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From Elements to Atoms:
A History of Chemical Composition

Robert Siegfried

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Design and composition
Andrew L. Sihler

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PREFACE

THIS BOOK was first conceived, and some portions written, for the students in the class of history of chemistry that I was teaching during the 1980s following the retirement of Aaron J. Ihde at the University of Wisconsin. My aim in teaching these chemistry and pre-med senior students was to enlarge their understanding of the nature of chemical science and explain how the concepts they were learning in their chemistry classes came to be. It is both to those students and to Aaron Ihde that I owe the inspiration for this attempt to present a simple, readable account of how in the eighteenth century chemical composition slowly abandoned the centuries-long tradition of metaphysical elements of EARTH, AIR, FIRE, and WATER, or the Paracelsan variation of MERCURY, SULPHUR, and SALT. By the end of the eighteenth century, chemical composition had become expressible in terms of operationally defined material simple bodies made verbally explicit by Lavoisier's successful new chemistry, wherein the elements were defined as any body not yet shown to be compound. Just twenty years after Lavoisier, John Dalton introduced the concept of atomic weight unique to each simple body, from which came the modern quantitative structure of chemical composition. Hence the story of the movement of chemical theory from metaphysical ELEMENTS to operationally-functional ATOMS.

About thirty years ago the late Betty Jo Dobbs and I published a paper[1] presenting the view that the fundamental accomplishment of Lavoisier's chemical revolution was the introduction of a material composition based

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[1] Robert Siegfried and Betty Jo Dobbs, "Composition: A Neglected Aspect of the Chemical Revolution," *Ann. Sci.* 24 (1968): 275-293.

on the concept of simple bodies, i.e., those that have not yet been shown to be compounded. The main theme of this book is to trace the slow and generally unconscious development of this operational concept of chemical composition in the seventeenth and eighteenth centuries, climaxed by Lavoisier's definition of simple body. The origin of my long-time focus on this theme is the chemical career of Humphry Davy, which I had been engaged with for more than fifteen years prior to that 1968 publication. It was Davy who first called my attention to the fundamental place of the idea of chemical composition:

> The most important part of the theory of Lavoisier was merely an arrangement of the facts relating to the combination of oxygen: the principle of reasoning which the French school professed to adopt was, that *every body which was not yet decompounded, should be considered as simple;* and though mistakes were made with respect to the results of experiments on the nature of bodies, yet this logical and truly philosophical principle was not violated; and the systematic manner in which it was enforced, was of the greatest use in promoting the progress of the science.[2]

My personal motivation for preparing this account comforms with the long tradition of scientists who wrote the history of their particular sciences for the educational benefit of their students. The history of a science was early offered in science textbooks with the thought that historical knowledge of the development of scientific ideas would give the student a deeper understanding of the science itself.

Antoine-François de Fourcroy, one of the outstanding chemistry textbook authors of the late eighteenth century, thought that the practitioner of every science ought to be familiar with its history. "For such a history, being a relation of scientific facts, fixes the dates of discoveries, points out the errors of our predecessors, and indicates the path that leads to success."[3] Historical introductions in scientific textbooks continued to be

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[2] H. Davy, "Historical View of the Progress of Chemistry," the Introduction to *Elements of Chemical Philosophy* [1812] in Davy, *Works,* vol. 4, 31. My emphasis.

[3] A.-F. de Fourcroy, *Elements of Chemistry and Natural History,* 5th ed., with notes by John Thomson, 3 vols. (Edinburgh, 1798), 92.

common well into the twentieth century. In the nineteenth century scientists began to expand interest in enlarging the understanding of the basic concepts of their own science by writing separate histories of their sciences, most thoroughly illustrated by the science of chemistry beginning with Thomas Thomson's *History of Chemistry* which appeared in 1830. By the end of the nineteenth century, many histories of chemistry had appeared in many different languages. The histories written by scientists were chiefly focused on the development of the ideas and concepts central to the science contemporary to the author's own time. Very little of the social circumstances of those developments was included. Matthew Moncrieff Pattison Muir early in the twentieth century perhaps best expressed the value of history of science when he opened the Preface to his *History of Chemical Theories and Laws* with the following statement: "The more I try to understand chemistry, the more I am convinced that the methods, achievements, and aims of the science can be realized only by him who has followed the gradual development of chemical ideas."[4] This educational attitude was expressed again by Colin Russell in 1984: "Science without its history is like a man without a memory."[5]

Scientists remained the chief writers of the history of science until the establishment of the field as a distinct academic activity in the twentieth century. Not surprisingly, it was mostly scientists who were responsible for the founding, at the University of Wisconsin in 1941, of the first independent department of the History of Science at any institution of higher learning in the USA.[6]

When I began my study of the history of science at the University of Wisconsin in the late 1940s, the policy of the graduate school was that because the advanced study of History of Science was a new discipline—when the department was founded, its purpose was undergraduate instruction—and had no established scholarly standards, I would have to complete my PhD jointly with another department. In this way the University

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[4] M.M. Pattison Muir, *A History of Chemical Theories and Laws* (New York: J. Wiley, 1907), v.

[5] Colin Russell, "Whigs and Professionals," *Nature* 308 (26 April 1984): 777-778, at 778.

[6] For an excellent and detailed account of "History of Science at the University of Wisconsin," see Victor Hilts, *Isis* 75 (1984): 63-94.

could be assured that proper academic quality was maintained. My choice was chemistry, in which I had completed two years of graduate study.

In that same spring of 1948 I was invited by chemistry Professor Aaron Ihde to be his Teaching Assistant in the newly organized program of Integrated Liberal Studies (ILS), dedicated to the concept of a general education in which the physical sciences were taught not as individual specialties, but as an integrated gathering of the fundamentals of several sciences. In the next four years I found that teaching in the ILS general science program, and the knowledge I was gaining in the history of science, were quite complementary to one another. That is, the history provided me useful examples for illustrating the development of scientific concepts, while the experience of teaching science provided me with insights into understanding the historical development of those same concepts.

When I finished my graduate work at Wisconsin, there were no academic positions for historians of science open anywhere. For eleven years my three academic positions were all obtained because of my experience in teaching science as in the Wisconsin general education program. My joint degree was a boon, as it provided me the qualifications to be an active member of the chemistry departments in two of the positions I held, at the Universities of Arkansas and Illinois, where I also taught courses in history of chemistry, the area of my research interests. Thus by the time I returned to Wisconsin as a member of the History of Science Department in 1963, I had eleven more years of experience in integrating history of science into the teaching of elementary physical sciences, an experience that had convinced me of its value in basic science education.

After returning to the University of Wisconsin I taught only within the History of Science Department, but the close association between history of science and science education was with me still. My chief aim while teaching undergraduates at Wisconsin has been to make the history of science the vehicle for conveying a basic understanding of the nature of the scientific enterprise as an open-ended search for scientific truth. The need for this understanding of science is just as great among the students who later become scientists as it is for the general literate public.

In the last thirty years, history of science publications have increasingly focused on the social and other contextual aspects in the development of scientific concepts. One of the early books written from one of these perspectives was *The Ferment of Knowledge: Studies in the Historiography of Eighteenth-Century Science.*[7] In my very positive review of that book in 1982 I made the point, illustrated by many of its contributors, that history of science needed *both* the internal *and* the contextual views.[8] Since a sequential account of the development of the concept of chemical composition has not been previously written, my historiographic justification for focusing on the internal history of scientific ideas is, paradoxically, that it will make possible a better contextual history of eighteenth-century chemistry than has yet been possible.

The content of this book is based on chemical writings of the seventeenth- and eighteenth-century chemists, and my references to recently published secondary works are intended for the benefit of readers who wish to enlarge their contextual perspectives on the development of early chemical thinking. In general I am not attempting to resolve any differences of perspective or interpretation.

It has been my aim in this account to tell a good story accurately—rational enough to make it easy to remember, faithful enough to the events to make it worth remembering, and challenging enough to make someone, some day, want to do it better.

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[7] S. Rousseau and Roy Porter, eds., *The Ferment of Knowledge: Studies in the Historiography of Eighteenth-Century Science* (New York: Cambridge University Press, 1980).

[8] *Ann. Sci.* 39 (1982): 201-203.

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This book is dedicated to the life and work of
Humphry Davy
the inspiration and model
for all my own scholarly aspirations

I

INTRODUCTION

In spite of the fact that composition is the singular organizational basis of modern chemistry, its history before Dalton's atomic theory has never been written. Though much of Ida Freund's pioneering work of 1904, *The Study of Chemical Composition: An Account of Its Method and Historical Development,* derived from historical development of chemical ideas and functions, she modestly denied that she had produced "anything sufficiently complete or even sufficiently proportioned to deserve the name of *history.*"[1] My theme in this book focuses on the eighteenth-century chemists' increasing use of material bodies as component parts of other material bodies, until at the end of the century, chemical composition became clearly organized by the functional introduction of simple body by Lavoisier. Other more recent studies with independently parallel perspectives on chemical composition will be treated later.[2]

Chemistry as Magic

There is something about chemical change that is magical. Bodies disappear and new bodies with different qualities appear in their stead. Two clear

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[1] Ida Freund, *The Study of Chemical Composition: An Account of its Method and Historical Development* [1904] (New York: Dover reprint, 1968), Preface, xv.

[2] Ursula Klein, "Origin of the Concept of Chemical Compound," *Science in Context* 7 (1994): 163-204, and her "E.F. Geoffroy's Table of Different 'Rapports' Observed between Different Chemical Substances—a Reinterpretation," *Ambix* 42 (1995): 79-100. See also J.B. Gough, "Lavoisier and the Fulfillment of the Stahlian Revolution," *Osiris* 4 (1988): 15-33.

liquids can be mixed and solid material appears; where did it come from? A piece of metal can be added to a clear, colorless liquid, the metal disappears, and a blue color appears. Based on direct experience alone there is no explanation available.

The gap between what we see and how we explain it today is bridged by a very elaborate and abstract invention. That our contemporary chemical theory is a powerful intellectual tool is obvious from the vast evidence of chemical success in our world today. Yet there is no apparent connection between this model and our direct experience of chemical change or of chemical properties.

For me, nothing illustrates this chasm between observation and chemical theory better than my experiences as a teaching assistant in the laboratory of a beginning chemistry course. Students were carefully following procedures described in the lab manuals, filling in the blanks to describe their observations. Then as a kind of climax they were asked to "Write the equation for this reaction." Students were often stunned by this request, for they could perceive no connection between what they had observed and the equation they were expected to write. This gap between the perceptual experience of events and their conceptual representation is wider and deeper than for any other of the basic sciences. That fact in large part accounts for the late arrival of chemistry at its maturity, with the work of John Dalton early in the nineteenth century.

Chemical change is so omnipresent in the world of experience that thinkers were struggling with ways to comprehend it from the beginning of philosophical history. But chemical change is so magical in its character that these attempts remained in metaphysical rather than in experiential language and concepts well into modern times. Finally in the eighteenth century we see the slow and largely undeliberate transformation of implicit operational concepts of composition into explicit definitions and statements of principle.

