disposed of, and it is plain that Avogadro's double hypothesis provides answers to all the difficulties to which Dalton called attention.

Avogadro's exposition of the important applications of his double hypothesis, continues.

> On reviewing the various compound gases most generally known, I only find examples of duplication of the volume relatively to the volume of that one of the constituents which combines with one or more volumes of the other; we have already seen this for water. In the same way, we know that the volume of ammonia gas is twice that of the nitrogen which enters into it. M. Gay-Lussac has also shown that the volume of nitrous oxide is equal to that of the nitrogen which forms part of it, and consequently is twice that of the oxygen. Finally, nitrous gas, which contains equal volumes of nitrogen and oxygen, has a volume equal to the sum of those of the two component gases, that is to say, double that of each of them. Thus in all these cases there must be a division of the molecule into two; but it is possible that in other cases the division might be into four, eight, &c. The possibility of this division of compound molecules might have been conjectured *a priori*; for otherwise the integral molecules of bodies composed of several substances with a relatively large number of molecules, would come to have a mass excessive in comparison with the molecules of simple substances. We might therefore imagine that nature had some means of bringing them back to the range of the latter, and the facts have indicated the existence of such means. Besides, there is another consideration that would seem to make us admit in some cases the division in question; for how could one otherwise conceive a real combination between two gaseous substances uniting in equal volumes without condensation, such as takes place in the formation of nitrous gas? Supposing the molecules to remain at such a distance that the mutual attraction of those of each gas could not be exercised, we cannot suppose that a new attraction could take place between the molecules of one gas and those of the other. But on the hypothesis of division of the molecule, it is easy to see that the combination really reduces two different molecules to one, and that there would be contraction by the whole volume of one of the gases if each compound molecule did not split up into two molecules of the same nature. M. Gay-Lussac saw clearly that according to the facts the diminution of volume in the combination of gases could not represent the closer approach of their molecules. The splitting of the molecules in such combinations explains how these two things can be rendered independent of one another.

Avogadro suggests that it is very difficult to construe the reaction

1 volume nitrogen + 1 volume oxygen → 2 volumes nitrous gas

except in terms of his double hypothesis. For the first stage of this reaction he proposes

$$N_2 + O_2 \rightarrow [N_2O_2],$$

where the N_2O_2 is to be regarded as an unstable intermediate, since "there would be contraction by the whole volume of one of the gases if each compound molecule did not split up into two molecules of the same nature." Therefore the over-all reaction has the form

$$\begin{array}{ccccccc} N_2 & + & O_2 & \rightarrow & [N_2O_2] & \rightarrow & 2\ NO, \\ n \text{ particles} & + & n \text{ particles} & & & \rightarrow & 2n \text{ particles.} \end{array}$$

This is entirely compatible with the observed fact that the reaction proceeds without apparent volume contraction, since the total numbers of particles present before and after the reaction are identical, even though a real combination has taken place.

III.

> Dalton, on arbitrary suppositions that appeared to him most natural [i.e., the rule of greatest simplicity] as to the relative number of molecules in compounds, has endeavored to establish ratios between the masses of the molecules of simple substances. Our hypothesis, supposing it well-founded, puts us in a position to confirm or rectify his results from precise data, and, above all, to assign the size of compound molecules according to the volumes of the gaseous compounds, which depends partly on that division of molecules of which this physicist had no idea.

Avogadro emphasizes that all of Dalton's atomic weights ultimately depend on the assignments of molecular formulas made with the aid of the not implausible, but entirely unsupported, "rule of greatest simplicity." Avogadro suggests that a superior method for the evaluation of these molecular formulas and atomic weights can be founded on his own double hypothesis. We have already remarked (see page 250) that the chief obstacle to the further extension and application of Dalton's atomic theory lay in that theory's inability to place its molecular formulas (and, thence, its atomic weights) on a rational empirical basis. Consequently, Avogadro's present proposal should be regarded as a crucial step in the development of the atomic theory.

> In what follows I shall make use of the exposition of Dalton's ideas that Thompson has given us in his *System of Chemistry*. Dalton sup-

> poses that water is formed by the union of hydrogen and oxygen, molecule to molecule. From this it results, according to the ratio by weight of the two components, that the mass of the molecule of oxygen should be to that of hydrogen about as 7½ to 1 or, according to Dalton's evaluation, as 6 to 1. This ratio on our hypothesis is, as we have seen, twice as great, namely, as 15 to 1. As for the molecule of water, its mass ought to be roughly expressed by $15 + 2 = 17$ (taking for unity that of hydrogen), if there were no division of the molecule into two; but on account of this division it is reduced to half, 8½, or more exactly 8.537, as may also be found directly by dividing the density of aqueous vapour, 0.625 according to Gay-Lussac, by the density of hydrogen, 0.0732. This mass only differs from 7, that assigned to it by Dalton, by the difference in the values for the composition of water; so that in this respect Dalton's result is approximately correct from the combination of two compensating errors — that in the mass of the molecule of oxygen, and that of neglecting the division of the molecule.

Caution must be exercised in making any comparison of Avogadro's results with those of Dalton. To begin with, the two sets of calculations were based on somewhat different analytical data. More important, we have now reached the very point at which Avogadro's suggestion of a distinction between the *physically* "smallest particle" (i.e., the *molecule* of an element) and the *chemically* "smallest particle" (i.e., the *atom* of an element) leads to a reorganization of the atomic-weight scale proposed by Dalton.

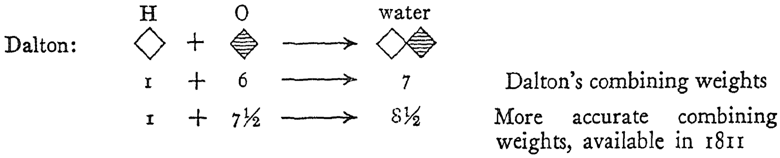
Observing that the experimental data indicated the density of oxygen to be 15 times that of hydrogen, Avogadro deduced, with the aid of his "equal volumes–equal numbers" hypothesis, that the molecular weight of oxygen was 15, relative to the hydrogen molecule taken as 1. He then made use of Gay-Lussac's data on combining volumes — 2 volumes of hydrogen react with 1 of oxygen to give 2 of water vapor — as the basis for the following formulation of the reaction in which water is so produced

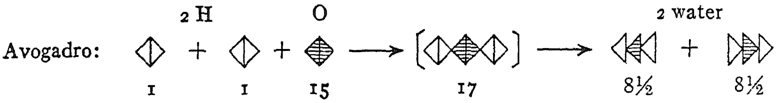
$$2\,H_2 + O_2 \rightarrow [H_4O_2] \rightarrow 2\,H_2O$$

The spontaneously unstable aggregate H_4O_2 is composed of two hydrogen molecules (each, by definition, of weight 1) and one oxygen molecule (whose relative atomic weight has been calculated as 15). Therefore the unstable aggregate must have a relative weight of 17; and when it splits in half to form two water molecules (H_2O) each of these will have a molecular weight of 8½, relative to the hydrogen *molecule* taken as 1. This value is confirmed by the fact that water vapor is 8½ times as dense as hydrogen gas.

Compare this with Dalton's procedure. Taking the formula of water as HO, Dalton used his combining weights — 6 of oxygen combine with 1 of hydrogen to give 7 of water—to calculate the relative atomic weight of oxygen as 6. This evaluation leads to a molecular weight of water of 7 (i.e., 6 + 1), relative to the hydrogen *atom* taken as 1. Numerically, this value, 7, differs from that deduced by Avogadro, 8½, only "by the difference in the values for the composition of water." Thus, had Dalton employed the more accurate combining weights cited by Avogadro (7½ of oxygen combining with 1 of hydrogen to give 8½ of water) his value for the atomic weight of oxygen would have been 7½, and for the molecular weight of water, 8½.

However, despite this agreement of the numerical values assigned to the molecular weight of water, Avogadro very properly remarks that Dalton obtained the "correct" figure only through "the combination of two compensating errors—that in the mass of the molecule of oxygen, and that of neglecting the division of the molecule." The way in which these errors cancel in the present case can best be illustrated by the following diagram:





All these numbers refer to the hydrogen "particle" (Dalton  ; Avogadro ) taken as 1.

Avogadro now continues with his consideration of a variety of specific applications of his new methods for the evaluation of molecular formulas and molecular weights. He carefully shows how his own values are derived, with the aid of his double hypothesis, from combining *volume* and density data for gases, while Dalton's figures are seen to derive from combining *weight* data, interpreted with the aid of the "rule of greatest simplicity."

