areas of society but are remembered primarily for their scientific contributions. Many parallels appeared, which might be expected for two well-educated and intelligent men of that time. Differences were due largely to the chance of birth: Lavoisier wealthy and "in" socially, Priestley poor and outside the establishment. In summary:

- Both names became household words.
- * Both men were visionaries, making proposals that were ahead of their time in the areas of education, economics, government, human rights, and religion.
- * Both were scientific revolutionaries, earning recognition as outstanding scientists and making lasting contributions to science.
- * Both men were destroyed by political revolution but for opposite reasons: Priestley because he supported it, and Lavoisier because he was seen as a representative of the system against which it was directed.

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LAVOISIER AND THE CONSERVATION OF WEIGHT PRINCIPLE

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It is generally agreed today that when Antoine Laurent Lavoisier overthrew the phlogiston conception of combustion, he achieved a revolution in chemistry. In its simplest outline the story goes like this. In the phlogistic view that widely prevailed when Lavoisier began his chemical work in the 1760's, sub-

stances owed their combustibility to the presence of phlogiston in their make-up. When the body was actually burned, the phlogiston departed, leaving behind the other components - the acid in the cases of sulfur and phosphorus, and the calx in the case of metals. In this view both combustion and calcination were decomposition processes. In this regard, the phlogistic view was an 18th century sophisticated version of a centuries-old tradition of fire analysis, that the application of great heat reduced any body to its simpler components, if not necessarily to its true elements. Thus, in the cases illustrated, the acid was simpler than the sulfur and the calx simpler than the metal.

Lavoisier was able to force the inversion of this compositional relationship by keeping a balance-sheet account of the weights of all the participants in the reactions. For example, when he heated a weighed quantity of mercury in a closed container, he was able to show that the weight gained by the metal in becoming a calx was equal to the weight lost by the air in which the reaction took place. Lavoisier carried out similarly monitored experiments on the combustion of sulfur and phosphorus and again was able to account for the weights of all the participating materials. From these kinds of experiments he was able successfully to argue that combustion was a process whereby something in the air (later named oxygen) combined with the combustible, rather than something leaving it. In Lavoisier's view, appropriately named the "anti-phlogistic chemistry," a metal was simpler than its calx, and sulfur and phosphorus were simpler than their acids. Until Lavoisier made weight a primary criterion for the recording of chemical change, the phlogistic view had been a useful way of organizing a large number of important chemical relationships in a qualitative way. But Lavoisier's persistent application of balance-sheet accounting made the older view untenable, and phlogiston rather quickly disappeared from the chemical scene.

Lavoisier was very conscious of his method in these events and stated the principle quite explicitly in his famous *Traité Élémentaire de Chimie* of 1789, whose bicentennial we are celebrating this year (1):

We may 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 ...

With weight as his measure of the "quantity of matter," his persistent and imaginative application established the conservation of weight as the standard principle in chemical investigations, for which he has very properly received full credit.

I have no intention either of challenging that judgment or of further illustrating Lavoisier's systematic use of that principle. Rather, I wish to address the question of why the conservation of weight had not been more vigorously used in chemistry before Lavoisier's time, for the idea of conservation is as old as Western philosophy. As early as the 5th century B.C. Anaxagoras laid it out that, "nothing comes into being or is

destroyed; but all is an aggregation or secretion of pre-existing things; so that all becoming might more correctly be called becoming mixed, and all corruptions, becoming separate."

Other examples from antiquity are readily found in the writings of Democritus, Lucretius, and any number of other philosophers. Marcelin Berthelot, the great pioneer of synthetic organic chemistry and historian of early chemistry, pointed out that "even the alchemists never did pretend to create gold or metals, but only to transmute the fundamental and pre-existing metal."

Closer to Lavoisier's own time, Francis Bacon offered a more operational version of this principle in the early 17th century, clothing it metaphorically in the language of the bookkeeper (2):

Men should frequently call upon nature to render her account; that is, when they promise that a body which was before manifest to the sense has escaped and disappeared, they should not admit or liquidate the account before it has been shown to them where the body has gone to, and into what it has been received.