In antiquity, problems relating to chemistry were approached by two philosophies held to be mutually exclusive. The compositional view is best illustrated by the four elements as developed by Aristotle. The opposing view of structure, represented by the atomic theory of Democritus, lost out in antiquity because its materialism left no room for the spiritual. The so-called elements of this story were not the material ones of today, but metaphysical causes of the properties of the various bodies experienced.

Chemical thought in the centuries after Aristotle was almost completely dominated by variations of the compositional view. The most significant variation came from the Swiss alchemist/physician Theophrastus Bombast von Hohenheim, known to posterity as Paracelsus, who in the sixteenth century introduced the *tria prima* of MERCURY, SULPHUR, and SALT as (slightly) more material principles than the four elements, which retained their metaphysical status behind the more experiential *tria prima*. His transfer of the alchemical goal from the making of gold to that of preparing chemical medicines gave alchemical practice a great increase in its material emphasis under the name of Iatrochemistry (from the Greek ἰ̄ᾱτρός (*īātrós*) "physician").

Two additional material principles were added to the *tria prima* in the seventeenth century to form the five-principle view that characterized the iatrochemistry until the middle of the eighteenth century, when the four Aristotelian elements returned largely through the influence of the French chemist Pierre-Joseph Macquer. Robert P. Multhauf has given a splendid account of these pre-modern years in *The Origins of Chemistry*.[3]

The central theme of this book lies in offering evidence that from the middle of the seventeenth century chemists were consciously dealing primarily with their operational familiarity with real, material bodies, even while retaining some of the conceptual consequences of the metaphysical tradition they had inherited. What they did and what they said were based on distinctly inconsistent philosophies. The intellectual and verbal expression of the operational concepts as substance, compound, and element, were not achieved until near the end of the eighteenth century. The compositional format was fully materialized by Lavoisier's concept of the operational element, or simple body, which only two decades later was combined with atomism through John Dalton's concept of atomic weight. Chemical composition has had no fundamental conceptual change since that time, for in spite of all the detailed developments in atomic structure, chemical bonding, etc., modern chemical formulas represent the same com-

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[3] Robert P. Multhauf, *The Origins of Chemistry* (New York: Franklin Watts, 1967).

positional data as did Dalton's formulas of symbolic circles, as will be seen in the last chapter. Dalton's quantization of weight units also made possible the nineteenth-century development of molecular structure, an open-ended view that remains today at the frontier of chemical science, whether in molecular biology or polymer plastics. It is pleasantly ironic that chemistry achieved its successful organization by combining philosophies that the great minds of antiquity had considered incompatible.

Discontinuity and Identity

> What is "a chemically distinct substance"? What happens when chemically distinct substances interact? These are the two main questions of chemistry and they have always been the two main questions of chemistry.[4]

When Muir wrote that the idea of a chemically distinct substance had always been one of the main questions of chemistry, he acknowledged that the question had not always been stated so clearly and directly. The successful clarification of the distinction between material and immaterial bodies largely occurred in the eighteenth century, and can be seen as a fundamental part of this story. Even within the realm of material bodies, the idea of a chemically distinct body remained undefined, though long recognized in practice. I have not found a clear statement earlier than that of Torbern O. Bergman near the end of the eighteenth century: "In general, any body which differs in properties from every other, and can be always had *similar to itself,* I consider as a separate and distinct body."[5] As Muir implies, the implicit usage of something like this is as old as philosophy, yet its importance was slow in becoming consciously recognized and defined. Even Bergman failed to insist on the central importance of this concept. Ursula Klein has recently published more detailed studies on this subject of the development of modern chemical identities, such as sub-

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[4] M.M. Pattison Muir, *A History of Chemical Theories and Laws* (New York: J. Wiley, 1906), Introduction, ix.

[5] T.O. Bergman, *Physical and Chemical Essays*, trans. Edmund Cullen, 2 vols. (London, 1788), vol. 1, xxix.

stance, compounds, components, elements, that were only slowly becoming conscious in the eighteenth century.[6]

The world of experience is filled with material bodies quite distinct from one another, bodies of sufficient importance and commonality that as children we are taught their names. At the gross level, where we readily distinguish rocks from flowers and dogs from cats, there is no problem and there is no need for deliberate definitions. At the same time our lives are even more abundant in experiences that grade imperceptibly into one another without generating stages distinct enough to receive names; shades of blue or red. Here is the fundamental question, is the world a continuum or a discontinuum? In ancient Greek philosophy, both answers were generated in answer to the question: How are we to account for change and permanence in the world of our experience?

Aristotle's response to the question of what is permanent behind observed changes in the natural world, offered a single undifferentiated but permanent matter. This matter, however, carries properties which give it form, forms manifested fundamentally in the four elements, EARTH, WATER, AIR, and FIRE.

> Aristotle insisted that the primary matter was not an *addition* to the elements; it was not corporeal as they were, but neither was it separable from them.... The primary matter itself only existed potentially that it might have form; it never actually existed without form or quality. This ultimate underlying subject, common to all things of nature, and presupposed by them, was thus a pure abstraction because, though it existed in various items, united with various "forms", it was not knowable in itself.[7]

The emphasis on external properties and the consequent de-emphasis on the underlying matter is highly significant, for it established the pattern in the history of chemical thought for the next two thousand years. By the

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[6] Klein, "Origin of the Concept of Chemical Compound," and her "Geoffroy's Table." Her accounts provide detailed illustrations of my general story of the move from metaphysical to experiential composition.

[7] Joshua C. Gregory, *Combustion from Heracleitos to Lavoisier* (London: Edward Arnold, 1934), 17-18.

seventeenth century, chemists had become quite committed to the use of "principles" as metaphysical concepts, each of which explained a particular property. By the sixteenth century, each of the four elements of Aristotle was presumed to be the metaphysical principle present in bodies to explain the particular properties directly observed. Simple examples include that of a solid being dominated by the presence of EARTH, as liquids were by the presence of WATER, and combustibles by the presence of FIRE.

The choice is natural enough, for the external properties are directly perceived and in that sense constitute the reality of experience. In the naive early days of science there was no evidence of a conscious hypothetico-deductive procedure by which the material component might be assigned hypothetical properties from which manifest, external properties might be deduced and compared with experience. Even the equally old atoms of Democritus failed to gain sufficiently credible attributes to become a theory in the modern sense, such that clear deductions made from them could be compared to experience. The atomic conception too remained little more than a way of explaining anything by simply assigning to the atoms whatever invisible qualities were needed.

What are some of the consequences of the emphasis on properties? External ones such as color, hardness, texture, etc., are all perceptions whose differences are those of degree; one shade of gray fades off into another with no clear boundary to be marked. Distinctions tend to be subjective, for there is nothing to count or measure, even if one were philosophically committed to counting and measuring.

All this is related to the distinction between chemical and physical properties. Physical properties describe what a body is, as it is now. Chemical properties describe what a body can become, how it can react with other identifiable bodies. When bodies mix physically their properties blend; properties common to both may be intensified, others are more or less cancelled out or diluted, but the original properties are still there in the mix. Black and white paint can be mixed to any shade of grayness; some shades might be distinctive enough to be given names, but there are no sharp boundaries.

When bodies react chemically their properties disappear, for new substances are formed, each with its own external physical properties by which it will normally be recognized. Today we say chemical changes are changes in composition, a rearrangement of the atoms in the molecules of the reactants into the molecules of the products. Chemistry's task is to correlate observed changes in properties with accompanying changes of composition. A fully functional distinction between physical and chemical properties and changes was not achieved until the introduction of Dalton's atomic theory made possible straightforward theoretical predictions.

The fact that the Aristotelian view emphasizing continuity won out over the discontinuous atomic view provided the tradition which chemists of the seventeenth and eighteenth centuries only slowly abandoned. For the most part, however, there is little deliberate discussion of this topic in these transforming centuries. The changes that ultimately took place came about chiefly from the exigencies of chemical practice, not from focused thought on such problems. Chemists generally have been an unphilosophic lot with a long and strong tradition of chemical manipulations often totally removed from the kind of philosophy that might have useful application to that practice.

In spite of a dominant philosophy for the continuity of change, chemical practice always required the recognition of distinct bodies. The list of such bodies in alchemical times included not only the seven familiar metals and their ores, but both natural minerals such as the vitriols, gypsum, and quartz, and a number of artificially prepared bodies, sal ammoniac, nitre, vitriolic acid, etc. By the end of the seventeenth century, the textbooks of chemistry were organized chiefly into chapters headed by those discrete substances whose chemical behavior was sufficiently well known to fill a chapter. These make a class of bodies I refer to later as "privileged bodies," a seventeenth century proto-equivalent to what we later call substances. But much of the natural world is not easily categorized into neat identities. (Workers in other areas of investigation were perhaps more conscious of this problem than were the chemists.) In any case, in order for the empirical concepts to surface and become explicitly admitted, a great deal of philosophical preference for continuity and unity had to be overcome or abandoned. There will be some accounts of this question of discontinuity and identity in Chapter 12, following the chapters treating the details of seventeenth- and eighteenth-century chemistry.

When most history of science was still focused on the intellectual development of science, its internal history, the eighteenth was perhaps the most neglected of modern centuries. Placed inescapably between the century of genius that preceded it and the coming of age of modern science that followed, it could at best be seen as a period of transition, the adolescence between the childhood of science and its arrival at maturity that followed. Historians of science, like many retrospective parents, have tended to treat such adolescence as a time best forgotten, and devoted their enthusiastic attention to more dramatic epochs. The study of the rise of the mechanical philosophy in the seventeenth century and its climax in the figure of Isaac Newton had become a veritable industry while Darwinian studies have become much the same. Studies of science in the eighteenth century have increased significantly in the last twenty years, though largely in the contextual, social patterns, rather than focused on the development of fundamental scientific concepts. This book is in the earlier tradition of presenting the detailed account of fundamental scientific conceptions which are necessary before contextual studies can be fully reliable. It also attempts to isolate and analyze the interests of the scientific community itself.

Eighteenth-century science, like human adolescence, was a formative period. It was chaotic and disorderly because still undefined. Basic rules and definitions of limits and procedures were being slowly and painfully worked out. Different sciences were roughing out their boundaries and creating the framework of concepts that would make each science distinct. Mineralogy, geology, crystallography, calorimetry, electricity, biological taxonomy, and chemistry all found their defining organizing concepts in the eighteenth century. In the language of Thomas Kuhn, many of these sciences in the eighteenth century were pre-paradigmatic; they needed not so much a revolution as a definition. The rapidly growing quantity of data required systematic organization for which older patterns, if they existed at all, had become inadequate or irrelevant. Like human adolescence it is a difficult area to work with, but it makes the challenge so much the greater. The excitement of the Enlightenment matches that of the newly awakened intellect of the adolescent, and the chaos of revolutions matches that of the teen-age rebellion.