> Dalton supposes that in nitrous gas the combination of nitrogen and oxygen takes place molecule to molecule: we have seen that this is effectively so on our hypothesis. Thus Dalton would have found the same molecular mass for nitrogen as we have, always supposing that of hydrogen to be unity, if he had not set out from a different evaluation of that of oxygen, and if he had taken precisely the same evaluation of

> the quantities of the elements in nitrous gas by weight. But in supposing the molecule of oxygen to be less than half what we find, he had also to make that of nitrogen equal to less than half the value we have assigned to it, viz., 5 instead of 13. As for the molecule of nitrous gas itself, his neglect of the division of the molecule again makes his result approach ours; he has made it $6 + 5 = 11$, whilst according to us it is about $\frac{15 + 13}{2} = 14$, or more exactly $\frac{15.074 + 13.238}{2} = 14.156$, as we also find by dividing 1.03636, the density of nitrous gas according to Gay-Lussac, by 0.07321 [the density of hydrogen]. Dalton has also determined in the same manner as the facts have given it to us, the relative number of molecules in nitrous oxide and in nitric acid, and in the first case the same circumstance has rectified his result for the magnitude of the molecule. He makes it $6 + 2 \times 5 = 16$, whilst according to our method it should be $\frac{15.074 + 2 \times 13.238}{2} = 20.775$, a number which is also obtained by dividing 1.52092, the density of nitrous oxide gas according to Gay-Lussac, by the density of hydrogen gas.
>
> As for ammonia, Dalton's supposition as to the relative number of molecules in its composition is on our hypothesis entirely at fault. He supposes nitrogen and hydrogen to be united in it molecule to molecule, whereas we have seen that one molecule of nitrogen is in it joined with three molecules of hydrogen. According to him the molecule of ammonia would be $5 + 1 = 6$; according to us it should be $\frac{13 + 3}{2} = 8$, or more exactly 8.119, as may also be deduced directly from the density of ammonia gas. The division of the molecule, which does not enter into Dalton's calculations, here again corrects in part the error that would result from his other suppositions . . .

Avogadro goes on to extend his new mode of calculation to a wide variety of other concrete cases. Up to this point practically all his statements and deductions are essentially correct, but in his further discourse he rather overextends himself, in venturing out over more slippery ground. Some of his later conclusions are not entirely free from error, though they still constitute an impressive demonstration of the power of his new technique for the evaluation of the molecular formulas and molecular weights so essential to the further progress of the atomic theory. In his concluding paragraph Avogadro very appropriately indicates the satisfaction of this need as one of the chief fruits of his investigation. In this closing statement Avogadro also bears testimony to the profound contemporary impression made by Berthollet's conception of compound formation in *in*definite proportions. Just as did Gay-Lussac under similar circumstances (see page 262) Avogadro attempts to supply some reconciliation of Dalton's new conceptual scheme — of which he so obviously approves — with the older views of Berthollet that he is still reluctant to abandon entirely.

> It will have been in general remarked on reading this Memoir that there are many points of agreement between our special results and those of Dalton, although we set out from a general principle, and Dalton has only been guided by considerations of detail. This agreement is an argument in favour of our hypothesis, which is at bottom merely Dalton's system furnished with a new means of precision through the connection we have found between it and the general fact established by M. Gay-Lussac. Dalton's system supposes that compounds are made in general in fixed proportions, and this is what experiment shows with regard to the more stable compounds and those most interesting to the chemist. It would appear that it is only combinations of this sort that can take place amongst gases, on account of the enormous size of the molecules that would result from ratios expressed by larger numbers, in spite of the division of the molecules, which is in all probability confined within narrow limits. We perceive that the close packing of the molecules in solids and liquids, which only leaves between the integral molecules distances of the same order as those between the elementary molecules, can give rise to more complicated ratios, and even to combinations in all proportions; but these compounds will be so to speak of a different type from those with which we have been concerned, and this distinction may serve to reconcile M. Berthollet's ideas as to compounds with the theory of fixed proportions.

6. EPILOGUE

Avogadro's proposals were essentially sound, yet in the years between 1811 and 1858 they were almost completely ignored by the vast majority of chemists. Instead, a number of other methods were employed in various attempts to establish molecular formulas and atomic weights. By 1840 the variety and fallibility of these methods had led to a number of basically contradictory results. The resulting confusion engendered an increasingly strong feeling that atomic weights could never be unambiguously determined, and that the whole atomic theory might be no more than a speculation that had outworn its usefulness as a quantitative concept, though everyone recognized its ancient value as a way of thinking about natural phenomena.

In 1858 Cannizzaro revived and slightly, but very importantly, extended Avogadro's ideas. His formulation rapidly won widespread acceptance for Avogadro's original proposals and the position of the atomic-molecular theory has since then steadily become more secure. Although we cannot consider them in detail it may be of interest to examine some of the factors that contributed to, and some of the salient events in, this long period of uncertainty.

Some Persisting Objections to Avogadro's Proposals. Avogadro's contribution was a very real one. It led to a reasonable method for the derivation of molecular formulas — the very information of which Dalton's atomic theory stood most in need. But its importance could not disguise the shortcomings of Avogadro's work. We have already mentioned that his presentation was anything but lucid. More important, the applicability of Avogadro's proposal was severely limited. It could be applied only to elements and compounds that could be readily obtained in a gaseous condition, and unfortunately the vast majority of materials do not exist as gases under normal conditions of temperature and pressure. Very possibly Avogadro recognized this shortcoming, for in the latter part of his first paper, and in his subsequent papers, he attempted to extend his methods to the determination of the formulas of solid substances. However, such a gross overextension of methods that rather clearly applied only to gases and vapors simply weakened the effect of those arguments in which Avogadro was quite correct.

While such factors may have reduced the initial impact of Avogadro's work, there were other more fundamental objections to his proposal. It should be recalled that this proposal rested on two assumptions. The first of these, the "equal volumes–equal numbers" idea, was not intrinsically unlikely, though it was distinctly *ad hoc* and unsupported. The second closely related assumption was that, even as stable groupings of *atoms of different kinds* were capable of coördinated existence and action in the *molecule of a compound*, there could also be a stable grouping of *atoms of the same kind*, to form a *molecule of an element*. Let us now examine three of the graver difficulties that beset this postulation of polyatomic molecules of the elements, at the time it was proposed by Avogadro.

(1) Although there was no evidence definitely *against* this *ad hoc* assumption, neither was there much evidence *for* it. To be sure, it reconciled Avogadro's first assumption with the known volume relations and the indivisibility of the chemical atom. But Avogadro's first assumption was very tenuously supported, so that his second assumption must have appeared to represent the piling on of one unsupported speculation in an attempt to maintain another conjectural notion.

Furthermore, there is some irrationality in the suggestion that the physically "smallest particle" (molecule) of a gas is not *the* "smallest particle" — the chemical atom — but rather an aggregate of such atoms.

(2) The suggestion that there were definite molecules of elements, containing two, four, six, or more atoms of the same kind, raised certain problems. If gaseous "atoms" can so combine, it means that there must be some attractive forces between atoms of the same kind. Speculation about such attractive forces seemed utterly ridiculous to Dalton, among others, and three years *before* Avogadro's paper appeared we find him animadverting on this point. In connection with a criticism of some work of Berthollet's he says in his *New System*:

> The author means to say, that the parts of elastic fluids *are* endued with the force of cohesion; but this he applies only to heterogeneous [different kinds of] particles. He certainly does not mean that particles of homogeneous elastic fluids possess the force of cohesion. [Note the complete confidence with which this "absurd" possibility is rejected.]
>
> Newton has demonstrated from the phenomena of condensation and rarefaction that elastic fluids are constituted of particles, which repel one another by forces which increase in proportion as the distance of their centres diminishes: in other words, the forces are reciprocally as the distances. This deduction will stand as long as the Laws of elastic fluids continue to be what they are. What a pity it is that all who attempt to reason, or to theorize respecting the constitution of elastic fluids, should not make themselves thoroughly acquainted with this immutable Law, and constantly hold it in their view whenever they start any new project.

Although Newton's "Law" was not so "immutable" as Dalton believed (see page 223) it *was* difficult to imagine how gaseous particles might sometimes repel each other to produce the "spring of the air" expressed in Boyle's law, yet on other occasions attract each other to form groups of atoms of the same kind.

Even allowing that some attractive forces might exist, why should they stop with the formation of O_2, rather than continuing in action to form O_3, O_4, and so on? That is, why should one atom of oxygen *attract* another atom of oxygen, to form O_2, while one O_2 particle *repels* another O_2 particle (producing the behavior expressed in Boyle's law) rather than combining with it to form O_4? No satisfactory answer to these last questions could be given by Avogadro and, indeed, no "good" answer could be given until about 1925. It is little wonder, then, that Avogadro's proposition provoked a skeptical response from his contemporaries.

(3) Avogadro himself recognizes that it is possible that larger numbers of atoms of the same kind may be combined in a single gaseous particle. Thus it is quite possible that instead of O_2 molecules

we have O_4 molecules. Instead of writing, as we did in the last section,

$$2\ H_2 + O_2 \rightarrow 2\ H_2O,$$

perhaps we should have written

$$2\ H_2 + O_4 \rightarrow H_2O_2.$$

The then available data did not allow of a decision between these alternatives, and it was almost 50 years before Avogadro's countryman, Cannizzaro, suggested a simple way of securing a highly probable (though not "certain") experimental distinction.