There are two major reasons why the chemical application of this principle was so long delayed. The first and more immediately significant was the general ignorance of the existence of gases as chemical agents. The other was the more fundamental question of how the quantity of matter is to be measured. The two problems are closely linked, but we can treat them most easily by dealing first with the problem of "airs," and then seeing how the philosophical problem permeated the practical one without being directly addressed.

Pneumatic chemistry hardly existed when Lavoisier began his work, and from the beginning his chemical interests were focused on what was just then beginning to be the "hot topic" of the fixing and liberation of "air", as all gases were then called. Without a knowledge of the role of gases in chemical change, many familiar reactions defied a meaningful application of the principle of conservation. Descriptions of some early 18th century experiments will illustrate the difficulties of applying the conservation principle when unaware of the role of gases.

Wilhelm Homberg, the most vigorous experimental chemist of the Paris Academy in the late 17th century, was curious to know how much "solid acid salt" was in the acid solutions available at that time. Such solutions were prepared by heating an appropriate salt and collecting the "spirit of salt" in water. Thus the heating of marine salt (NaCl) with a vitriol, or more commonly with a clay, yielded the "spirit of marine salt" (HCl) which was captured in an aqueous solution. Homberg, in order to determine the "quantity of solid acid salt" contained in the solution, carried out a very simple experiment based implicitly on the concept of conservation of weight. He added a solution of spirit of marine salt to a weighed quantity of dry alkali until the cessation of effervescence indicated the alkali to be satu-



Stephen Hales

rated. The resulting neutral salt was then dried and weighed. Since all the water had been driven off, Homberg reasonably assumed that the weight of the neutral salt was equal to the sum of the weights of the alkali and the solid acid salt whose quantity he sought (3):

alkali + spirit of acid = neutral salt + water
$$(K_2CO_3)$$
 (HCl + water) (KCl) (H_2O)

By the end of the 17th century, "air" as one of the traditional Aristotelian elements had virtually dropped out of the chemists' considerations, though great progress had been made in characterizing its physical properties. Hence, Homberg was totally unaware of the loss of gaseous carbon dioxide in his reaction, so his results were meaningless. As Joseph Black pointed out a half century later, Homberg's "estimate was not accurate; because the alkali loses weight, as well as gains it" (4).

The irony of this experiment is that Homberg was staring right at the escaping gas all the time he was neutralizing the alkali. The effervescence that he monitored to determine the saturation point of the alkali was seen not as liberation of air, but as evidence of the "intestine motion" of the particles of acid and alkali in their vigorous strife of mutual destruction. Although vegetable indicators had been used by Robert Boyle before this time, they did not come into common practice until about the middle of the 18th century.

Stephen Hales first clearly established that "air" had to be taken into chemical account and, in doing so, implicitly utilized the conservation of weight principle as part of his argument. In his *Vegetable Staticks*, published in 1727, Hales reported at length on a series of experiments in which he

strongly heated a wide variety of substances from which he collected various quantities of air in an apparatus devised for the purpose. The loss in weight of the original body, which he attributed to the air emitted, was sometimes as much as half the weight of the original solid body. After finding air produced from such a wide variety of materials from all the kingdoms of nature, and often in such large quantities, he felt justified in summarizing his conclusions as follows (5):

[M]ay we not with good reason adopt this now fixt, now volatile *Proteus* among the chymical principles ... notwithstanding it has hitherto been overlooked and rejected by Chymists ...?

In spite of Hales' abundant evidence of the presence of air in a wide variety of substances, he saw it all as simply "air" with no chemical features to distinguish one from another. Hales, a great admirer of Isaac Newton and Robert Boyle, followed them in their view that air was simply air, that any differences that might be noticed in their properties were attributable to various impurities physically present. Nor was the chemical community much impressed by Hales' evidence, for air continued to be "overlooked and rejected by Chymists" (6).