Though the seventeenth century saw a return of atomic thinking along with the successful development of mechanical philosophy, its interaction with chemical experience was never fully successful. In this pre-paradigmatic period many writers felt free to expound their undisciplined conjectures, which most other writers properly ignored. This condition was lamented by Robert Boyle in the late seventeenth century in an account labelled *Certain Physiological Essays Written at Distant Times and on Several Occasions, London 1661. (Containing: (a) Concerning the unsuccessfulness of Experiments, (b) Specimens of an attempt to make Chymical Experiments Useful to Illustrate the Notions of the Corpuscular Philosophy, (c) The History of Fluidity and Firmness Begun).*

> [I]t has long seemed to me none of the least impediments of the real advancement of true natural philosophy, that men have been so forward to write systems of it, and have thought themselves obliged either to be altogether silent, or not to write less than an entire body of physiology ... it not unfrequently happens, that ... a writer, to vent some few peculiar notions or discoveries of his own, presumes to write a whole body of philosophy.[8]

Boyle's criticism of those who write no less than "an entire body of physiology" and his own reluctance to offer one of his own in spite of his vast exploration of mechanical and corpuscular models, testifies to the uncertain theoretical state of chemistry in the late seventeenth century.[9] In the absence of a clear body of universally accepted paradigms of chemical thought, every chemist felt free to write his own system. More than a century later, the situation had hardly changed, for according to Joseph Priestley men still created systems for their own vanity.

> [M]en can keep brooding over a new fact, in the discovery of which

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[8] Robert Boyle, *Certain Physiological Essays* (London, 1661), 3 & 4. The quotation is also given by James R. Partington, *A History of Chemistry*, 4 vols. (London: Macmillan, 1962–1970), vol. 2, 498.

[9] Our insights into Boyle's chemical attitudes have been recently enlarged by the following careful studies: Antonio Clericuzio, "A Redefinition of Boyle's Chemistry and Corpuscular Philosophy," *Ann. Sci.* 47 (1990): 561-589; and Michael Hunter, ed. *Robert Boyle Reconsidered* (Cambridge & New York: Cambridge University Press, 1994), 10.

> they might, possibly, have a very little real merit, till they think they can astonish the world with a system as complete as it is *new*, and give mankind a high idea of their judgment and penetration....

But the acquisition of new facts had far outstripped the capacity of chemical theory to absorb them rationally.

> At present all our *systems* are in a remarkable manner unhinged by the discovery of a multiplicity of *facts*, to which it appears difficult, or impossible, to adjust them.[10]

Antoine-François de Fourcroy, writing with an additional ten-year perspective, saw the 1770s in the same condition as had Priestley:

> [W]hile [chemistry] became enriched with innumerable facts, its theory proceeded but slowly: it even appeared to lose ground, and to be embarrassed amidst these immense acquisitions. Every chemist had his particular theory; and no complete system was to be found, no certain connection between these results of which the multiplicity actually overwhelmed the science.[11]

Of the new eighteenth-century sciences, chemistry has probably received more of the historian's attention than any of the others, chiefly because only chemistry has a magisterial figure at all comparable to Newton and Darwin, whose works dominate studies of the seventeenth and nineteenth centuries respectively. The view that Antoine Lavoisier had achieved a revolution in chemistry was initiated by the great man himself, and acknowledged by his contemporaries, followers and opponents alike. A century later, Marcellin Berthelot's book, *La Révolution Chimique-Lavoisier*, made official the identification of the chemical revolution with the work

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[10] Joseph Priestley, *Experiments and Observations on Different Kinds of Air*, 3 vols. (Birmingham, 1790), Kraus Reprint edition (New York, 1970), vol. 1, xvii-xviii, and xliii.

[11] A.-F. de Fourcroy, *Système des Connaissances Chimiques*, 15 vols. (Paris, 1800-1801); from the English translation by William Nicholson, *A General System of Chemical Knowledge*, 11 vols (London, 1804), vol. 1, 49.

of Lavoisier, and modern scholars maintain the tradition, sometimes calling it "Lavoisier's chemical revolution."[12]

In what had become virtually a canonical view, Lavoisier's accomplishments consisted chiefly of replacing phlogiston, an imaginary principle of combustion, with real oxygen. His sustained arguments based on the systematic application of the principle of the conservation of weight convincingly demonstrated the imaginary nature of phlogiston and the material existence of real oxygen. In the last two decades many new publications have improved our perspective on Lavoisier and the chemical revolution,[13] but a careful discussion of the development of the operational definition of chemical composition is still needed for a full comprehension of the chemical revolution, and that is what this book aims to provide.

In 1968 Betty Jo Dobbs and I proposed, rather too cautiously it now seems, an alternative interpretation of the events of the late eighteenth century.[14] We suggested that the really important consequences of Lavoisier's work lay not in his overthrow of phlogiston and its replacement with an oxygen-centered explanation of combustion, but rather in the resultant inversion of the order of compositional simplicity that accompanied that replacement, and the introduction of the concept of the materially defined element, or simple body. We further suggested that the revolution itself might be redefined in terms of the events that established *composition* as the defining characteristic of chemical organization. In this view Lavoisier's achievments are only the the beginning of a revolution which reaches its

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[12] For example, I. Bernard Cohen, *Revolution in Science* (Cambridge, Massachusetts: Harvard University Press, 1985), 236.

[13] Only a few of the most relevant need be mentioned. Maurice P. Crosland, "Chemistry and the Chemical Revolution," in G.S. Rousseau and Roy Porter, eds., *The Ferment of Knowledge* (Cambridge & New York: Cambridge University Press, 1980); Arthur Donovan, ed. "The Chemical Revolution: Essays in Reinterpretation," *Osiris* 4 (1988); Arthur Donovan, *Antoine Lavoisier: Science, Administration and Revolution* (Cambridge & New York: Cambridge University Press, 1993; Marco Beretta, *The Enlightenment of Matter: The Definition of Chemistry from Agricola to Lavoisier* (New York: Science History Publications, 1993); William H. Brock, *The Norton History of Chemistry* (New York: W.W. Norton, 1993); Bernadette Bensaude-Vincent & Isabelle Stengers, *A History of Chemistry* (Cambridge, Massachusetts: Harvard University Press, 1996).

[14] Robert Siegfried and Betty Jo Dobbs, "Composition: A Neglected Aspect of the Chemical Revolution," *Ann. Sci.* 24 (1969): 275-293.

completion with the introduction of Dalton's atomic theory. This book is an attempt to fulfill the implications of that view without redefining the chemical revolution.

The compositional story begins in the seventeenth century and reaches its climax in the early nineteenth with Dalton's atomic theory. The first half of the eighteenth century has been so little examined that almost any serious study would provide surprises. The compositional theme gives secure coherence and continuity to a century that on the surface has looked rather chaotic and uninviting. Some other writers have contributed recently to this compositional theme, and will be treated briefly later.[15] New historical perspectives appear for many fundamental chemical concepts and processes. Because the scope is large and the theme is new I have not attempted a comprehensive exploration of all the nooks and crannies along the way. In the absence of an existing body of good scholarship and significant amounts of research on broad topics in eighteenth-century chemistry, it has seemed advisable to pioneer an exploratory path through what has remained an intellectual swamp; by defining a few islands of solid intellectual footing, I trust that others might more securely explore their own particular interests. I hope that this new perspective will allow other younger scholars to see opportunities that I have either overlooked or have not the time, patience, or inclination to pursue. My aim is more to stimulate new research than to attempt definitive answers.

Thematic Outline

In the late seventeenth century the chemical community, in France at least, had arrived at a pretty clear sense of identity. In the textbooks of that time we can also see the beginnings of the drift away from metaphysical toward material composition, a drift more apparent to the historian than to the chemists of the time. The evidence of this development is found in the

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[15] Frederick Lawrence Holmes, *Eighteenth-Century Chemistry as an Investigative Enterprise* (Berkeley, California: Office for History of Science & Technology, 1989). These were five lectures delivered at the International Summer School in History of Science, Bologna, August 1988. See also Klein, "Origin of the Concept of Chemical Composition" and Klein, "Geoffroy's Table" as well as Gough, "Stahlian Revolution," at 15.

empirical descriptions based on implicit concepts we can see in chemical practice that do not become explicit before the end of the eighteenth century. My story recounts the struggle to create order in the absence of clear conceptual goals under the metaphysical tradition that had long before ceased to be progressively useful. The struggle proceeded in the absence of any stated alternative either metaphysical or empirical. The recognition of the utility of the empirical relationship came slowly and almost reluctantly, for the habit of metaphysical rationalism was an old and honored habit and few openly challenged it. But empirical practice shows a pattern of material components that slowly emerged most successfully around the concept of neutral salt as the combination of an acid with a base. Acids, metals, earths, and alkalies had long been known as the material components of the neutral salts, without anyone suggesting that such a relationship was fundamentally significant. In 1782, however, Louis-Bernard Guyton de Morveau proposed a systematic nomenclature based on this empirical compositional relationship. The extension of this system in 1787 to include Lavoisier's evidence that acids and bases were not simple, required the invention of the concept of "simple body," i.e., any body not yet known to be compound. By the end of the century chemical bodies had come to be identified by their composition expressed in "simple bodies" and the beginning of quantitative analysis was under way.

Though the struggle for definition had become conscious, and composition had been identified as *the* fundamental chemical property, the science of chemistry had yet to find a way to organize itself as a coherent system. In the absence of standard analytical procedures, one chemist's analysis might be claimed to be as good as another's, and a researcher selected his best results more by intuition than by established standards. But more discouraging than the uncertainties of analytical processes was the fact that every tediously performed analysis stood in rational isolation from every other analysis. Chemistry lacked an organizing theory for its rapidly multiplying quantitative data. Only with the appearance of Dalton's atomic hypothesis was the often-expressed hope fulfilled that chemical knowledge would prove to be as calculable as astronomy.

The laws of chemical composition (conservation of weight, definite and multiple proportion) so slowly being defined as empirical rules were instantly illuminated and rationalized by Dalton's hypothesis. Even more important was the unification of chemical composition by the concept of atomic weight. Each element or simple body was assigned an atom having a fixed weight characteristic of that element (a quantum of weight). By expressing the composition of a compound by the number of these quanta (atomic weights) the quantitative composition of every compound became mathematically related to the composition of every other compound through the intermediation of a table of atomic weights. A true unity of chemical knowledge was achieved for the first time and composition was confirmed as the organizational basis for chemistry and has remained so every since.

Most chemists immediately utilized the compositional relationships derived from the atomic hypothesis, but for most of the century they continued to dispute the ontological reality of the atoms that rationalized their useful consequences.[16] Even those most doubtful of the reality of the atom found its operational utility indispensible. Humphry Davy was expressing composition by the relative numbers of "proportions" by 1810, and William Wollaston attempted a calculus of chemical equivalents in 1814. Jöns Jakob Berzelius undertook a systematic determination of the most accurate values to assign each of the atomic weights, publishing his first list in 1813.