These are formidable difficulties. The first — the highly speculative character of the double assumption — was an entirely unavoidable, but none the less serious, shortcoming. However, the second and third difficulties — the unexplained stability of the polyatomic molecules of the elements, and the indeterminacy of the number of atoms that they contained — were, then and later, even more serious obstacles. Had Avogadro's proposal been the only obvious way of reconciling the atomic theory and the law of combining volumes perhaps these difficulties could have been taken in stride. However, as we shall see, there was at hand an alternative explanation of the data which, at the time, presented a much more prepossessing appearance.

The second difficulty — the unexplained stability of the polyatomic molecules of the elements — was, in 1811, a particularly annoying one. The postulation of such molecules appeared to be a flagrant contradiction of the most alluring explanation that could then be given of the striking chemical effects brought about by electricity. These effects and this explanation were very much in the minds of contemporary investigators, since they had developed very recently. A brief examination of some of the more important aspects of this work may now be appropriate.

The Electrochemical Investigations of Davy and Berzelius, and the Development of the Dualistic Theory. The vigorous activity in the field of electrochemical investigations largely stemmed from the invention of the voltaic pile. This pile was, in effect, a primitive battery not essentially different from batteries that are used today. It produced much stronger electric currents than had previously been available, and the application of this new tool to the study of chemical phenomena was undertaken with great celerity and astonishing results.

Volta's description of his pile was communicated early in 1800 in the form of a letter to Sir Joseph Banks, then president of the Royal Society. Within a few months two English investigators had found that the establishment of an electric current in water led to the decomposition of this substance and the formation of hydrogen and oxygen in roughly the proportions in which they normally combined to form water. Apparently the electric current had resolved the compound into its component elements. Similar decompositions of other compounds were rapidly discovered, notably in an important series of observations reported in 1803 by Berzelius and Hisinger. But the most important discoveries on the "Chemical Agencies of Electricity" were made through prolonged and systematic studies carried on with great virtuosity and notable éclat by Sir Humphry Davy, working at the Royal Institution.[6]

Davy's further work resulted, in 1807, in his spectacular discovery of the alkali metals, to which he was guided by a belief that the stability of chemical compounds was due to *electrical* forces between the elementary particles (i.e., atoms) of which they were composed. Davy's remarks in this connection retain a remarkable cogency even today:

> If chemical union be of the [electrical] nature which I have ventured to suppose, however strong the natural electrical energies of the elements of bodies may be, yet there is every probability of a limit to their strength; whereas the powers of our artificial instruments seem capable of indefinite increase . . . [Consequently, we may] hope that the new [electrical] method of analysis may lead us to the discovery of the *true* elements of bodies.[7]

Using a much enlarged voltaic pile, Davy succeeded in breaking down several previously undecomposed substances, and found among their components the alkali elements — "true" chemical elements whose existence Lavoisier had formerly been able at most to suspect. In this connection we may note a remark of Dalton's that has already been cited (see page 228): "We may not know what elements are absolutely indecomposable, and what are refractory, because we do

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[6] Indeed, in 1806 a paper on this subject won for Davy a prize offered by Napoleon for the most important electrical work of the year. Coming shortly after the Battle of Trafalgar and in the same year as the "Continental System" of blockading England, this award may occasion rather melancholy reflections today. To the cultural historian remains the interesting task of explaining how, in the development of Western civilization, the growth of science, from a harmless and relatively useless avocation of a few amateurs, to its present eminence as a major contributor to national welfare, entailed the loss of its once-vaunted supranational character.

[7] There is an almost perfect parallelism between these views of Davy's and opinions that are entertained today. Believing as we do that electrical forces are responsible not only for the existence of chemical compounds, but also for the existence of the chemical "elements" themselves and the various "particles" of which these "elements" are now presumed to be composed, we are still seeking, as by the construction of bigger and better cyclotrons, to achieve an "indefinite increase" in the power of our instruments. We hope that with such instruments it will be possible to resolve the "elements" that we already know into yet more subtle "materials," to find the "*true* elements" of which, we now believe, the chemical "elements" are themselves compounded.

not apply the proper means for their reduction." Davy had discovered the "proper means" to apply to some of these "refractory" materials.

Davy's demonstration of the ability of electrical influences to work a separation of even the most resistant chemical compounds was very impressive. Duly considered, it lent force to the idea that chemical compounds owed their stability to the electric forces between the atoms of which they were composed. In Davy's experiments, these forces were simply overcome by the more powerful disruptive forces generated by the enlarged voltaic pile. This electrochemical theory of chemical combination received its most elaborate formulation and most vigorous expression in the dualistic theory of the Swedish chemist Berzelius. In this theory Berzelius made the new findings on electrochemical phenomena the basis of a revision and revival of another (acid-base) dualistic system that had been suggested by Lavoisier, who had in turn derived his dualistic views from even more ancient natural philosophers.

The decomposition of compounds by an electric current (called *electrolysis*) was brought about by inserting in the substance, or in a solution of it, two terminals (called *electrodes*) that were, in turn, connected to the voltaic pile. The products of the decomposition then appeared at the electrodes. Thus, in the electrolysis of water, it was found that at one electrode only hydrogen was liberated, and at the other only oxygen. This behavior, when considered in the light of what was already known about the forces acting between charged bodies, naturally suggested that all the hydrogen particles bore one characteristic charge, while all the oxygen particles carried an equally characteristic charge of opposite polarity. In the attractive forces known to exist between such oppositely charged particles Berzelius saw the origin of the stability of the chemical compound, water. Furthermore, his work on the electrolysis of a number of other compounds showed that some of the decomposition products always appeared at one electrode, and the others at the oppositely charged electrode. This seemed to be a fairly clear indication that the different constituents of all compounds were always oppositely charged, and suggested that *all* chemical compounds owed their stability to the electric forces between the oppositely charged particles of which they were composed. This was the heart of Berzelius' dualistic theory — the dualism inhering in the juxtaposition of positively and negatively charged bodies. In this theory electrolysis was construed as a simple reversal of normal chemical combination. That is, the charges characteristic of the free elements, which had been lost or neutralized in their combination, were restored at the appropriate electrodes; and, thereby, the compound was broken down and the free elements were regenerated.

An early intimation of Berzelius' dualistic theory appeared in the same year, indeed in the same journal, in which Avogadro's proposal was published. However, it is easy to see how Berzelius, and the many who acceded to the dualistic conceptions of this preëminent theoretician, would be inclined to take a very dim view of Avogadro's postulation of polyatomic molecules of the elements. They readily "understood" the stability of water in terms of the aggregation of the oppositely charged particles that composed it. But how could one, with this dualistic conception, imagine the stable existence of the hydrogen molecules and oxygen molecules hypothesized by Avogadro? Electrolytic experiments seemed to show clearly that all the hydrogen particles bore the *same* charge. They should, therefore, *repel* each other, and there appeared to be no basis for Avogadro's postulation of hydrogen *molecules* formed from two or more hydrogen atoms. Similarly, all the oxygen atoms appeared to be alike in bearing some other characteristic charge, so that they too should repel each other rather than aggregating in stable polyatomic molecules. Consequently, Avogadro's speculations, founded on the supposition that such polyatomic molecules had a real existence, appeared to be excessively farfetched when viewed in the light of a dualistic conception that arose quite straightforwardly from well-established observations of the chemical effects of electricity. Thus the dualistic theory struck a telling blow at the very foundation of the conceptual structure reared by Avogadro.

Berzelius' Conception and his Efforts to Secure Accurate Atomic Weights. Unlike Dalton, Berzelius accepted as exact Gay-Lussac's law of combining volumes. However, being unimpressed by Avogadro's attempt to reconcile the atomic theory with the law of combining volumes, Berzelius devised an alternative method of reconciliation that appeared to be much more prepossessing. This method did *not* entail the postulation of the polyatomic molecules of the elements, so repugnant to the dualistic view of chemical combination. Berzelius avoided all necessity for any such postulation by adopting the "equal volumes–equal numbers" notion only in a severely restricted form. He granted that there were equal number of gaseous particles (here assumed to be atoms) in equal volumes of the *elementary* gases, but he denied the extension of this supposition to the particles of the compound gases formed by the combination of the elements. Instead, he believed that the numbers of particles (molecules) in equal volumes of compound gases were *not* equal, but varied with the effective sizes of the molecules. In general he assumed, quite plausibly, that a molecule containing two or more atoms must have a greater effective volume than the individual atoms themselves, so that there ought to be fewer molecules in a volume of a compound gas than there were atoms in an equal volume of one of the component elementary gases. He allowed the molecular sizes to assume any values that brought the "predicted" numbers of molecules into line with the volume relations observed by Gay-Lussac. Let us consider a few examples of the results that are secured from this line of reasoning.