Before pneumatic chemistry could be said to exist, some distinctions between "airs" had to be made. This was first accomplished by Joseph Black shortly after the middle of the century. In his study on magnesia alba, a naturally occurring hydrated magnesium carbonate, Black noted first its similarity to lime and conducted parallel experiments on both. He was able to show that when limestone was strongly heated, the resulting calx (quicklime) weighed only a little more than half as much as the initial limestone. As had Hales before him, Black tacitly assumed the conservation of weight and concluded that the loss in weight was owing to the loss of the air, a conclusion strongly supported by the fact that the quicklime did not effervesce with acid as had the original limestone. The original weight of the limestone could be recovered from the quicklime by reacting its solution with the mild alkali, that is, potassium carbonate. Black was able to characterize this "fixed air" as distinct from common atmospheric air:

quicklime + mild alkali = limestone + caustic alkali
$$(Ca(OH)_2)$$
 (K_2CO_3) $(CaCO_3)$ (KOH)

From these he could conclude that mild alkali was equivalent to caustic alkali plus fixed air.

Here for the first time it had been demonstrated that the presence of a particular air was explicitly related to the presence or absence of particular properties. Although Black never weighed the emitted air directly, all his arguments are based on the assumption that the weight of the emitted air would be

equal to the loss in weight from the original limestone. By assuming that weight is conserved, he was able to demonstrate the consistency of the cycle of chemical changes involved (7).

But even Black's work did not immediately cause chemists to turn their attention to the chemistry of gases. In the years between 1735, when the *Vegetable Staticks* was translated into French, and about 1770, the *Mémoires* of the Paris Academy show no significant attention to the role of air in chemistry. Nor does Diderot's *Encyclopédie* reflect a more perceptive response. The ten-page article "Air" in the first volume (1751) is devoted almost entirely to the physical properties of air, with a brief paragraph merely announcing that Hales had shown air to be obtainable from a wide variety of substances. Two examples are offered without suggesting that the work is of chemical significance.

What I have offered up to this point is evidence that, long before Lavoisier, the principle of the conservation of weight in chemical change was sufficiently well known that at least three workers could apply it without feeling obligated either to justify it or even mention it as a distinct principle. But in the absence of a general awareness that gases enter into many common chemical processes, it is not surprising that no one saw the systematic application of the principle as a promising chemical procedure. Even Black's work, as significant as it was historically, did not utilize the principle as a challenging principle against which *all* chemical changes must be measured. This vision was put into practice first by Lavoisier. Although he first stated it as a fundamental principle only in 1789, his experimental practice had from the beginning been designed on that principle. In the famous *Traité*, he wrote (8):

As the usefulness and accuracy of chemistry depends entirely upon the determination of the weights of the ingredients and products both before and after experiments, too much precision cannot be employed in this part of the subject; and, for this purpose, we must be provided with good instruments ...

In this manner of operating, we have always a very material proof of the accuracy of the analysis, as the whole weights of the products taken together, after the process is finished, must be exactly equal to the weight of the original substance submitted to distillation.

Needless to say, Lavoisier himself did not always follow his own precepts (that's a story for another time and place). But the conservation of weight principle had entered the toolbox of deliberate and conscious chemical argumentation and the science would never be without it again.

Recall that Lavoisier in the main body of the *Traité* stated the conservation principle in the most general terms; that "an equal quantity of matter exists both before and after the experiment" (9). For us today it is a perfectly obvious procedure to balance the quantitative books with weight as the proper measure of the quantity of chemical matter. In the 18th century, matter without weight was not a self-evident contra-



Isaac Newton

diction as it would seem to us today.