Historians have not given much attention to the place of Dalton's work in the sequence of compositional developments, focusing their attention rather on the detailed analysis of the origins of his particular hypotheses, and the problems associated with the determination of a consistent set of atomic weights. Perhaps because the concept of atomic weights, by whatever name, was so quickly absorbed into chemical practice with little debate, historians have given this aspect of his work little attention. Whatever the reasons, the connection between Dalton and the eighteenth-century empirical chemical background has remained largely unexplored. The establishment of orderly composition through the atomic theory seems to me the most important event in the history of chemistry. It is the aim of

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[16] William H. Brock, ed., *The Atomic Debates* (Leicester: Leicester University Press, 1967); Alan J. Rocke, *Chemical Atomism in the Ninetenth Century* (Columbus, Ohio: Ohio State University Press, 1984).

this book to offer a first step toward a fuller undertanding of that connection by providing an account of the history of compositional chemistry in the eighteenth century and its incorporation into Dalton's atomic theory.

Dalton's atomic theory marks a watershed in the history of chemical thought, dividing its history into a clear and permanent PAST and a changing but perpetual PRESENT. The PAST is permanent because the atomism that Dalton presented provided so complete a solution to the century-long problem of composition, one so satisfying to the contemporary chemical community that it quickly assumed the status of having always been that way. There were dirty debates about whether the atomic weights ought to be doubled or halved and much other specific uncertainty in the actual application, but there seems to have been little doubt about the utility of expressing composition in terms of some kind of quantized weight units, whether called atomic weights, proportions, or equivalents.

The other side of the divide created by the atomic theory I call the perpetual PRESENT because nearly two centuries later we are still witnessing the exploitation of the chemistry of molecular structure made possible by that theory. The initial development of this opportunity in the nineteenth century has been sufficiently described that it needs no further interpretation here.[17]

The story I want to tell is that of how the appearance of the atomic theory suddenly gave clarity to many discoveries and concepts that had accumulated in the previous century without having yet acquired coherence and unity. In the eighteenth century chaos, many ingenious ideas had appeared, but the atomic theory established an order that clearly allowed the vast accumulation of undifferentiated data to be sorted between the significant and the incidental, and assigned systematic and unambiguous status within a defining framework.

Author's Historical Perspective

Because this story is new and necessarily individualistic, it seems appropri-

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[17] A highly focused account is found in O. Theodor Benfey, *From Vital Force to Structural Formulas* (Philadelphia: American Chemical Society, 1964). A broader account is found in chapter 7 of Brock, *Norton History of Chemistry.*

ate to give the reader a sense of where the author stands. The historian has two mutually conflicting duties that must be resolved as best they can be. The first obligation is to the integrity of those workers whose lives and thoughts the historian is attempting to understand. We seek to re-create and understand the way their world was organized, its unity and coherence. Within the limits of our own abilities we shall misrepresent neither their ideas and intentions nor their achievements and limitations. Just as the physician's obligation is to do the patient no harm, so the historian's first obligation is to do the past no injustice.

Whatever the historians' successes in gaining personal understanding of the past, they are still members of the contemporary culture that has supported their efforts. The historians' second obligation, then, is to conduct the contemporary audience to that same understanding. We historians have dwelt a long time in the land of the past; our audience has not. We must constantly endeavor to compensate for that inescapable difference of perspective. Our efforts to gain the insider's view of an earlier century must not be so all-consuming that we cannot translate that perspective into language comprehensible to our readers. Our obligation to write intelligibly for our readers is as great as our obligation to the integrity of the past we have studied.

At the present time, historians of science have become quite good at maintaining the integrity of the past. Standards of scholarship are high; new sources of information and confirmation are being diligently discovered and exploited. The obligation to our readers, however, is not in so healthy a state. Our current fear of writing "Whiggish" history is so great that we may be unconsciously reverting to the belief that we are telling it "as it really was." But such efforts are doomed to failure and possible self-deception. The historian's profession has many adages that reflect the tentative nature of historical scholarship: "history is a bag of tricks we play on the dead" is no less accurate than it is cynical.[18] The interpretive advantage from the hindsight of years or centuries gives the historian ample temptation to in-

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[18] One of my history professors about fifty years ago attributed this statement to Voltaire, but I have never confirmed its origin.

terpret the evidence either deliberately or unconsciously in ways the original players might not recognize.

Another such adage states that every generation must write history for itself. Time and circumstance change our views of the world's meaning and/or purposes, and inevitably we see the world differently than did our fathers or grandmothers. If the past has any meaning for us at all, it must bear some relevance to the present we are born and bred into. Even as the present changes, so also does the significance of the past that somehow led us to it. Regardless of how the present world-view changes, our need to make it consistent with the past requires that we persistently rewrite the past to provide an appropriate ancestry to the present.

The recognition of this inescapable pattern creates the temptation to write history with a self-justifying bias, to demonstrate by historical scholarship how today's world, or some selected part of it, has come to reach some kind of epitome of values and virtues, what has become known as Whig history.[19] I do not wish here to defend Whig history for its own sake, but rather to urge the point that a certain amount of such interpretation is unavoidable. We are products of our time and there is no way that we can free ourselves so thoroughly from the contemporary perspective that a later generation cannot detect a self-serving tendency. Our obligation then is not to the impossible task of eliminating whiggish tendencies, but to maintain a constant state of awareness of the inevitable provincialisms of our times, and try to keep that awareness before our readers as well.

We have come to think of progress in science as taking place through sharp changes in fundamental conceptions called scientific revolutions.[20] The change need not be rapid, for the classic case of *the* scientific revolution encompasses nearly a century and a half between Copernicus and Newton. Unlike the example from astronomy, chemistry before its revolution in the eighteenth century had not found a theoretical structure at all comparable to the Ptolemaic system that had served astronomy so well and

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[19] Herbert Butterfield, *The Whig Interpretation of History* [1931] (New York: W.W. Norton, 1965).

[20] Thomas S. Kuhn, *The Structure of Scientific Revolutions* (Chicago: Chicago University Press, 1962). See also Cohen, *Revolution in Science.*

so long before Copernicus. Because of the magical nature of chemical change, attempts to rationalize chemical phenomena were generally made by imposing externally conceived systems onto them. In antiquity the combination of Aristotelian patterns and metallurgical knowledge had produced alchemy; the attempt to subsume chemical practice under the mechanical philosophy of the late seventeenth century produced promise without success. Thus the story of composition is not about the demise of one system and its replacement by another. Though the body of detailed chemical knowledge continued to grow, no systematic ordering of chemistry by concepts intrinsic to its experience appeared until the end of the eighteenth century. It has therefore seemed appropriate to organize the story in terms of modern concepts that in the eighteenth century were only implicit. This story is that of how they became explicit, how unrationalized empirical practices ultimately became explicitly stated theoretical principles.

Parallels Between Science and History

> But modern Scientific inquiry in any case comes to rest only provisionally.... By its own nature the inquiry cannot reach a final term in any direction. So it is something of a homiletical commonplace to say that the outcome of any serious research can only be to make two questions grow where one question grew before.
>
> Thorstein Veblen, "The Evolution of the Scientific Point of View"[21]

When, in graduate school, I switched my primary allegiance from chemistry to the history of science, my first reaction was to note that in the main there was little difference in the intellectual processes of the two fields. It is the aim of both a science and its history to create as good a story as possible from the data available.

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[21] A paper read before the Kosmos Club at the University of California on 4 May 1908, and subsequently printed in the *University of California Chronicle* 10, no. 4 (October 1908): 395-416 at 396. The quotation, always truncated to the last nineteen words, is usually referred to Veblen's essay "The Place of Science in Modern Civilization," *American Journal of Sociology* 11 (1906), 585-609. It does not occur there.

Veblen's comment illustrates only one of several parallels between science and history, though perhaps the most important. The search for truth and understanding, whether it be in science, in history, or in any other human endeavor, is a never-ending activity. To assume, even unconsciously, that we have reached some kind of finality is to betray the enterprise altogether. Those who attempt to eschew interpretation and write history "as it really was" are doomed to failure and disillusionment. Historical truth is no less tentative than scientific truth.

Good history, like good science, should do more than simply answer questions. Its explorations of the past should also raise new questions whose investigation will further enlarge our understanding, not only of the past, but of our own selves. It is this attitude that keeps both science and history open-ended where the spirit is more in the seeking than in the finding, which is always tentative. Both science and history, however, at times become clogged with details, which must be put into some kind of order and perspective that makes possible a comprehension of the whole. Science has been successful in identifying areas of nature that seem more amenable to simplification and rigorous ordering than most of history. The human factor in history seems to make such technique forever unavailable to the historian. But science too has its intractable topics, such as the weather. Even now with powerful computers we have found prediction almost as elusive as ever, but we have found a kind of order by inventing "chaos theory."

When I was teaching elementary meteorology to the Navy primary flight cadets during World War II, one of them asked one day why they had to learn the patterns represented by the idealized cyclonic system with its neatly positioned warm front followed by the triangular warm sector, followed by the blue-line cold front; this and the sequence of cloud patterns, wind shifts, and temperature changes associated with these events as the cyclone passed by. "Why," he asked, "do we have to learn this model when we never see anything so neat and clear-cut on our daily weather maps?" A good question indeed! Why are we taught idealized forms that we never encounter in real life? In the particular instance I was lucky, for though far from being an experienced scientist or an experienced teacher, the answer came to me that I would still defend. We need that idealized form so that the real-life deviations from it can be identified and perhaps explained. By focusing on the deviations, the big problem has been divided into more manageable small ones, some of which may also initiate new research.

Newton's law of gravitation played that ideal role for planetary astronomy during the eighteenth century. Once a planetary orbit had been calculated, based on the ideal relation between a planet and the sun, any deviation from the calculated path was immediately seen as a challenge to the law and became a focus of concerned attention to seek an explanation, usually found in the gravitational effects of other planets. The most spectacular example of this was the discovery of the planet Neptune from the deviations in the orbit of Uranus.

Lavoisier's systematic application of the axiom of the conservation of weight played a similar role in his investigations. By assuming the constancy of the weight before and after chemical change, Lavoisier could know immediately that there was a point to be investigated or explained away whenever the before and after weights did not equate. Deviations from a well-chosen ideal are the red flags that gain our attention, that create the investigations that make science an ever expanding enterprise. As we shall see, Dalton's atomic theory gave chemistry just such a model that allowed the perfection of compositional representation.

Just as an ideal scientific law or theory can serve creativity in the investigation of nature, so will modern concepts of chemistry serve as our idealized standard against which we will assess the state of chemical thought in the seventeenth and eighteenth centuries. We will not use our modern knowledge as a judgment upon earlier inadequacies, but as a way of gaining our own comprehension of their problems and how they coped without modern concepts that we take for familiar truths. The principle of the conservation of weight was used functionally in a few cases in this period before Lavoisier made it explicit near the end of the eighteenth century. (See the example of Homberg in Chapter 4, p. 87.) This illustrates my point that our familiarity with well-established principles allows us to see how scientists of the eighteenth century were sometimes using modern principles implicitly before—sometimes well before—they became explicit.