For the combination of nitrogen and oxygen to form nitrous gas Avogadro would have written, as we do today,

$$\begin{array}{ccccc} \text{1 volume oxygen} & + & \text{1 volume nitrogen} & \rightarrow & \text{2 volumes nitrous gas,} \\ n \text{ particles} & + & n \text{ particles} & \rightarrow & 2n \text{ particles,} \\ O_2 & + & N_2 & \rightarrow & 2\,NO. \end{array}$$

He suggests, in his text (see page 287), that it would be very difficult to construe the reaction in any other terms. But Berzelius found no difficulty in so doing. He would write

$$\begin{array}{ccccc} \text{1 volume oxygen} & + & \text{1 volume nitrogen} & \rightarrow & \text{2 volumes nitrous gas,} \\ n \text{ particles} & + & n \text{ particles} & \rightarrow & n \text{ particles,} \\ O & + & N & \rightarrow & NO. \end{array}$$

Berzelius thus acknowledged that there were equal numbers of the respective atoms in equal volumes of nitrogen and oxygen. However, he regarded the molecules of nitrous gas as correspondingly bigger than the atoms constituting them. Indeed, in this case the volume of the molecule appeared to be just equal to the sum of the volumes of its component atoms — a most attractively reasonable relation. There would then be only half as many molecules in a given volume of nitrous gas as there were atoms in an equal volume of nitrogen or oxygen. Consequently, if there were n atoms in *one* volume of oxygen or nitrogen, there would be but n molecules in *two* volumes of nitrous gas. The "predictions" of the atomic theory can thus be brought into line with the volume relations observed by Gay-Lussac, and this concordance involves neither the subdivision of the chemical atom nor the assumption of polyatomic molecules of the elements.

Reasoning in the same way, Berzelius would have written

$$\begin{array}{ccccc} \text{1 volume oxygen} & + & \text{2 volumes hydrogen} & \rightarrow & \text{2 volumes water,} \\ n \text{ particles} & + & 2n \text{ particles} & \rightarrow & n \text{ particles,} \\ O & + & 2\,H & \rightarrow & H_2O \end{array}$$

and

$$\begin{array}{ccccc} \text{1 volume nitrogen} & + & \text{3 volumes hydrogen} & \rightarrow & \text{2 volumes ammonia,} \\ n \text{ particles} & + & 3n \text{ particles} & \rightarrow & n \text{ particles,} \\ N & + & 3\,H & \rightarrow & NH_3. \end{array}$$

In each case the effective volumes of the product molecules were taken to be just those that would permit the number of available molecules to fill the experimentally determined volumes of product. Thus Berzelius proposed to retain both the atomic theory and the law of combining volumes. He viewed the latter as highly significant as far as the numbers of atoms of the *elementary* gases were concerned, but he regarded the volumes of the product gases as more or less accidental factors which shed no great light on the numbers of compound molecules present.

It seems probable that, had he not been diverted by his interpretation of the physical phenomena through which he first made his oblique approach to the atomic theory, Dalton might have arrived at the well-formulated views adopted by Berzelius. These physical considerations (see page 226) so strongly suggested to Dalton that the effective diameters of no two gaseous species could be *exactly* the same that he was never able to credit the idea that equal volumes of different gases contained precisely the same number of particles. Consequently, he could never bring himself to accept the law of combining volumes as an exact relation, as Berzelius did. Thus, although he was the originator of the modern atomic theory, Dalton was outstripped by Berzelius in the appreciation of the significance and usefulness of the relations discovered by Gay-Lussac. Indeed, it might be even more correct to say that *because* Dalton was the originator of the modern atomic theory, and because of the way in which he received his original inspiration from the study of physical phenomena, he was less able to contribute to the subsequent elaboration of the chemical atomic theory.

It will be observed that this mode of approach gave Berzelius the "correct" formulas for water, ammonia, nitrous gas and a number of other compounds formed from gaseous elements. Unfortunately, only four of the then known elements are gases under normal conditions of temperature and pressure, so that the usefulness of this method of establishing molecular formulas was severely restricted. In the attempt to determine the atomic weights of the nongaseous elements Berzelius was thus forced to set out with a body of working rules reminiscent of Dalton's rule of greatest simplicity. Berzelius' rules were a great deal more sophisticated, and he applied them with flexibility and wisdom, guiding himself with a variety of crosschecks based on the analogies in the chemical behavior of the various elements and compounds. Even so, the atomic weights that he so deduced were often in error. However, they differed from Dalton's in one pivotally important respect—in practically all cases they diverged from the "correct" (i.e., modern) values only by some small whole-number factor.

This crucial difference obtained because the *combining* weights on which Berzelius' *atomic* weights were based were vastly more accurate than those used by Dalton. Berzelius secured these combining weights by the most laborious experimentation. He set himself to this immense task because he recognized it as a vital preliminary to the further progress of the atomic theory that had so favorably impressed him (see page 275). As he later wrote:

> By new experiments I soon convinced myself that Dalton's figures were wanting in that accuracy that was required for the practical application of his theory. I perceived that if the light that was now shed upon the whole of science was to be increased, the atomic weights of as large a number of elements as possible, and especially those of the commonly occurring elements, must be determined with the greatest accuracy attainable.

Perceiving that these accurate *atomic* weights would have to be based on accurate evaluations of the *combining* weights, Berzelius devoted the greater part of 10 years of his life to the careful determination of some 2000 combining weights of elements and compounds. These results he collected and published in 1818.

Let us contrast the state of affairs before and after Berzelius' work. Prior to his excellent determinations of combining weights there was a wide range of values for each atomic weight. For example, the weights of hydrogen and oxygen that combined to form water were so uncertain that the atomic weight of oxygen relative to that of hydrogen was very seriously in doubt, as may be seen from Table 2.

TABLE 2. Atomic weight of oxygen (relative to hydrogen as 1) according to various combining weights and formulas for water.

If the combining proportions are		*Then* the assumption of the following formulas leads to the atomic weights shown		
		HO	H_2O	HO_2
6:1	Dalton 1806	6	12	3
7:1	Dalton 1810	7	14	3½
7½:1	Avogadro 1811	7½	15	3¾

There is obviously a great diversity of possibilities and, although the conjectures based on any one set of combining weights are simply related to one another, those drawn from different evaluations of the combining weights are not.

After Berzelius' work became available the situation was quite different. The possible values of the atomic weights were strictly delimited and very simply related to one another even when, as in his work with solid elements, Berzelius did not have Gay-Lussac's data to guide him. The restricted degree of uncertainty attaching to the atomic weight of silver (symbol, Ag) will serve to illustrate the new state of affairs. It should be remarked here that Berzelius, unlike Dalton and Avogadro, referred all of his atomic weights to the weight of the oxygen, not the hydrogen, atom. Allowing the oxygen atom its present standard weight of 16, Berzelius' considerations might be formulated as follows:

The fact is that 13.516 grams of silver combine with 1 gram of oxygen. *Therefore, if* the formula of silver oxide is AgO,

$$\frac{\text{atomic weight of silver}}{\text{atomic weight of oxygen}} = \frac{\text{atomic weight of silver}}{16} = \frac{13.516}{1},$$

then

$$\text{atomic weight of silver} = 16 \times 13.516 = 216.26;$$

if the formula of silver oxide is Ag_2O,

$$\frac{2 \times \text{atomic weight of silver}}{\text{atomic weight of oxygen}} = \frac{2 \times \text{atomic weight of silver}}{16} = \frac{13.516}{1},$$

then

$$\text{atomic weight of silver} = 8 \times 13.516 = 108.13;$$

if the formula of silver oxide is AgO_2,

$$\frac{\text{atomic weight of silver}}{2 \times \text{atomic weight of oxygen}} = \frac{\text{atomic weight of silver}}{2 \times 16} = \frac{13.516}{1},$$

then

$$\text{atomic weight of silver} = 32 \times 13.516 = 432.52;$$

if the formula of silver oxide is Ag_pO_q, where p and q represent any small integers,

$$\frac{p \times \text{atomic weight of silver}}{q \times \text{atomic weight of oxygen}} = \frac{p \times \text{atomic weight of silver}}{q \times 16} = \frac{13.516}{1},$$

then

$$\text{the atomic weight of silver} = \frac{q}{p}\,16 \times 13.516 = 216.26\,\frac{q}{p}.$$

These possibilities are summarized in Table 3, which is similar to Table 2. However, it is immediately apparent that the range of possible atomic weights is much more restricted in Table 3.

Making the best possible use of his very tenuous criteria for the selection of the correct formula, Berzelius tentatively adopted the formula AgO_2, and the corresponding atomic weight of 432.52. In this choice he was mistaken, and it might appear that the range of possibilities was still so great that little positive progress had been made. However, Berzelius' careful experimental work had at last removed serious doubts about the accuracy of the primary data, and the residual uncertainties all arose in the interpretation applied to them. Thus, in the present case, it was at least possible to say that if the atomic weight of silver were *not* 432.52, then it must be some simple multiple or fraction of that figure. Even this broad definition of the possibilities was such a notable advance over the previous uncertainties that it was rapidly fruitful of new advances.

TABLE 3. Atomic weight of silver (relative to oxygen as 16) according to various formulas for silver oxide.