The fundamental justification for identifying the quantity of matter with its mass (or on the earth's surface, its weight) came with Newton's law of universal gravitation. The weight of a body is the force of attraction between it and the earth. Hence all massive bodies on the earth should experience that attraction and be ponderable. But Newton himself gave ambiguous exception to this seemingly restrictive meaning of matter when he added the General Scholium to the second edition of the *Principia* in 1713 (10):

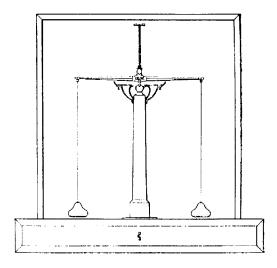
And now we might add something concerning a certain most subtle Spirit, which pervades and lies hid in all gross bodies; by the force and action of which Spirit, the particles of bodies mutually attract ... and electric bodies operate ... as well repelling as attracting the neighbouring corpuscles, and light is emitted, reflected, refracted, inflected, and heats bodies; and all sensation is excited, and the members of animal bodies move at the command of the will, namely, by the vibrations of this spirit, mutually propagated along the solid filaments of the nerves, from the outward organs of sense to the brain, and from the brain into the muscles. But these are things that cannot be explained in a few words, nor are we furnished with that sufficiency of experiments which is required to an accurate determination and demonstration of the law by which this electric and elastic spirit operates.

Newton's "most subtle spirit" is itself ambiguous on this point. The word spirit in Newton's time derived from the earlier usage as anything volatile, an ethereal spirit. It was associated with the Paracelsian mercury, symbolic representa-

tive of the volatility of all such, the very essence of ethereal spirits. Was it material, or was it spiritual in the theological, non-material sense of the word? Also Newton clearly allows repulsive as well as attractive forces, from which some bodies might show absolute levity by being repelled from the earth.

18th century philosophers and scientists found in this passage justification for dealing with imponderable matter generally. Treating heat, electricity, magnetism, and light as imponderable fluids provided the 18th century with at least a vocabulary for discussing phenomena which then still lacked the energy concepts of the 19th century. For the chemist, heat or the matter of fire was the most important of the imponderable fluids, taking on a material or instrumental quality while retaining something of the elusive nature of the ancient element of fire - nonisolable and known only by its effects. Of similar conceptual existence was the equally imponderable, but more elusive, phlogiston. In this guise the tradition of imponderable matter was to be directly confronted by the newly emphasized ponderable aspect in the work of Lavoisier.

That some metals gained weight when calcined in the air had been known for a long time. This had not been perceived as a problem early in the 18th century, for as we have already seen, the conservation of weight had not yet become a consciously applied axiom. But from about the middle of the century sufficient attention began to be given to the particular fact of weight gain in calcination that various explanations began to appear. These often showed much confusion between specific and absolute weights. As the question became more focused and the phlogistic view of composition became more widely held, serious proposals were made to assign that elusive material a negative weight or an absolute levity, thereby explaining a gain in weight in spite of a loss of material (11).



Small balance constructed for Lavoisier by Mégnié after a design by Truchot. Sensitivity: 0.1 g. Original now in the the Musée des Techniques, Conservatoire National des Arts et Méties in Paris (18).

However heroically perverse negative weight might seem to us today, its introduction derived from the implied application of the conservation of weight principle to the calcination of metals. Putting arbitrary figures on the reactants, the implied argument becomes clear:

$$Metal = Calx + Phlogiston$$

$$10 12 -2$$

In the absence of the knowledge of the role of oxygen, there is no other way to balance the weights.

When Lavoisier first encountered the problem of the gain in weight by metals in calcination, he had already created a theory of the gaseous state and recognized the possibility that the gain was due to the fixing of air (12). Because Lavoisier's approach was new to the problem, he was not trapped into futile attempts to tinker with new concepts of gravity, but focused on the air which, unlike phlogiston, was already known to be ponderable and thus conformed with the positive gravity or weight in the ordinary sense of usage. When he was able to show that the weight gained by a calcined metal was equal to the loss of weight of the ambient air, even the phlogistonists soon accepted the evidence and admitted that oxygen (or dephlogisticated air as they called it) did indeed combine with the metal. They too were inheritors of the conservation principle and were not about to argue with it when used in such convincing fashion. Some still held that, since Lavoisier had not demonstrated the non-existence of phlogiston, it combined with the oxygen and in that combination remained a part of the calx or the acid. Thus, they were able to maintain the faith of their early training.