When we look at eighteenth-century chemistry with a conscious twentieth-century perspective, the discerning eye will find many modern concepts hidden in the still inadequate language of the eighteenth century.

Many have long latent histories, their significance unrecognized. They seeped into the collective subconscious until some event or individual insight clarified relationships long familiar at the subliminal level, but not consciously recognized until the right moment.

Perhaps the concept the slowest to become verbally deliberate was that of expressing chemical composition in material rather than pre-existing metaphysical terms. The seventeenth-century textbook pattern introduced the traditional metaphysical elements in an opening chapter, followed by experimental procedures. These latter passages, however, show a growing tendency to ignore philosophy in favor of referring to the material components of material bodies. The same tendency is even more clearly visible in the papers published in the Paris Academy *Mémoires*. This practice found its most successful application with the neutral salts whose composition came increasingly to be represented in terms of the material acids and bases from which they could be made, and into which they could be resolved.

My theme traces concepts of chemical composition through its implicit stages in the eighteenth century until such concepts become subsumed and unified by the atomic theory. I recognize that the development of concepts of chemical composition is an idealized theme and that to some extent I am imposing on the scientists of the eighteenth century one of the bag of tricks we play on the dead. But it is a theme with lots of support from contemporary evidence from those chemists themselves, though only toward the end of the century is it evident that their implicit usage had become consciously and verbally explicit. Ursula Klein's recent work offers detailed examples consistent with my theme.[22]

The chemists of the eighteenth century, like their contemporary astronomers, believed that they were dealing with reality. The law of gravitation was a law of Nature, not a human invention. It is the same attitude among the chemists whose works we study here. They were looking for reality and often thought they had found it. Looking back from the advantage of two centuries of perspective we know that their realities are our history, that their faith was often misplaced. We have constructed a new reality from

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[22] See note 6 above.

what they left us, discarding some concepts, redefining others, adding new ones.

But are the truths we teach in the classroom today any more secure than those of the past? Are these truths discovered, or were they invented out of a need to gain some practical utility or intellectual satisfaction? Just as history is a bag of tricks we play on the dead, scientific theory is a bag of tricks we play on ourselves if we believe it represents nature as it *really* is. Here I am echoing the perspective of the late Richard Feynman, Nobel Laureate in Physics, who wrote that

> Scientific knowledge is a body of statements of varying degrees of certainty—some most unsure, some nearly sure, but none ***absolutely*** certain.
>
> Now, we scientists are used to this, and we take it for granted that it is perfectly consistent to be unsure, that it is possible to live and *not* know. But I don't know whether everyone realizes this is true. Our freedom to doubt was born out of a struggle against authority in the early days of science. It was a very deep and strong struggle: permit us to question—to doubt—to not be sure. I think that it is important that we do not forget this struggle and thus perhaps lose what we have gained. Herein lies a responsibility to society.[23]

How can we put all this insight to pedagogical advantage? A modern educator has said, "The most important single factor influencing learning is what the learner already knows."[24] But Mark Twain warned that "It ain't what you don't know that hurts you, it's what you know that ain't so."[25]

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[23] Richard Feynman, *What Do* ***You*** *Care What Other People Think?* (New York: Bantam Books, 1989), 245.

[24] Quoted by George M. Bodner, "Constructivism: A Theory of Knowledge," *J. Chem. Educ.* 63 (1986): 873-878, at 877.

[25] This aphorism, with slight variations in wording (e.g., "...know for certain that ain't so"), is usually attributed to Twain. He may have said some such thing, but he seems never to have written it down. It is attributed less often to Will Rogers, in whose published work it also cannot be found; and to Josh Billings, which ditto. Its attribution to Satchel Paige cannot be verified.

Its popularity is deserved.

Taking both these views seriously, let us look in the eighteenth-century history for "what they knew for sure that wasn't so." We will be better prepared to deal with the parallels we find in the twentieth-century classroom.

1

THE SEVENTEENTH CENTURY: CHEMISTRY COMES OF AGE

MODERN CHEMISTRY has its roots in many sources, but its historical continuity is most clearly traced in alchemy, which assumed its identity about 300 AD when ancient metallurgical practices gained a rationale from the ambient Aristotelian philosophical environment. The coloring of metals, in a sequence from black through white to yellow, provided the operational basis for illustrating the transformation believed to be indigenous beneath the earth as metals grew towards their teleological goal of perfection in the form of gold.[1] With time, these practices not only provided an ever-increasing knowledge of chemical behavior, but also gave credence to the possibility of actually achieving the goal of making real gold artificially. Belief that gold-making was really possible is evidenced by the fact that some rulers tried to suppress the practice of alchemy, being worried about the power gained by anyone who might be successful. Even greater evidence is provided by the success of those who gained more modest wealth by their false claims of successful alchemical practice. As early as the fourteenth century, Geoffrey Chaucer recounted the fraudulence of alchemy in his *Canon's Yeoman's Tale.*

Continued failure of the alchemists' labors in their efforts to transmute metals into gold may have forced them to expand their aims to provide

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[1] Arthur John Hopkins, *Alchemy, Child of Greek Philosophy* (New York: Columbia University Press, 1934). There has been a revival of historians' interest in alchemy in recent years. Note especially W.R. Newman and L.M. Principe, "Alchemy versus Chemistry. The Etymological Origins of a Historiographical Mistake," *Early Science and Medicine* 3 (1998), 32-65.

further justification for their efforts. The search for the philosopher's stone that would accomplish the transmutation of metals was paralleled by the search for the elixir that would provide eternal life. The alchemists' ability to perfect the colors and texture of metals made that practice into a ritual symbolizing the search for moral perfection. By the sixteenth century alchemy had gone about as far as it could go, without having achieved any demonstrable successes in its original aims.

Although alchemical practice became widespread after its introduction to the Latin West, it lacked significant organizational identity. Alchemy was never a part of the Scholastic corpus of the universities of the West. As long as alchemical philosophy and its goal of transmutation dominated the purposes of chemical practitioners, they necessarily worked in isolation, writing in symbolic and secret languages, designed as much to mislead as to enlighten.[2]

In spite of the failure of alchemy to reach its goals of transmutation, there was a positive gain from the fifteen centuries of alchemical practice. The accumulated knowledge of the particular behavior of metals and their compounds was considerable, and the invention of the art of distillation led to the isolation and characterization of alcohol and the inorganic acids. In its broadest application, distillation became the standard method of analysis by fire.[3]

In the sixteenth century alchemy received a new direction from Paracelsus, who urged the application of its knowledge and skills to the making and purification of chemical medicinals. This change also increased the focus on specific materials and their purity, reinforcing the distinctness of their separate identity, moving slowly toward the concept of chemical substance.

As chemical practice became increasingly associated with medicine, its practitioners became a part of a larger, open community. In the latter half

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[2] More detailed accounts of alchemy in the middle ages can be found in William R. Newman's work on Geber, *The Summa Perfectionis of Pseudo-Geber* (Leiden: Brill, 1991).

[3] Excellent readings on the history of distillation can be found in Allen G. Debus, "Fire Analysis and the Elements in the Sixteenth and the Seventeenth Centuries," *Ann. Sci.* 23 (1967), 127-147; and in Robert P. Multhauf, *The Origins of Chemistry* (New York: Franklin Watts, 1967).

of the sixteenth century a few chymists were giving extramural lectures in quasi-association with medical schools, though chemistry did not become a part of the medical curricula for another century. Chemical textbooks offering recipes for the preparation of medical drugs became quite common in the seventeenth century. When later in that century scientific societies offered even broader opportunities for the dissemination of specific knowledge, chemistry had become a distinct and well established activity. The iatrochemical practice acquired the name of "chymistry," while "alchemy" retained its earlier association with gold-making and fraud.

From a general historical perspective we can characterize Paracelsus and iatrochemistry as a kind of counter-culture of the sixteenth century, a revolt against the rigidity of the University curriculum and its isolation from experience. Similar movements can be found in religion, politics, the arts, and economics, the whole period being characterized by changes and upheaval that we call the Renaissance.

The concept of element, as viewed in the four-element Aristotelian tradition, was chiefly a metaphysical one, their names being chiefly symbols for the general properties the bodies themselves possessed. Paracelsus' *tria prima* of MERCURY, SULPHUR, and SALT, while still essentially metaphysical in meaning, carried a somewhat greater material implication than the four elements of Aristotelian tradition. The clearest evidence of an increased concern with materiality appears in the early years of the seventeenth century, when practicing iatrochemists felt obliged to add two more principles to the *tria prima* of Paracelsus. The standard practice of analyzing bodies by fire had taught them that both EARTH and PHLEGM (water) were almost always obtained in this procedure, and they were accordingly added to make a total of five principles. This pattern became established in the developing textbook tradition and was standard by the end of the seventeenth century.

Libavius and Didactic Chemistry

During most of its history, chemical and alchemical practice had not been much conducted at the universities or by members of the university community. There the Aristotelian tradition had become rigidly established in what became known as Scholasticism, basically a rationalized synthesis of Aristotelian natural philosophy and Christian orthodoxy. Alchemical practice lay outside that tradition, however well educated its practitioners may have been. Paracelsus (1493?–1541) himself had received considerable university training, but came to disdain much of what he had learned, especially the medical writing of the ancients still taught there. He publicly burned the writings of Galen and Avicenna to symbolize his rejection of ideas that had degenerated into dogma far removed from nature. In the Aristotelian tradition of the universities, the four elements still dominated what might have passed for chemical interest among the schoolmen, but little experimental activity seems to have taken place there.

This began to change toward the end of the sixteenth century when Andreas Libavius (1540?–1616) published his influential *Alchymia*. Libavius had received a medical degree from Jena, but spent most of his life teaching history and poetry and publishing books in philosophy and other widely diverse subjects while simultaneously practicing medicine as well. He was thus in a good position to present alchemical practical knowledge as a rational, Scholastic pedagogy. In its emphasis on chemical operations and the preparations of chemical drugs, his text represents the Paracelsian medical tradition. By elimination of most of the Paracelsian mystical cosmology and the avoidance of the obscure writing of the alchemists, *Alchymia* reflected the scholastic tradition. Hannaway, indeed, calls him "anti-Paracelsian."[4]

Libavius agreed with Paracelsus' reliance on nature rather than on authority as in the Scholastic tradition. He also shared Paracelsus' Christian commitment, but sought to discipline the wild-eyed extravagances of the chemico-religious ecstasy that made Paracelsian ideology into what amounted to a chemical counter-culture. By this Libavius achieved "the obvious divorce and independence of the textbooks from Paracelsian ideology."[5] Libavius in a sense virtually *invented* chemistry as a distinct activity by organizing it in a format congenial to contemporary educational traditions.

It is not clear why this demystified brand of Paracelsianism won favor

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[4] Owen Hannaway, *The Chemists and the Word: The Didactic Origins of Chemistry* (Baltimore: Johns Hopkins University Press, 1975), xi.