The combining ratio of silver to oxygen in silver oxide is known to be	The possible values for the atomic weight of silver, deduced from the following formulas, are			
	AgO	Ag_2O	AgO_2	Ag_pO_q
13.516:1	216.26	108.13	432.52	$216.26 \frac{q}{p}$

Petit and Dulong Link the Atomic Theory to the Theory of Heat. Perhaps the most significant development arising from Berzelius' 1818 publication was the work of two French investigators, Petit and Dulong, who announced the discovery of a most significant empirical generalization in a paper presented to the French Academy of Science on April 12, 1819. We have seen Berzelius' important dualistic theory growing out of the new interest in the recently discovered electrochemical phenomena; the next episode in our story occurred because of a continuing scientific interest in *thermal* phenomena, Dalton's response to which had already played a prominent role in shaping his atomic theory (see, for example, pages 224-226).

It has not been our intent to provide extensive documentation for this epilogic summary. However, Petit and Dulong's account of their discovery of a generalization that related thermal phenomena to the atomic theory, is at once so clear and so revealing that we can scarcely forego its consideration.

> *Investigations of Several Important Aspects of the Theory of Heat*
>
> Considerations grounded on the totality of the laws relating to the properties of chemical compounds now allow us to form ideas about the constitution of bodies that, although they are arbitrarily established at several points, cannot be regarded as vague and absolutely sterile speculations. We are persuaded that certain of the properties of matter would appear in simpler form, and could be expressed in more regular and less complicated laws, if one could relate them to the elements on which they are immediately dependent. We have tried to introduce the most probable

> results of the atomic theory [presumably Berzelius' figures] in the study of several of these properties that seem to be more intimately connected with the individual action of the particles of matter. The success that we have already attained makes us hope that this kind of reasoning will not only contribute to the ultimate progress of physics, but that also the atomic theory will in its turn receive from it a new degree of probability, and that it will there find sure criteria for the distinction of the truth among hypotheses that appear to be equally probable [i.e., for the selection of the correct formulas and atomic weights].

Petit and Dulong now focus attention on the thermal properties, notably the specific heats, of various kinds of matter, to the study of which they had already made considerable contributions. The specific heat of a substance is here defined as the ratio between the quantity of heat required to produce a unit temperature change in a certain weight of the substance, and the quantity of heat required to produce the same temperature change in the same weight of water. Thus, a statement that the specific heat of some substance is 0.1 signifies that, for example, the quantity of heat required to warm one pound of this substance by 1°F would be only one-tenth as great as that required to warm one pound of water by 1°F. Petit and Dulong point out the inadequacies of the then current theories dealing with the specific heats of bodies, and further suggest that the available methods for the experimental determination of specific heats also leave much to be desired. After describing an improved method that they had devised for these measurements, they continue:

> We now present, in a single table, the specific heats of several elements, restricting ourselves however to those determinations about which we no longer entertain doubt [Table 4].
>
> To bring out the law that we propose to make known we have, in the preceding table, joined to the specific heats of the different elements the relative weights of their atoms. As is known, these weights are deduced from the relations that one observes between the weights of the elements that combine with each other. The care that has been exercised for several years in the determination of the [weight] proportions in the majority of chemical compounds cannot leave more than slight uncertainties in the results of which we have made use. However, since there exists no rigorous method for the discovery of the real number of atoms of each species that enters into the compound [that is, there is no method of establishing the formula of the compound], one understands that there is always some arbitrariness in the establishment of the relative weights of the elementary molecules [atoms]. Nevertheless, the indeterminacy that so results does not extend to more than two or three numbers that are very simply related to one another [see page 302]. The reasons that have guided us in our choice will be sufficiently explained by what

> follows. [Petit and Dulong simply chose the simplest fractions of Berzelius' figures that yielded results in accord with the generalization they sought.] For the moment we will say only that there is no figure on which we have settled that is not in accord with the best established chemical analogies.

The type of cross check implied by this statement is particularly clear and significant in the case of sulfur. The analogies between the chemical behavior of sulfur and oxygen — both as free elements and in their compounds with other elements — are striking. The prevalence of these similarities led quite naturally to the supposition that the compounds of sulfur and oxygen were analogous in general, and that they had analogous formulas in particular. Now in the case of water, Berzelius' use of Gay-Lussac's combining volume data led to the modern formula, H_2O. It was then not unnatural to accept for the formula of the corresponding compound of sulfur with hydrogen the expression H_2S. The use of this formula and the corresponding combining weights then leads to an atomic weight for sulfur of 32. This agrees well with the indication of the Petit and Dulong "law,"

TABLE 4. Petit and Dulong's table of specific heats, atomic weights (converted to O = 16), and the products of these two numbers.

[Element]	Specific heat (relative to water)	Relative weights of the atoms	Products of the weight of each atom multiplied by the corresponding specific heat	Petit and Dulong's "relative weights of the atoms" as derived from Berzelius' 1818 figures *
Bismuth	0.0288	212.8	6.128	283.8 × ¾
Lead	.0293	207.2	6.070	414.2 × ½
Gold	.0298	198.9	5.926	397.8 × ½
Platinum	.0314	178.6	5.984	178.4 × 1
Tin	.0514	117.6	6.046	253.3 × ½
Silver	.0557	108.0	6.014	432.5 × ¼
Zinc	.0927	64.5	5.978	129.0 × ½
Tellurium	.0912	64.5	5.880	129.0 × ½
Copper	.0949	63.31	6.008	126.62 × ½
Nickel	.1035	59.0	6.110	118.3 × ½
Iron	.1100	54.27	5.970	108.55 × ½
Cobalt	.1498	39.36	5.896	118.3 × ⅓
Sulfur	.1880	32.19	6.048	32.19 × 1

* This column does not appear in the table given by Petit and Dulong. It has been added to exhibit their (unacknowledged) indebtedness to Berzelius. The figures to the left in this column represent Berzelius' atomic weights which, when they are multiplied by the simple fractions on the right of the column, yield products that are in all cases close to, if not identical with, Petit and Dulong's relative atomic weights, as they are given in the third column of the table.

and presumably this "law" was originally framed with some attention to the inferences drawn from just such analogies.

> By means of the data contained in the preceding table it is now possible to make a simple calculation of the relations that exist between the [heat] capacities of the different kinds of atoms. Observe, in this connection, that to pass from the experimentally observed specific heats to the specific heats of the particles themselves, it will suffice to divide the former by the numbers of particles contained in equal weights of the substances to be compared. Now it is clear that in equal weights of matter the numbers of particles are inversely proportional to the densities [weights] of the atoms. Thus the desired results will be secured by multiplying each of the experimentally determined specific heats by the weight of the corresponding atom. These products are gathered together in the fourth column of the table.

This reasoning is only superficially complicated. The measured specific heats refer to the relative quantities of heat required by *equal weights* of the different substances. What Petit and Dulong sought were the quantities of heat required by *equal numbers of atoms* of the different substances. They remark that the heavier the atoms of an element, the smaller will be the number of its atoms contained in a certain weight of the element. Thus, for example, if the atoms of element *A* are ten times as heavy as those of element *B*, it is plain that in *equal weights* of *A* and *B* there will be only one-tenth as many atoms of *A* as of *B*. *Equal numbers of atoms* of the two species would be present only if we had ten times as great a weight of *A* as of *B*. In general, then, to study equal numbers of atoms of the different elements we must consider weights of these elements that are directly proportional to the relative weights of their atoms — that is, to their so-called atomic weights. Consequently, to convert the heat requirements of *equal weights* of the different elements (i.e., the specific heats) to the heat requirements of *equal numbers of atoms* of the different elements, we have only to multiply the specific heats by the atomic weights. This is what Petit and Dulong did in arriving at the figures given in the fourth column of their table.

> Mere inspection of these numbers reveals a relation so remarkable in its simplicity that in it one immediately recognizes the existence of a physical law capable of being generalized and extended to all the elements. In fact, the products in question, which express the [heat] capacities of different kinds of atoms, are so nearly equal to each other that it is impossible that the very slight observed differences are not attributable to the inevitable errors, whether these errors be in the measurement of the specific heats or in the chemical analyses. [This was an overly optimistic appraisal. The "law" is, in fact, far from exact.] This

> is especially probable when it is observed that in certain cases the errors arising from these two sources may be in the same direction, so that they may be multiplied in the results. The number and diversity of the substances with which we have worked exclude the possibility of considering as simply fortuitous the relation that we have just indicated, and justify the deduction of the following law:
>
> The atoms of all the elements have exactly the same capacity for heat.
>
> Recalling what we have said previously about the type of uncertainty that still attaches to the determination of the relative weights of atoms, it is easily seen that the law that we have just established might be changed if one were to adopt an assumption about the weights of the atoms that is different from the one we have used. In all cases, however, that law will embody the expression of a simple relation between the weights and the specific heats of the elementary atoms. Having to choose between equally probable hypotheses, we have felt obliged to decide in favor of the one that established the simplest relation between the elements that we compared.
>
> Whatever may be the final opinion adopted with regard to this relation, it can henceforth serve as a control of the results of chemical analysis. In certain cases it may even offer the most exact method of arriving at information about the proportions of certain combinations. And if, in the continuation of our work, no fact arises to impair the probability of the opinion that we now hold, this law will also offer the advantage of establishing in a certain and uniform manner, the relative weights of the atoms of all the elements that can be subjected to direct examination.