Lavoisier recognized his inability to prove the negative and, in his most thorough-going attack on the phlogistic doctrine, argued chiefly that phlogiston was inconsistent and unnecessary. Following a summary of his own demonstration of the role of oxygen in calcination, he wrote (13):

... if everything in chemistry is explained in a satisfactory manner without the help of phlogiston, it is by that reason alone infinitely probable that the principle does not exist; that it is a hypothetical body, a gratuitous supposition; indeed, it is in the principles of good logic, not to multiply bodies without necessity.

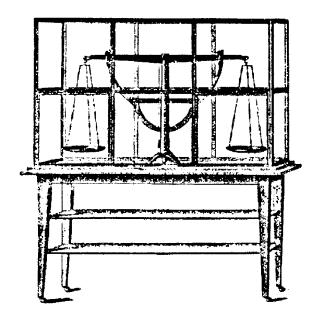
But if Lavoisier found the imponderable phlogiston hypothetical and useless, he found good use for his own equally imponderable caloric or the matter of heat. The idea that all gases were combinations of the matter of heat with different chemical substances was the earliest and most persistent of Lavoisier's scientific concepts. Caloric was for him the principle of the gaseous state even as phlogiston was for Priestley the principle of inflammability. In Lavoisier's list of elements or simple bodies, the imponderable bodies, caloric and light are listed in the first group along with the ponderable

oxygen, hydrogen, and nitrogen (14).

Indeed, caloric was probably more materially real for Lavoisier than phlogiston was for Priestley, for he had established its quantitative existence by carefully measuring not its weight, but the amount of ice it could melt. In a long series of calorimetric experiments carried out in 1783, Lavoisier and his colleague, Pierre-Simon de Laplace, determined heats of combustion and specific and latent heats, all measured on the assumption that the quantity of heat or caloric is conserved (15). When we recall Lavoisier's later statement that "an equal quantity of matter exists both before and after the experiment ..." [my emphasis], can we not reasonably infer that he had imponderable caloric in mind as well as the ponderable elements? The utility, not to say the necessity, of the imponderable fluids remained in science well into the 19th century, when energy concepts were able to make them unnecessary.

In summary, we have seen that, though the principle of the conservation of matter was well known long before Lavoisier introduced it as a decisive tool in chemical investigation, the ignorance of the chemical role of gases made its application meaningless. Noting also the deep philosophic and procedural uncertainties concerning the nature of matter, we can appreciate even more deeply Lavoisier's greatness in establishing weight as the operating criterion by which the quantity of matter is to be measured and conserved in chemistry.

Postscript - The history of science can teach fundamental lessons about the nature of scientific thought itself. One such lesson from this particular story has not always been under-



Large balance built for Lavoisier by Fortin in 1788 after a design by Truchot. Capacity: 10 kg, sensitivity: 25 mg. Original in the Musée des Techniques, Conservatoire National des Arts et Méties (18).

stood by those charged with teaching the science to new generations of students. Witness the following quotation from a contemporary general chemistry text (16):

Antoine Lavoisier (1743-1794), a French chemist, insisted on the use of the balance in chemical research. His experiments demonstrated the law of conservation of mass, a principle that states that mass remains constant during a chemical change (chemical reaction). A flash bulb gives a convenient illustration of this law.

The author completes his point by indicating that the flash bulb weighs the same before and after it is ignited.

But what will the student learn from this passage? First, that Lavoisier demonstrated the law of conservation of mass or weight, presumably in a manner like that utilized in the flashbulb experiment. As we have seen, Lavoisier did no such thing, but took the principle as "an incontestable axiom" incapable of direct experimental demonstration.

But the important point here is not the author's misrepresentation of Lavoisier's work (though that is lamentable enough), but that in so doing he misrepresents the manner by which such broad general principles are established in science. By implying that Lavoisier arrived at this principle by generalization from a large number of cases, presumably some 18th century equivalent of flash bulbs, the author is promoting the Baconian or inductive method, a view long recognized as inadequate and misleading. As we have seen, Lavoisier assumed an axiomatic validity for the principle from which he drew the conclusion that "the whole weights of the products taken together, after the process is finished, must be exactly equal to the weight of the original substance submitted to distillation" (17). Since all his measurements were consistent with the conclusion derived from his axiomatic principle. Lavoisier could feel confident of its validity and justified in its continued use. This procedure has since become familiar as the hypothetico-deductive method, a practice that might lead to the falsification of the assumption, but not to its direct demonstration. It is unfortunate that a modern textbook writer would promote a scientific methodology a century and a half out of date.