[5] Hannaway, *The Chemists,* x.

type of the new chemical texts that began to appear soon thereafter. Its pattern of organization was followed by nearly all texts of the seventeenth century, both French and German. All are chiefly descriptive and procedural, largely devoid of the Paracelsian cosmological mysticism and religion, but retaining the iatrochemical tradition of the making of chemical drugs from metals and other inorganic sources. The German texts of the seventeenth century are more academic than the French equivalents, "But all have a common form of organization: the definition of the art, a description of its instruments, a discussion of operations, followed by preparations—that is the basic structure of the *Alchemia*."[6]

Although Libavius' *Alchymia* provided the organizational pattern of the many texts that followed, it was Jean Beguin's *Tyrocinium Chymicum* (chemistry for beginners) that made the pattern popular.[7] Beguin's book was shorter, more simply written, and easily accessible. The first edition appeared in 1610 in Latin, with a French edition in 1615. There were many ever-larger editions and translations during the century. A French edition appeared as late as 1660 and an English one in 1669, based on the Latin of 1612.[8]

A brief examination of Beguin's book provides us with a pretty clear sense of the earliest days of the iatrochemical textbook tradition, which changed surprisingly little through the seventeenth century. Much of the earlier mysticism has faded away, and the emphasis on nature and laboratory experience is very evident in the full title of his book: *Chymical Essays Acquired from The Fountain of Nature and Manual Experience.* That the reader might not miss the message, Beguin followed his opening dedication to God with a quotation from Paracelsus.

> Paracelsus in his Book of Tincture of Natural things, Chapter 1, saith. First, you must Learn Digestions, Distillations, Sublimations, Reverb-

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[6] Hannaway, *The Chemists,* 155.

[7] Robert P. Multhauf, "Libavius and Beguin," in *Great Chemists,* ed. Eduard Farber (New York: Interscience Publishers, 1961). See also Multhauf, *Origins* for a good broad account of this period.

[8] Hélène Metzger, *Les doctrines chimiques en France du début du XVII à la fin du XVIII siècle* Paris, 1923) remains the basic reference work for this period.

> erations, Extractions, Solutions, Coagulations, Fermentations, and Fixations; and you must also know what Instruments are required for use in this Work; as Glasses, Cucurbits, Circulatory vessels, Vessels of *Hermes*, Earthen Vessels, Balneums, Wind Fornaces, Fornaces of Reverberation, and other such like: as also a Marble, Mortars, Coals &c. So may you at length proceed in the Work of Alchimy, and Medicine.
>
> But as long as you shall by Phantasie and Opinion adhere to feigned Books, you will be apt for, and Predestined to none of these.[9]

A few procedures and drug recipes had become standard by the early seventeenth century and these constitute the major contents of the book. They are arranged chiefly by process. Those materials prepared by distillation come first; water from vegetables, *aqua fortis* and other acids and spirits; then extracts and tinctures; and various calcinations, mostly of metals. The third book is briefly devoted to the preparation of quintessences, i.e. vaporous distillates. "Chymistry," he says, "is the Art of dissolving natural mixt bodies, and of coagulating the same when dissolved, and of reducing them into salubrious, safe and grateful Medicaments,"[10] thus illustrating both the nature of the science and its purpose. He defends metallic remedies, though admitting they "generally are more sharp, more corrosive, and more hot than is convenient, and also very strongly smell of the fire."[11]

To implement his definition of chemistry as the art of analysis and synthesis, Beguin adopts the MERCURY, SULPHUR, and SALT of Paracelsus' *tria prima,* as the principles or components of chemistry, and provides the traditional illustration of their escape from the burning of a piece of green wood. Analysis by fire was still the only method available. Note especially his claim for the superiority of evidence over rational argument:

> Moreover, every mixt body may be, and by us is resolved into these three principles (so according to the Pythagoreans, every thing, and all things are terminated in three) fixed in the sacred ternary. Although

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[9] Jean Beguin, *Tyrocinium Chymicum, or, Chymical Essays Acquired from the Fountain of Nature, and Manual Experience,* translated by Richard Russell from the Latin edition of 1612 (London, 1669).

[10] Beguin, *Tyrocinium,* 1.

[11] Beguin, *Tyrocinium,* 4.

> this might be proved by weighty reasons, yet ocular and evident inspection doth far exceed all these. Therefore, by example taken from the various kind of mixt things, we shall, for the benefit of young Beginners delucidate every thing. We will first begin with green Woods, which if you burn, there come forth a certain Wateriness, which is plainly unapt for taking flame; and if gathered when converted into flame, it is resolved easily into water (and by the same reason, to seek drink from a flame is not impossible) and this is called Mercury: then there goes forth an oleaginous substance easily inflammable, which resolved into vapours, if taken, will pass into Oil, and that is called Sulphur: at length a dry and terrestrial substance remains, which from the ashes, by the benefit of water is extracted and in the humid and cold it is dissolved, but in heat congealed, and it obtains the name of Salt. So milk contains a Sulphureous buttery substance, then Mercurial Whey, and at length saline Cheese, or Curds. In Eggs, the White exhibits Mercury, the Yolk Sulphur, the Skins and Shells Salt. In like manner from Linseed are drawn Oil by expression; Water by separation from the Oil; and Salt from the remaining feces, by extraction. [Cloves, Nitre, Sea Salt are taken through similar analyses.] Of Antimony a *Regulas* is made, which is the Mercury thereof; then a Red Sulphur conceiving flame; and at length a Salt, which is vomitive. And thus may you of all other things judge the same. But you are chiefly to note that none of the aforementioned principles can be found simple, and alone, that doth not participate with the other. For Mercury contains a Sulphureous and saline substance; Sulphur a Salt and Mercurial substance: And Salt an oleaginous and Mercurial substance.[12]

To the modern reader, this passage illustrates the absence of any sense of a distinct chemical species or substance. But we must remember that the dominant philosophy was not yet material; observed properties were not generated so much from material composition as by spiritual presence.

> But the said principles [i.e. mercury, sulphur, and salt], to speak properly, are neither bodies, because they are plainly Spiritual, by reasons of the influx of celestial Seeds, with which they are impregnated; nor Spirits, because corporeal, but they participate of either nature....[13]

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[12] Beguin, *Tyrocinium,* 22-23.

[13] Beguin, *Tyrocinium,* 21.

This conflation of spiritual and material is preserved in the ambiguity implicit in the names used for the three principles of chemical composition. SULPHUR could refer either to the common, yellow brimstone (throughout called *sulfur*, here) or to the principle that gave a body its oily texture or its imflammability. Similar ambiguities are associated with MERCURY and SALT, both of which have both material and spiritual referents. The conflation of spiritual and material expressed so clearly in Beguin persists in chemistry throughout the seventeenth and eighteenth centuries, in spite of the later Cartesian distinction. The road to a functional chemical materialism was long and slow.

Note also that the properties of identifiable bodies are seen to be blended from those of the composing principles. "Salt consists of divers parts; earthy, aqueous, and fiery. Its consistency and solidity, is from earth, its Liquidity from Water, and its biting property from fire."[14] It is almost as if Beguin was thinking of composition of properties rather than of a particular chemical material. The habit of viewing the properties of a material body as a blend of the properties of its ingredients continued through the eighteenth century, and was finally abandoned only after the integration of the atomic weight concept into chemical expression early in the nineteenth century.

An early step in the direction of viewing composition in material terms was taken by Beguin when he suggested that two empirically identified components might be added to the *tria prima:*

> [In addition to] these three principles truly active, there are two other substances which by Chymists are not admitted into the number of principles, because they are only as it were the Shells or Coverings of the said principles, and are destitute of all Hypocratick virtue; one of which is dry, a sandy Earth or lifeless ashes, and it is called damnate Earth, and *Caput mortuum*, endowed with no other virtues then, than drying and emplastick, and it is easily converted into Glass. The other

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[14] Beguin, *Tyrocinium*, 66.

> is humid and accidentally airy, viz. insipid and unsavory phlegm, which only moistens, without any other Energy or medicinal activity.[15]

In spite of the lack of spiritual powers, these two empirically originated bodies of earth and water became widely accepted into the list of principles as the seventeenth century progressed, finally making five the most common number for compositional theory. EARTH and WATER, however, were often distinguished from the others by being labelled passive compared to the active nature of MERCURY, SULPHUR, and SALT. That they were so accepted shows a significant move toward a materially based chemistry.[16]

Beguin's book initiated a series of similar books by other writers. All followed the pattern of opening with a brief introductory treatment of metaphysical theory followed by extended discussions of procedures and recipes for chemical drugs. As specific knowledge accumulated from their laboratory practice, later writers added large amounts of descriptive information without significant changes in the brief introductory sections on theory. Early in the century many of the books in France were written to accompany private lectures in Paris, and later to accompany public lectures at the Jardin du Roi. These latter were generally given by the King's personal physician, the first being a Parcelsian Scotsman named William Davidson whose name was gallicized to Guillaume Davisson (1593?–1669?). He was followed in that position in 1651 by Nicolas Le Févre (1615–1669) who published his text *Traicté de la chymie* (1660), and by Christoph Glaser (1615?–1672?) in 1660, publishing *Traité de la chymie* in 1663. The climax of this French textbook tradition came with Nicholas Lemery (1645–1715) whose *Cours de chymie* appeared in 1675. The pattern illustrated by these three writers became a tradition of French chemical outlook and practice that continued well into the eighteenth century. The many editions of

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[15] Beguin, *Tyrocinium,* 23-24. Partington credits the French physician Sebastian Basso with being the first to introduce the five principles group into chemistry in 1621. See J.R. Partington, *A History of Chemistry,* 4 vols. (London: Macmillan, 1962-1970), vol. 3, 7. But Beguin suggests the two passive elements in the French edition of his *Les élémens de chymie* (Paris, 1615), 47-48.

[16] Beguin was not the first to suggest the addition of earth and phlegm to the *tria prima,* but his is the first text in which it appeared.

Lemery's *Cours de chymie* remained the standard text in France for more than three quarters of a century, providing the major continuity that connects iatrochemistry with the so-called chemical revolution.

The spiritual cosmology that gave chemistry it philosophical order was derived from Paracelsus, and most clearly presented in Le Févre's text. Because vestiges of it survive well into the next century, we need to provide a brief exposition here. Le Févre's reverence for Paracelsus is revealed in his reference to him as "our *German Trismegistus,*"[17] a symbolic identification with the ancient traditional founder of alchemy, "thrice-great Hermes."