Petit and Dulong now go on to consider the degree to which the data of other investigators agree with their law, and conclude with an exposition of the importance of their work for the general theory of heat. For our purposes, however, their most important contribution is alluded to in the last paragraph above, where it is suggested that the new "law" provides an important method of determining molecular formulas and atomic weights. The great significance of this new possibility will be better appreciated after a closer examination of the key relation that lay at the bottom of all the earlier work on the atomic weights.

The Interrelation of Atomic Weights, Molecular Formulas, and Combining Weights. The combining weights (or proportions) of the elements in chemical compounds are determinable by direct measurements with the analytic balance. These *combining weights* are so related to two other items — the *atomic weights* of the elements and the *molecular formulas* of their compounds — that if any two of these three factors are known the third can be computed. We may visualize this relation in the form of an equilateral triangle: if the positions of any two of the apexes of the triangle are known, the third can be located.

Now of the three interrelated factors only one — the combining weights — could be measured directly. Yet before use could be made of this crucial relation one of the other two factors had to be determined. The combining weights having been established, the molecular formulas could be calculated if the atomic weights were known; or the atomic weights could be calculated if the molecular formulas were known. But neither the atomic weights nor the molecular formulas *were* known, nor could they be determined by direct experimentation. Under these conditions there appeared to be no alternative to a resort to guesswork, and Dalton, Avogadro, Berzelius, and their contemporaries were constrained to adopt such a course. In general, they sought to guess at the molecular formulas by the use of a discordant variety of arbitrary working rules, the observed combining volumes of gases, the analogies between the chemical behaviors of the different elements, and so on. With these formulas and the known combining weights they then calculated the corresponding atomic weights. However, although the few formulas that could be deduced from the combining volumes of gases were largely correct, the greater number of molecular formulas were very poorly established, and largely rested on extremely conjectural foundations. There thus remained the gravest doubt about the validity of the calculated atomic weights, as may be seen from an examination of the various possible values for the atomic weight of silver given on page 302.

Petit and Dulong's new generalization sharply reduced the conjectural element in the appraisal of atomic weights. Even though their "law" was neither as general as they had hoped nor as accurate as they had supposed (its fallibility was very properly recognized by Berzelius at an early date), this "'law" did at least provide *approximate* values of the atomic weights. Curiously enough, the availability of these quite crude values made possible a fruitful return to the "triangular" relation, and through it led to the derivation of *accurate* atomic weights that were more firmly rooted against the winds of speculation.

This new possibility is well illustrated in the case of silver. Reference to page 302 shows that the combining weights of the elements in silver oxide were well established. However, in the absence of sure criteria for the selection of the proper molecular formula, there was a series of possible values for the atomic weight of silver. Now let us take advantage of Petit and Dulong's "law" — that the product of the atomic weight and the specific heat is approximately constant. The average value of this "constant," deduced from their figures, was 6.0. For the specific heat of silver they cite the figure 0.0557. According to their "law," then, it should be true that

$$\text{Atomic weight of silver} \times \text{specific heat of silver} \doteq 6.0;$$
$$\text{Atomic weight of silver} \times 0.0557 \doteq 6.0;$$
$$\text{Atomic weight of silver} \doteq \frac{6.0}{0.0557} = 107.7.$$

This is not the exact value that Petit and Dulong had supposed it would be — both because of the serious experimental difficulties besetting the accurate determination of specific heats, and because of their "law's" inherent failings. But this *approximate* value is all we need!

Looking back to page 303 we see that of the various possible formulas for silver oxide only one, Ag_2O, leads to the deduction of an atomic weight of silver that is *anywhere in the vicinity* of the approximate value. Thus it appears that we are justified in settling on Ag_2O, rather than Berzelius' choice of AgO_2, as the most probable formula of silver oxide. *Now* we have both the combining weights and the molecular formula, so that we can solve for the third factor — the atomic weight of silver — by the routine method shown on page 302. It is plain that the approximate value of the atomic weight has played the limited but crucial role of providing a more reliable criterion for the selection of the proper molecular formula; and once this was established, the calculation of the atomic weight could be carried out by the standard methods used by Dalton, Berzelius, and others.

Petit and Dulong's "law" thus opened up an important avenue of approach to the determination of atomic weights and molecular formulas. It provided a vital complement to the suggestions furnished by the data on gas densities and combining volumes which, as they were used by Berzelius, could be applied only to the relatively few elements that were normally gaseous. The atomic weights of the vast majority of elements had previously been deduced with the aid of various arbitrary working rules, but these rules could now be discarded in favor of the more objective indications drawn from the "law" of Petit and Dulong. To the methods founded on this "law" and on the data on gas densities and combining volumes Berzelius joined two others, one based on the analogies in the chemical behavior of the elements (see page 305), the other based on analogies in the crystal structure of compounds. By judicious selections from among the various possibilities offered by these methods he had, by 1840, arrived at atomic weights and molecular formulas that are in most cases in excellent agreement with those we now accept as correct. But alas, by this time a flood tide of skepticism was already lapping around the foundations of the atomic theory, and Berzelius' fine work did not receive the attention it deserved.

Perplexing Results of Dumas' Vapor-Density Studies (1827). Many factors contributed to the outburst of a long-latent skepticism about the "reality" of the whole structure of matter postulated by the atomic theory. One in particular is worthy of our closer attention. Avogadro had suggested that the relative weights of the particles of the gaseous elements could be inferred from the corresponding relative gas densities. Until 1826 this method had had a very limited application, since only four of the then known elements were gaseous under normal conditions of temperature and pressure. The Petit and Dulong "law" could not be efficiently applied to these gaseous elements and, consequently, there had been no satisfactory check on the consistency of the atomic weights derived from the Petit and Dulong "law" and those secured from gas-density data. But in 1827 enough data became available to permit a limited comparison of the atomic weights indicated by these two methods. The results then obtained, far from showing the eagerly anticipated concordance, manifested an apparent incompatability that shook the atomic theory to its very roots. The involuntary engineer of this deplorable denouement was the French chemist J. B. A. Dumas, then at the threshold of a brilliant career.

Dumas began by being very favorably impressed by the possibilities of the gas-density method, and he proposed to extend its usefulness. For this purpose he devised a simple yet elegant procedure (which is still used today) for the determination of gas densities at such high temperatures that a considerably increased number of elements could be studied in the gaseous state. This method he applied to a variety of substances. Let us consider the surprising results he obtained for the elements mercury, sulfur, phosphorous, and arsenic.

The density of mercury vapor was found to be just about 100 times that of hydrogen at the same temperature and pressure. The application of the "equal volumes–equal numbers" idea to this datum leads to the conclusion that the particles of mercury are 100 times as heavy as those of hydrogen. But the Petit and Dulong "law" and the combining-weight data indicate an atomic weight of mercury in the vicinity of 200.

To Berzelius the "particles" in a gaseous element were atoms. (It will be recalled that his dualistic theory had induced him to neglect the possibility of polyatomic molecules of the elements.) Therefore the gas-density data would indicate that the mercury atom was 100 times as heavy as the hydrogen atom, a serious contradiction of the value of 200 obtained from the other sources. This discrepancy, together with others discussed below, impelled Berzelius to break off the struggle. He simply concluded that the "equal volumes–equal numbers" idea applied *only* to the elements that were gaseous at room temperature, and he denied the validity of its application to the less volatile elements studied by Dumas. Such an artificial distinction was repugnant to

Berzelius' contemporaries, as it probably was to him, but he saw no more palatable alternative.

Dumas was more willing than Berzelius to consider the possibility of polyatomic molecules of the elements, but whether one says that the gaseous particles of mercury (symbol, Hg) and hydrogen are Hg and H, or Hg_2 and H_2, or Hg_4 and H_4, or Hg_n and H_n, it is plain that if there are equal numbers of these particles in equal volumes of the respective elements, there must also be equal numbers of the corresponding atoms. Thus the problem is still unresolved — the total weight of a number of atoms of mercury is only 100 times the weight of an equal number of atoms of hydrogen. The indicated atomic weight of mercury is then 100, only half that suggested by the Petit and Dulong "law."

A discrepancy of the same sort, but in the opposite direction, arose in the case of sulfur. The Petit and Dulong "law" indicated that the atomic weight of sulfur was 32, which agreed with the value obtained from the combining weights when the formulas of sulfur compounds were so assigned as to bring out the chemical analogies between sulfur and oxygen. But the measured density of sulfur vapor was 96 times that of hydrogen. Acceptance of the "equal volumes–equal numbers" notion then implied that the sulfur particles were 96 times as heavy as those of hydrogen. Whether to these particles one assigned the formulas S and H, or S_2 and H_2, or S_n and H_n, it was all too clear that if the numbers of these particles were equal, the numbers of the corresponding atoms would also be equal. Hence the atomic weight of sulfur was indicated as 96, three times the then accepted value derived from other sources. The vapor-density studies of phosphorus and arsenic led to similar contradictions, since these densities proved to be twice as great as had been expected. The cumulative inconsistency is impressive, and it is little wonder that Berzelius adopted the easy way out — completely rejecting the application of the "equal volumes–equal numbers" idea to these cases.