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- 5. S. Hales, *Vegetable Staticks*, London, 1727. Quotation from the Oldbourne reprint edition, London, 1961, pp. 179-180.
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LAVOISIER THE EXPERIMENTALIST

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Historians have paid more attention to Lavoisier the theorist than to Lavoisier the experimentalist. His conceptions of heat, the gaseous state and the composition of the atmosphere, his theories of combustion and of oxygen as the acidifying principle, his definition of an element and the reordering of chemical composition, his attacks on the phlogiston theory and his reform of the nomenclature of chemistry have all been thoroughly analyzed. Much scholarship has been devoted to the origins of his interest in these subjects, to the genesis of his ideas concerning them, and to the influences of other thinkers on his views. In part because the Chemical Revolution is treated as the construction of a new conceptual foundation for that science, Lavoisier has been viewed predominantly as a great theorist. It is frequently pointed out that at critical points he borrowed the experimental findings of others - especially those of the experimentally brilliant Joseph Priestley - and reinterpreted their results to fit his emerging theoretical framework. Some have even maintained that Lavoisier himself did not make major experimental discoveries.

Lavoisier is also known as the author of the fundamental principle of the conservation of mass. In the *Traité Élémentaire*, whose bicentennial we are celebrating this year, he wrote (1):

... nothing is created, either in the operations of art, or in those of nature, and one can state as a principle that in every operation there is an equal quantity of material before and after the operation.

It is recognized that this statement was the operating principle on which Lavoisier based his "balance sheet" method of experimentation; but the priority given to Lavoisier as a theoretician has prompted historians to wonder why he located the statement of so general a principle in a detailed discussion of fermentation rather than in a broader context. If one follows closely Lavoisier's prolonged investigation of fermentation, however, a very reasonable explanation for this connection becomes apparent. The fermentation reaction he viewed as a difficult, almost climactic test of his experimental method. As he put it in an earlier paper on fermentation that he did not publish, for a simple case there is no difficulty following a chain of reasoning in which the equation between the materials and the products of a chemical change is implicit. It is in handling a complicated case like fermentation that it is most important to keep this principle firmly in mind (2). That example alone should suggest that it would be fruitful to place more emphasis than is commonly done on the details of Lavoisier's experimental practice.

Historians here frequently noted that Lavoisier practiced quantitative "balance sheet" methods long before he stated the general principle on which they are based. His first notable experiments on the transmutation of water in 1768-70 relied on that method, and it pervaded all of his experimental investigations through the next two decades. There has been, however, an implicit assumption that Lavoisier's most significant experimental achievement was simply to adopt this criterion and the quantitative methods necessary to implement it. Making them actually work has not been viewed as a major problem once the "airs" in which Lavoisier was interested had been incorporated into the balances. When we follow Lavoisier's investigative pathway, however - in particular when we reconstruct his experimental ventures at the intimate level recoverable from his laboratory notebooks - we find that he did not have a global method for ensuring that his balance sheets would balance out; that they frequently did not; that he encountered myriad errors, the sources of which he could not always identify with certainty; that he often had to calculate indirectly what he could not measure directly; that he exerted great ingenuity in the management of his data so as to make flawed experiments support his interpretations; and that he devoted much care and effort to the design of experiments so as to obviate such difficulties, but that he often settled for results he knew to be inaccurate, using his faith in the conservation principle to complete or correct the measured quantities. Much of his scientific success, I would claim, is rooted in the resourcefulness with which Lavoisier confronted the many pitfalls that lay along the quantitative investigative pathway he had chosen. He was, in fact, the most innovative experimental chemist of his age. He invented a whole new way to perform chemical experiments, and it required all of his considerable technical skill and critical judgment to make it succeed.

Recently there has been some discussion over the question