Le Févre was trained as a pharmacist and his book, according to its dedication, is devoted "to the study and disquisition of the Contexture and Compound, and of the resolution of Natural bodies: whereby these wonderful Virtues, and specifical Properties hath hidden in their Center, may be discovered and laid open." But such practical aims are placed within a more cosmological setting, for "Chymistry is nothing else but the Art and Knowledge of Nature itself," a residue of Paracelsian chemical cosmology. Chapter 1 treats "Of the Universal Spirit," that truly creative essence that generates all the particular bodies found in the corporeal world. In Chapter 2 he treats "Of several Substances which are found after the dissolution and Anatomy of the Body or Compound." Le Févre very explicitly continues the dualistic pattern of spiritual and corporeal that we have already seen in Beguin:

> Chymists assign to Nature two Elements, in their description of them; *viz.,* the one Spiritual, the other Corporal; the virtue of the one being hid in the bosom of the other.
>
> [The] "universal spirit," the creative cause of all things, has many names. Vital substance, a Spirit of life, Light, Balsom of life, Vital Mummy, Natural heat, Univeral Spirit, Mercury of life.... These are the principal appellations. [Paracelsus taught us] that the strength of Nature is not included in the mortal and corruptible body; but that it is to be sought in that wonderful seed which hides it self under the

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[17] Nicholas Le Févre, *A Compleat Body of Chymistry ... rendered into English by P.D.C., Esq., one of the gentlemen of His Majesties Privy-Chamber.* (London, 1664), 14.

> shade of the body, who of it self hath no strength or virtue, but fetches it all from that seminal spirit which it contains;...[18]

> [The universal spirit] hath a threefold denomination; for in respect to its natural heat and fire, it is called Sulphur; in respect to its moysture, which is the food and aliment of this fire, Mercury; and finally, in respect to the radical drought, which is, as it were, the knot and cement of the fire and moysture, it is called Salt; which we shall clear more particularly when we treat hereafter of the three Principles by themselves.[19]

> The Heaven doth by the assistance of his Stars, communicate unto her heavenly, spiritual and invisible virtue, which descends first unto the Air, where it beginneth to assume a kinde of body; the Air sends it into the Water or the Earth, where this celestial virtue and influence beginneth to operate more materially, and associate it self to matter, thereby to frame a body to it self by means of those various natural fermentations which are the cause of alteration in sublunary things.[20]

Thus the traditional elements of Aristotle become for the iatrochymists the matrices of creation rather than the components of corporial bodies of chemical interest.

> The chief use which the *Chymists* do assign to this Element [air], is, that it serves as Matrix to the Universal Spirit, which doth begin in it, to be some bodily Idea before it be wholly corporified in the Elements of Water and Earth, who produce Mixed Bodies, that are as fruits of the said Elements.[21]

WATER is the second general Matrix, "containing in it self many particular Matrixes." But the EARTH is the source of most of the bodies of interest to the chymist.

> [If the Universal Spirit] meet with a Vitriolic Matrix, it turns it self to Vitriol; if with Sulphur, it becomes Sulphur, and so of the rest, and

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[18] Le Févre, *A Compleat Body,* 32.

[19] Le Févre, *A Compleat Body,* 14-15.

[20] Le Févre, *A Compleat Body,* 44.

[21] Le Févre, *A Compleat Body,* 36.

> that by virtue and efficacy of several natural fermentations: In a Vegetable Matrix, it become Plant; in a Mineral, Stone, Mineral, Metal; in an Animal, whether living or not living, it produces an Animal, as is daily seen in the generation of such creatures as are produced by the corruption of some Animal or other Mixt; as for Example, Bees degenerated out of young Bulls flesh; and Worms out of the corruptions of several Fruits....[22]

No chymist after Le Févre dealt so fully with the spiritual aspects of the universal spirit and its interaction with the matrices, but their language makes it clear that their thoughts are still working within this same spiritual frame, well into the eighteenth century, especially in the influential work of Nicholas Lemery.

In the typical seventeenth-century text these discussions of spiritual chemical cosmology were confined to short, introductory chapters followed by the extensive descriptions of medicinal preparations. These iatrochemical texts served strongly to establish a clearly recognizable community of chymical practitioners which we can properly call "Chymists." They continued in the practice of drug preparations within the rationale of cosmic order and creativity, but with a growing range of descriptive, material information.

This seventeenth-century iatrochemical tradition gained its coherence from its Paracelsian sources of their definition of chymistry as the analysis and recombination of bodies to make purer and more efficacious drugs. Their knowledge became a part of public knowledge in the form of public lectures and textbooks. The appearance of scientific academies toward the end of the century provided yet another and quicker vehicle for the dissemination of chymical knowledge through their periodical publications.

Note that all three of these authors, along with Beguin earlier in the century, use the term "bodies" when referring to chemical materials, for they lacked the concept of chemical substance as having a fixed, quantitative composition, hence in effect everything was, by modern standards, a mixture. Indeed, as long as the conception of composition was primarily

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[22] Le Févre, *A Compleat Body,* 38-39.

metaphysical, quantitative composition was impossible. From a modern perspective, it was the idea of a material element that was still lacking.

The difficulty in gaining useful compositional knowledge at this early stage was neatly expressed by Paul Walden. "In the early days every new *compound* body represented a new riddle."[23] The only method of analysis available was that by fire, and the products were necessarily assumed to be simpler than the body that had been heated and perhaps to be the actual components of that body. This has been the most naive assumption as we saw presented and argued by Beguin.

Partington suggests the importance of Le Févre's role was in transmitting knowledge of German chemistry into France and England, chiefly through his influence on Glaser, who was his student, and Lemery, who was briefly a student of Glaser.[24]

In the opening chapter of his *Traité de la chymie* in 1663, Christoph Glaser proclaims the same empirical emphasis as Beguin and Le Févre, but he wrote more easily and clearly with less of the spiritual context.

> As for myself, who profess to say nothing but what I know, and to write nothing but what I have done, I propose only in this little *Treatise,* to publish a short and easy method for the happy attainment of all the most necessary preparations of Chymistry.[25]

He offers several names for the chymical art, including "Spagyrick," a word credited to Paracelsus from Greek (supposedly), meaning to take apart and put together; "pyrotechnia" from fire being the chief agent of operations; "Hermetic" from Hermes Trismegistus (not the Greek god Hermes but a quite different being), the most famous but mythical practitioner of the art. He finally states that he will stick with "chymistry," but in his definition he comes closest to the implications of the term Spagyrick when he says that chymistry is "A Scientific Art, by which one learns to dissolve

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[23] Paul Walden, *Salts, Acids, and Bases: Electrolytes—Stereochemistry* (New York: McGraw-Hill, 1929).

[24] Partington, *History of Chemistry,* vol. 3, 19.

[25] Christophe Glaser, *The Compleat Chymist,* translated from the 4th French edition (London, 1677), 1.

bodies, and draw from them the different substances of their composition, and how to unite them again, and exalt them again to an higher perfection."[26]

Glaser here illustrates the pattern expressed by most seventeenth-century chemists, the age-old idea that chemistry is the science of analysis, and the iatrochemical goal of reuniting the components into medicaments of greater purity and perfection than can be found in nature. The implied mysticism in this statement is made explicit when Glaser claims chymistry to be

> the key which alone can unlock to all Naturalists the door of Nature's secrets; by reducing things to their first principles; by giving of them new forms, and by imitating Nature in all its productions and Physical alterations.[27]

The climax of French iatrochymistry was the work of Nicholas Lemery, whose *Cours de chymie* of 1675 will be treated in Chapter Three. But two other chymists of the mid-century deserve comment. Le Févre identified them as "The *subtil van Helmont,* and the *laborious Glauber,* the two Beacons and Lights which we are to follow in the Theory of Chymistry, and the best practice of it."[28] These two, Johann Glauber and Joan Baptista van Helmont, are significant exceptions to the textbooks tradition of seventeenth century chemistry. Both maintained an extraordinary emphasis on experimental observations, even while returning to mystical philosophical positions.

Johann Rudolph Glauber (1604–1670) was born in Germany, but the Thirty Years' War (1618–1648) that so devastated the German states led him to seek more peaceful conditions in Holland where he spent all but five of his last thirty years. Unlike most of the other well-known chemical workers of the seventeenth century, Glauber did not have a university education, and his chemical activities were directed toward technical and commercial applications as well as medical ones. He took his philosophical stance from an even earlier tradition than Paracelsus, that of alchemy itself. His devotion

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[26] Glaser, *Compleat Chymist,* 2.

[27] Glaser, *Compleat Chymist,* 3.

[28] Le Févre, *A Compleat Body,* 3.

to the ideals of alchemy he kept secret, and attempted to express them through the perfection of the material world. By tying "the hermetic art ... to specific aspects of laboratory practice ... he interpreted the symbols of alchemy so concretely as to destroy their esoteric appeal."[29] His skills in devising and manipulating new apparatus led to significant improvements in the preparations of basic chemicals and made possible preparations not previously accomplished.

His writings are mines of particular information and his works are more frequently quoted and referred to by later writers than any of the textbook writers. His *New Philosophical Furnace* (1646–1649) takes its title from the descriptions of new designs that allowed the achievement of much higher temperatures than before. Of particular note is the production of the acid spirit of marine salt (hydrogen chloride) by heating the sea salt (sodium chloride) with potters clay, a much cheaper mode of production than the heating of marine salt with vitriol, though requiring a higher temperature. He examined different methods of producing each of the other mineral acids as well and recognized loosely that the products were similar though the methods of preparation were different. As we shall see later, it was not until well into the next century that it became common to recognize that different procedures might yield identical substances.

Glauber, perhaps more than any other seventeenth-century chemist, was responsible for greatly increasing the practical knowledge of salts. Walden notes first, "his efforts and his success in increasing the number and kinds of salts"; but more importantly that his work initiated the beginning of a conscious recognition of the "purity and individuality, that each salt has its own type and properties and always exhibits these properties, no matter how it may have been prepared." Much of Glauber's work also exhibits a clear but implicit recognition that salts are composed of "two chemically opposite parts—an alkali (base) and an acid." Glauber's insights about the idea of constancy of chemical type, i.e. chemical substance, must be viewed as implicit in the manner of his manipulation of the materials.[30] An ex-

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[29] Kathleen Ahonen, "Johann Rudolph Glauber," *Dictionary of Scientific Biography*, vol. 5, 423.

[30] Walden, *Salts*, 43-45.

plicit definition of a chemical substance hardly appears before Bergman a century later. But the explicit recognition of the nature of salts was to come soon from the consequences of van Helmont's acid-alkali theory of physiology.

Joan Baptista van Helmont (1579–1644) was the last serious Paracelsian to retain significant allegiance to the master's religious cosmology. Born into a well-to-do Flemish family, he travelled widely, received his MD in 1609, but spent most of his life in his native Netherlands, at that time still under the influences of Spain and the Spanish Inquisition. He was, of all the followers of Paracelsus, both the most religious and the most empirical, the most devoted researcher directly into nature's mysteries. Like so many workers of the sixteenth and seventeenth centuries he was dissatisfied with the traditional curricula he knew from his university education, and reflected in common with many others the determination to learn of nature from nature herself, hoping to rise above the "'dung' of traditional learning," rejecting what he called the "useless logic" of the schoolmen. Not surprisingly, Helmont was long in trouble with ecclesiastical authorities and was once briefly imprisoned (four days), and under house arrest for two years, for having written the heretical contents of a "monstrous pamphlet."[31]

In Helmont's religious cosmology, WATER was the ultimate material of the world, the first matter to exist.