There is, to be sure, one ingenious way in which all of these contradictions can be resolved without discarding Avogadro's attractive idea. This rationalization was proposed in 1833 by Gaudin, another French investigator; and, to some extent, it was apprehended by Dumas himself. Let us suppose that there *are* equal numbers of particles in equal volumes of the vapors of the different elements; but let us now further assume that these particles do *not* in every case contain the same number of atoms.

Turning to a concrete example, let us imagine that the "particles" of mercury and of hydrogen are Hg and H_2, respectively. Now, if there are *n* particles in unit volume of each of these gases, we are actually dealing with n atoms of mercury and $2n$ atoms of hydrogen. If we assign to hydrogen and mercury the accepted relative atomic weights of 1 and 200, then the following proportion will prevail:

$$\frac{\text{Weight of mercury in unit volume of mercury vapor}}{\text{Weight of hydrogen in unit volume of hydrogen gas}} = \frac{n \times 200}{2n \times 1}.$$

But, since the density of a gas is synonomous with the weight of unit volume of that gas, we may also write:

$$\frac{\text{Density of mercury vapor}}{\text{Density of hydrogen gas}} = \frac{n \times 200}{2n \times 1} = 100,$$

and the predicted ratio of the densities of mercury and hydrogen is then precisely that found in practice.

We may, in similar fashion, assign to the sulfur "particle" the formula S_6. Then, if the number n of these particles in unit volume of sulfur vapor is the same as the number of H_2 particles in unit volume of hydrogen gas, we will have present $6n$ atoms of sulfur as against $2n$ atoms of hydrogen. If, now, we assign to the atomic weight of sulfur its most probable value of 32, we come to the following proportion:

$$\frac{\text{Density of sulfur vapor}}{\text{Density of hydrogen gas}} = \frac{6n \times 32}{2n \times 1} = 96,$$

and the predicted ratio of the gaseous densities is then in full agreement with that found by the direct measurements. The extension of this type of reasoning to phosphorus and arsenic reveals that if the "particles" of these substances are polyatomic molecules with formulas P_4 and As_4, respectively, then there is again complete consistency between the atomic weights derived from the Petit and Dulong "law" and the combining-weight data on the one hand, and the relative gas densities and Avogadro's hypothesis on the other.

This apparently attractive reconciliation could be achieved only at a price that many found inordinately high. Not only would it have to be maintained that there are polyatomic molecules of the elements, but it would now have to be further conceded that the polyatomic molecules of the different elements contain different numbers of the respective atoms. The source of the stability of *any* polyatomic molecule was unknown — the whole conception was repugnant to the influential dualistic theory — and to this difficulty would now be added the inability to explain why the molecules of different elements contain different numbers of their respective atoms. It would be necessary to hypothesize not just one improbable, but a considerable variety of improbables; and the diversity of these formulas for the incongruous polyatomic molecules seemed a flagrant violation of the scientist's almost instinctive faith in the simplicity of nature.

An equally serious shortcoming was that, if the variation of the number of atoms per molecule of the gaseous elements were accepted, the usefulness of Avogadro's original proposal appears to be very seriously impaired. The postulated equality of the number of "particles" present in equal volumes of the different gaseous elements could *not* now be assumed to signify the equality of the number of *atoms* of these elements, so that measurements of the relative gas densities of the elements could no longer be construed as the basis of a distinct evaluation of the relative atomic weights. For such an evaluation it would be necessary to know the relative numbers of atoms present, and this in turn depended on a knowledge of the numbers of atoms present in the gaseous "particle" of each element. It will be recalled that one of the major weaknesses of Avogadro's original proposal was his inability to suggest any method of estimating the numbers of atoms in the molecules of the gaseous elements, and this deficiency now assumed major significance. One could infer these numbers *if* atomic weights drawn from other sources were used in the interpretation of the measured gas densities. However, the very fact that these other atomic-weight data were required suggested that gas-density values could not provide the basis for a significant *independent* method of determining atomic weights. One might adopt Berzelius' view, denying that the "equal volumes–equal numbers" notion applied to elementary gases except in special cases. Or one might, apparently, vitiate the significance of this notion by adopting the further conjecture that the "particles" involved contained different numbers of atoms. But in either case the conclusions appeared to involve the destruction of much of the value of Avogadro's proposals.

Confusion and Dawning Clarification of the Atomic Theory in the Period 1827–1857. Hastening toward our conclusion, let us once again examine three important weak points in Avogadro's scheme, with a consideration of which this epilogue began. These points provide some basis for a very rapid survey of the events that most affected the atomic theory during the period between the setback it experienced through Dumas' work in 1827 and its triumphant revival by Cannizzaro in 1858.

The first of these points was the conjectural character of the atomic theory in general, and of Avogadro's proposals in particular. This unavoidable characteristic caused a certain amount of skepticism in the earliest days of the atomic theory, and the doubts waxed stronger after Dumas' vapor-density work. Skepticism probably reached its peak a little after 1840, about the time of the accelerated decline of Berzelius' dualistic theory. Even as the bankruptcy of a major concern shakes the whole of the business world, the decline of Berzelius' towering conceptual scheme, brought about by some other experimental work of Dumas', inferentially involved in its ruin the atomic theory, of which Berzelius had been one of the foremost proponents.

The atomic theory was far from dead, but for a time it appeared quite infirm. Yet scarcely one of the years between 1827 and 1858 passed without the development of some more or less compelling evidence of the "correctness" of the corpuscular view of matter. A host of newly discovered properties and phenomena relating to the manifold compounds of carbon were very successfully construed in terms of the atomic theory. In particular, there were certain striking regularities in the vapor densities of the many gaseous compounds of carbon; and, in the years between 1843 and 1856, Gerhardt and Laurent repeatedly emphasized how easily these regularities could be understood in terms of simple relations based on the "equal volumes–equal numbers" idea. The originally limited scope of application of Avogadro's proposal was thus vastly extended, and the value and significance of this proposal were correspondingly increased. Then, too, by 1857 an impressive success was finally achieved in the long search for a method of deducing or deriving the properties of gases from the laws of mechanics. Among other things, the new "kinetic theory of gases" strongly indicated that gases consisted of minute particles of matter, widely separated from each other and present in equal numbers in equal volumes of elementary and compound gases. Perhaps even more striking was the intimation that some of these particles were polyatomic molecules of the elements, just as postulated by Avogadro.

Still another factor, less immediate in its action though probably of great importance, was the scientific world's increasing awareness of the profound fruitfulness and frequent "correctness" of a wide variety of other speculative schemes. By 1857 these new sentiments may have reduced the antipathy toward the conjectural character of the Dalton-Avogadro conceptual scheme, particularly since the plausibility of this scheme had been much increased by all the developments noted above, and many others as well. Though its conjectural character was still a distinct liability, it was probably no longer a major source of resistance to the free acceptance of this surpassingly useful conceptual scheme.

A second weak point to which attention has been directed was the lack of any adequate explanation of the stability of the polyatomic molecules of the elements postulated by Avogadro. With the decline and fall of Berzelius' dualistic theory the antipathy to such bodies was somewhat reduced; at least their postulation was no longer a flat contradiction of an influential contemporary theory. Moreover, there were a number of independent indications that such polyatomic molecules did "exist." We have already commented on the important inference drawn from the kinetic theory of gases, and the existence of such bodies was also suggested by the observed variety of the physical forms of some of the elements, by the heats and speeds of various chemical reactions, and by a number of other phenomena with which we need not now concern ourselves. Thus, although by 1857 there had been practically no positive progress toward a satisfactory *explanation* of the existence of these polyatomic molecules, there was at least an accumulation of bits of evidence that they "*did exist.*" Presumably the postulation of these particles was still not an entirely palatable proposal, but it was probably no longer a major item of reproach against the Dalton-Avogadro conceptual scheme.

We have also considered a third weak point — the lack of a well-defined method of determining the numbers of atoms in the hypothetical molecules of the elements. By 1857 this had become a particularly vexing shortcoming, in that it deprived Avogadro's proposals of much of their intrinsic usefulness as the basis for an independent evaluation of the atomic weights of the elements. After Dumas' work the measured values of the relative gaseous densities of the elements could no longer be regarded as a direct and certain indication of the relative atomic weights of those elements. In the preceding paragraphs we have seen how two other major sources of difficulty in Avogadro's conceptual scheme had, by 1857, become somewhat less pressing. However, this third weakness, connected not with the abstract plausibility but with the concrete usefulness of Avogadro's scheme, had, if anything, become a more serious problem than before. Yet the need for a trustworthy series of atomic weights and molecular formulas had never been more acute. It was just this problem on which the Italian chemist Stanislao Cannizzaro (1826–1910) threw great light. In 1858 he both minimized its importance and indicated its solution, in connection with a most penetrating analysis of the Dalton-Avogadro conceptual scheme.

The Final Act — Cannizzaro Revives and Emphasizes Avogadro's Concept. It is from the appearance of Cannizzaro's *Sketch of a Course of Chemical Philosophy* that we can date the beginning of the final triumph of the atomic-molecular theory. Cannizzaro's deceptively simple proposal was founded on nothing more novel than a *full* return to Avogadro's original position. We are to assume that the numbers of particles in equal volumes of all elementary *and compound* gases are equal. We must not, however, confuse these particles (molecules) with the atoms of which they are composed. Neither must we so far give way to our longing to find simplicity in nature as to suppose that the molecules of all the gaseous elements contain equal numbers of their respective atoms. This being granted, it is plain that we cannot expect to find equal numbers of *atoms* in equal volumes of the various elementary gases. Consequently the direct comparison of the relative densities of the gaseous elements leads *not* to the relative atomic weights, but only to the relative molecular weights of those elements. However, while depreciating this superficially attractive possibility, Cannizzaro suggested a much more promising approach — the comparison of the densities of the gaseous *compounds* of the elements.

Let us begin with the case of hydrogen. We can measure the densities (i.e., the weights of unit volumes) of a wide variety of gaseous compounds of hydrogen. By analysis we can determine what proportion of the weight of each of these compounds is due to the hydrogen it contains. If, now, we multiply the measured density of each compound by the measured fraction of its weight that represents its hydrogen content, then we find the weights of hydrogen that are present in equal (unit) volumes of the gaseous compounds of this element. Very significantly, *all these quantities prove to be integral multiples of one minimum value.*

How is this relation to be understood? First we must remember that we are dealing with unit volumes of each of the different gases, hence with equal numbers of the respective molecules. Let us call this (unknown) number n. Let us now assume — and this is still akin to a rule of simplicity — that the molecule of at least one of these gaseous compounds of hydrogen contains just one hydrogen atom. The total weight of hydrogen present in unit volume of that compound should then be given by the expression $n \times$ weight of an atom of hydrogen. An equal weight of hydrogen will be found in the unit volume of any other gas whose molecule contains but one hydrogen atom. Moreover, this should be the minimum weight of hydrogen ever found under these conditions, since we cannot readily conceive of a hydrogen compound whose molecule contains less than one atom of hydrogen. Symbolizing this minimum weight of hydrogen by M_H we may then write:

$$M_H = n \times \text{weight of an atom of hydrogen.}$$

Now if among the compounds studied we had one whose molecule contained two hydrogen atoms, then the weight of the hydrogen present in unit volume of this compound should be $2 \times n \times$ weight of an atom of hydrogen, or $2M_H$. Similarly, unit volume of a compound whose molecule contains three hydrogen atoms will contain a weight of hydrogen expressed by $3 \times n \times$ weight of an atom of hydrogen, or $3M_H$, and so on. Therefore we have every reason to anticipate what we actually find: that all the weights of hydrogen are integral multiples of a certain minimum weight, which we have called M_H. Incidentally, since the weight of unit volume of pure hydrogen is equal to $2M_H$, we have some justification for concluding that the gaseous "particle" of pure hydrogen is an H_2 molecule—i.e., the molecule contains two atoms.

Applying the same methods to the study of the gaseous compounds of oxygen, we find, as expected, that the weights of oxygen contained in unit volumes of these compounds are all integral multiples of some minimum value. This minimum weight of oxygen, which we shall designate as M_O, must represent the weight of oxygen present in n molecules of a compound that contains just one atom of oxygen in each of its molecules. Consequently we may write:

$$M_O = n \times \text{weight of an atom of oxygen.}$$

The experimentally determined value of M_O is just 16 times that of the analogous minimum weight of hydrogen, M_H. Now we are in a position to make a very significant calculation. From the two foregoing equations we may derive the following expression:

$$\frac{n \times \text{weight of an atom of oxygen}}{n \times \text{weight of an atom of hydrogen}} = \frac{M_O}{M_H}$$

or

$$\frac{\text{weight of an atom of oxygen}}{\text{weight of an atom of hydrogen}} = \frac{M_O}{M_H}.$$

But since experiment has shown that $M_O = 16M_H$ we may conclude that

$$\frac{\text{weight of an atom of oxygen}}{\text{weight of an atom of hydrogen}} = \frac{M_O}{M_H} = \frac{16M_H}{M_H} = \frac{16}{1}$$

whence it is plain that the atomic weight of oxygen, relative to the hydrogen atom taken as 1, must be 16. Finally, since the weight of unit volume of pure oxygen is $2M_O$, it appears that each molecule of gaseous oxygen must contain two oxygen atoms, and should be represented by the formula O_2.

Turning now to the element carbon, we encounter a material so very involatile (below 3000°C its vapor pressure is exceedingly small) that direct measurement of its density in the gaseous state was essentially impossible. However, carbon forms a large number of volatile *compounds*, so that we can easily determine its atomic weight by the method proposed by Cannizzaro. An experimental study reveals that the weights of carbon present in unit volumes of its gaseous compounds are always integral multiples of a minimum value, which is 12 times the corresponding minimum figure for hydrogen. Hence the atomic weight of carbon is established as 12.

Applying the new method to the many gaseous compounds of sulfur, we secure the expected series of weights that represent integral multiples of a minimum weight of sulfur M_S, and M_S is 32 times the value of M_H, so that the indicated atomic weight of sulfur is 32. This is in excellent agreement with the figure derived from the Petit and Dulong "law" and with the value deduced from the combining weights in sulfur compounds when the formulas of these compounds are assigned so as to bring out the chemical analogy between sulfur and oxygen. Incidentally, under the conditions prevailing in Dumas' vapor-density studies the weight of unit volume of pure sulfur vapor approximates $6M_S$, suggesting S_6 as the formula of the sulfur molecule.

The study of mercury by vapor-density methods alone is somewhat handicapped by the small number of readily volatile compounds of this element. When we have completed the examination of this limited series of compounds we cannot be too confident that we have at least one substance that contains but one atom of mercury in each of its molecules. For what it may be worth, however, M_{Hg}, the minimum weight of mercury of which all the others are integral multiples, proves to be $200M_H$. The value of 200 so indicated for the atomic weight of mercury then agrees with that predicted by the Petit and Dulong "law." The weight of unit volume of pure mercury vapor is just equal to M_{Hg}, so that for this element the gaseous "molecule" is identical with the chemical atom.

Continuing this type of examination of the compounds of all the common elements, Cannizzaro emphasizes that in every case to which both the Petit and Dulong "law" and his own treatment of the vapor-density data can be applied, *the two indications of the atomic weight are concordant.* So general and impressive is this self-consistency that it seems almost impossible to avoid the conclusion that it represents the inevitable agreement of the results of two equally valid methods for the determination of atomic weights. As already remarked, these two methods display a favorable complementarity. The atomic weights of the light nonmetallic elements — which form many volatile compounds — are most readily deduced from gas-density measurements; and the atomic weights of the heavy metallic elements — which do *not* form many volatile compounds — are indicated by the Petit and Dulong "law." Thus, by the combined action of these two methods, we can at long last derive a rational and coherent series of the atomic weights of the elements.

This development had many vital and widespread implications, but with its completion we may bring our present story to a close. We have seen how in 1808 Dalton called attention to "the importance and advantage of ascertaining *the relative weights of the ultimate particles of both* *simple and compound bodies.*" In 1858 Cannizzaro finally achieved the goal that had been indicated just half a century earlier. In the almost 50 years that had elapsed since the first enunciation of the Dalton-Avogadro conceptual scheme practically nothing essential in that scheme had been changed. However, during the intervening period of intense scientific activitv there had been (1) a dissipation of some of the original objections to this scheme; (2) an accumulation of much indirect evidence in favor of it; (3) the collection of many data of critical importance to it; and (4) the development of an acute need for it. Its revival by Cannizzaro, in his supremely lucid, powerful, and convincing statement, rapidly swept this scheme to the prominent position among the concepts of science that it has continued to occupy with honor until the present day.

CHRONOLOGY OF THE MAIN EVENTS OF OUR STORY

1774–1789	Period of the "chemical revolution" brought about by the introduction of Lavoisier's oxygen theory of combustion
1789	Wm. Higgins' proposal of an atomic theory
1792–1802	Richter's work on the law of equivalent proportions
1797–1808	Proust's work on law of definite proportions; challenged by Berthollet in 1801
1800–1803	Dalton achieves a clear formulation of his atomic theory
1803	Dalton's first public intimation of his atomic theory. Statement to Thomson in the following year
1807	First printed account of the atomic theory appears in Thomson's book
1808	Publication of the first part of Dalton's *New System of Chemical Philosophy*
1808	Thomson and Wollaston support the law of multiple proportions
1809	Publication of Gay-Lussac's work on the law of combining volumes
1810	Publication of second part of Dalton's *New System*, containing criticism of Gay-Lussac's work
1811	Avogadro's publication — the postulation of polyatomic molecules of the elements
1811	Berzelius presents a brief account of his dualistic theory
1818	Berzelius publishes a collection of a large number of combining and atomic weights

1819	Publication of Petit and Dulong "law"
1827	Dumas' vapor density work
1827–1857	Period of intense scientific activity and a rather confused response to the atomic theory
1858	Publication of Cannizzaro's *Sketch of a Course in Chemical Philosophy*

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