> The spirit of the Lord hovered on the waters, and from water every object takes its origin.... Water as such is "empty"; it is a general medium which precedes all differentiation. [On the other hand] all bodies are the fruit of water.[32]

This view is illustrated by Helmont's famous willow tree experiment. A small willow tree weighing five pounds was planted in a tub of earth weighing 200 pounds. For five years nothing was added to the soil but water. At the end of that time, the tree had grown to weigh more than 150

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[31] Walter Pagel, *Joan Baptista van Helmont, Reformer of Science and Medicine* (New York: Cambridge University Press, 1982), 12.

[32] Pagel, *Helmont*, 61.

pounds, while the earth had lost no weight at all. Van Helmont could conclude that the willow was made of nothing but water.[33]

Like Paracelsus, Helmont sought to obtain the spiritual essence of bodies, analyzing the smoke that lingers after combustion. In burning more than sixty pounds of coal, he obtained only about one pound of solid ashes, the rest having gone up in smoke. This smoke, he thought, was not like ordinary air or water vapor, but a distinct, previously unknown entity. He invented the term "gas" derived from the Greek *χάος chaos,* to present what he held to be the essence of a body.

Though Helmont's real interest in gases came from his religious views, he nonetheless recognized something of their materiality, for he reported that the appearance of a gas often produced destruction of the equipment, and he spoke of the "wild spirit" that could not be contained. Because he had no way of collecting and handling these gases, he could not explicitly characterize them. He was able to recognize that they were different from ordinary air, and in some cases different from each other. He obtained one or another of these 'gases' from many sources, getting most frequently what we now know to have been carbon dioxide, but also probably sulfur dioxide, carbon monoxide, chlorine, and methane.[34]

Perhaps because of the mystical religious context in which he embedded his descriptions of gases, his discoveries made little contribution to the later development of pneumatic chemistry. His term "gas" became standard usage only late in the next century.

Helmont was very much an experimental chemist, devising improved ways for the preparation of the mineral acids. He recognized that a metal dissolved in an acid has not been destroyed for the original metal can be obtained once again from the solution. Similarly, he recognized that when a piece of iron is placed in a solution of copper in nitric acid, the iron is not transmuted into copper as had been widely believed. These and other views he shared with some of his contemporaries, but he remains an enigmatic figure, both ahead of many contemporaries in his detailed knowledge

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[33] J.R. Partington, *A Short History of Chemistry,* 3rd ed. (London: Macmillan, 1957), 51-52.

[34] Partington, *History of Chemistry,* vol. 2, 227-234.

of material things, yet deeply immersed in a philosophy more characteristic of a century earlier than his own.

Chief of Helmont's chemical discoveries in medicine is that of the acid nature of the stomach juices, not only of humans but also of many other animals. His suggestion that acids were the initiating power of digestion and other bodily functions was turned into a universal theory of acid-alkali physiology by his pupils Sylvius and Tachenius.[35] This unifying theory of animal physiology involved a more material conception than the four humors of medical tradition, and gave new emphasis to the acid-alkali reaction for chymistry through the close relationship between medicine and iatrochymistry. As we shall see, the acid-alkali relationship initiated the most important organizing relationship of chemical knowledge in the eighteenth century, that of neutral salts.

Iatrochymistry had become a firmly established scientific activity by the end of the seventeenth century. Although most of the seventeenth-century chymists appealed to nature as the basis of belief, yet the science had not yet achieved a clear operationally-based rationale for the organization of the rapidly growing experiential knowledge of chemical behavior. Though able to describe their work with material bodies, the spiritual and empirical duality of their vocabulary reflects the ambiguity of their compositional conception still found in Nicholas Lemery's *Cours de chymie* of 1675, which climaxed the French chemical textbook tradition. This group of chymists nonetheless established the basis for the progress that led to the eighteenth-century chemical revolution.

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[35] Marie Boas, "Acid and Alkali in Seventeenth-Century Chemistry," *Arch. Int. d'Hist. Sci.* 9 (1956): 13-28.

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ROBERT BOYLE:
THE SCEPTICAL CHYMIST

> The doctrine of the four elements never led to any attempt actually to analyse bodies into their supposed elements: for composition was inferred from the resemblance of the qualities, not from the separate exhibition of the ingredients; the supposed analysis was, in short, a decomposition of the body into adjectives, not into substances.
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> William Whewell, *History of the Inductive Sciences*[1]

THE RISE OF A MECHANICAL PHILOSOPHY in the seventeenth century, climaxed by Isaac Newton's *Principia* in 1687, reflects a large scale revolt against the traditional Aristotelian system of qualities and forms. It shows up in different ways in different areas of intellectual endeavor, but in general the mechanical view is a much more materialistic view than the one it was replacing. The leading advocate of this philosophy in the chemical world was Robert Boyle (1627–1691), the seventh and youngest son of the kingdom's richest man, the first Earl of Cork. As the youngest, he had neither political obligations nor financial concerns and was able to devote his life to the experimental and intellectual investigation of nature and the ways of God that he found therein. In his will he provided funds for a series of lectures to be given in defense of Christianity against unbelievers. He was deeply involved in the founding of the Royal Society of London in 1662 and remained active in its affairs. His range of interests was very wide, finding the mechanical philosophy preferable in nearly every area of

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[1] W. Whewell, *The History of the Inductive Sciences from the Earliest to the Present Time*, 3rd ed. (New York, D. Appleton & Co., 1858), vol. 2, 261.

scientific investigation. Chemistry was his favorite science and he persisted in it even though his efforts to mechanize its theory were unsuccessful.

Robert Boyle's *Sceptical Chymist* (1661) has long been identified with the beginning of modern chemistry, and Boyle himself has been called the Father of modern chemistry. But paternity is more easily claimed than established, and we should take him at his own word and see him not as the creator of modern chemistry but as the "Sceptical Chymist," the critic of the chemical thought of his time. The old way of thinking about things chemical was two thousand years old, and seventeenth-century thought was drifting away from Aristotelian patterns. The revival of ancient atomism and its seventeenth-century development led to a vigorous mechanical philosophy epitomized in the writings of René Descartes. Boyle's own philosophical preference was distinctly mechanical, but it was his direct frontal attack on traditional scholastic thought and its Renaissance-modified derivatives that helped clear the way for chemical practice to develop its own indigenous ways of explaining and describing chemical behavior.[2] In spite of Boyle's obvious mechanical preferences, recent studies have shown his belief in some supernatural, non-mechanical forces.[3]

The *Sceptical Chymist* is written as a dialogue, in which Boyle presented his own views through Carneades. The attack centered on the dubious reality of both the four elements of Aristotelian tradition and the Paracelsian *tria prima,* and it challenged the validity of the fire analysis that produced them. As a mechanical philosopher, a believer in the reality of matter and in that sense a materialist, he insisted that a component part of a body ought to be demonstrable—it ought to be obtainable in some visible, palpable form. Furthermore, he asks, how does it happen that there are just four, or three, or any determinate number of fundamental bodies, when so many analyzed bodies yield sometimes fewer than three or more than five? Some, such as gold and silver, show no signs of decomposition at all. And Boyle vigorously raises the question of whether the results may not be created by the fire rather than simply being liberated by it.

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[2] A fine summary of Boyle's chemistry can be found in Marie Boas, *Robert Boyle and Seventeenth-Century Chemistry* (Cambridge & New York: Cambridge University Press, 1958).

[3] Antonio Clericuzio, "A Redefinition of Boyle's Chemistry and Corpuscular Philosophy," *Ann. Sci.* 47 (1990): 561-589.

> Notwithstanding the subtle reasonings I have met with in the books of the peripatetics, and the pretty experiments that have been shewed me in the laboratories of chymists, I am of so diffident or dull a nature, as to think that if neither of them can bring more cogent arguments to evince the truth of their assertions than are wont to be brought, a man may rationally enough retain some doubts concerning the very number of those material ingredients of mixt bodies, which some would have us call elements and others principles.[4]

Boyle says these important questions have been obscured by the imprecise language in which both the peripatetics (Aristotelians) and the chymists (Paracelsians) have clothed their writings. They manipulate words without insight or understanding. Just as knowing the letters of the alphabet is not enough to ensure literacy, so playing with the esoteric words of alchymy does not assure understanding. Their imprecise language reflects their imprecise thinking. Carneades hopes by his efforts to draw "the chymists' doctrine out of the dark and smokie laboratories" so that "judicious men" might see how inadequate are the proofs offered for their *tria prima,* and thus disbelieve them; or to oblige the "abler chymists" to speak plainer than they have done.[5] Eleutherius, a neutral participant in the discussion, says to Carneades

> I am not a little pleased to find that you are resolved on this occasion to insist rather on experiments than syllogisms. For I, and no doubt you, have long observed, that those dialectical subtleties, that the schoolmen too often employ about physiological mysteries, are wont much more to declare the wit of him that uses them, than increase the knowledge or remove the doubts of sober lovers of truth.[6]

The agreed subject of the discourse is "the number of the elements, principles, or *material ingredients* of bodies."[7] By focusing on the material ingredients Boyle may have been moving the reader toward his own me-

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[4] Robert Boyle, *The Sceptical Chymist* (New York, Everyman ed., 1949), 15. Carneades speaking.

[5] Boyle, *Sceptical Chymist,* 6.

[6] Boyle, *Sceptical Chymist,* 17.

[7] Boyle, *Sceptical Chymist,* 13, my emphasis.

chanical position. But the concern of the chymists at that time was already largely focussed on material bodies, for their text books were chiefly collections of recipes for the preparations of real drugs. Whatever the residue of Platonic conception that remained in the minds of chemists in the seventeenth century, and we find evidence of it in their language, their operations were consistently with real material bodies, stones, earths, acids, metals, and salts, and the distillates of fire analysis.

Boyle's discussants all agreed that "elements" and "principles" have the same meaning, specifically, "those primitive and simple bodies of which the mixt ones are said to be composed, and into which they are ultimately resolved."[8] Themistius, the Aristotelian, justifies the peripatetic view by asserting that "it is much more high and philosophical to discover things *a priore* than *a posteriore.*" For this reason the peripatetics have "not been very solicitous to gather experiments to prove their doctrines, contenting themselves with a few only, to satisfy those that are not capable of nobler conviction. And indeed they employ experiments rather to illustrate than to demonstrate their doctrines...."[9] He offers at this point the familiar example of the burning of the green stick, which produces the four peripatetic elements of earth, water, air, and fire.

> [I]f you but consider a piece of green wood burning in a chimney, you will readily discern in the disbanded parts of it the four elements, of which we teach it and other mixt bodies to be composed. The fire discovers itself in the flame by its own light; the smoake by ascending to the top of the chimney, and there readily vanishing into air, like a river losing itself in the sea, sufficiently manifests to what element it belongs and gladly returnes. The water in its own form boiling and hissing at the ends of the burning wood betrays itself to more than one of our senses; and the ashes by their weight, their firiness, and their dryness, put it past doubt that they belong to the element of earth.[10]

Carneades responds by claiming that no one has ever proved that the products of such an analysis *must* have been pre-existent in the body analyzed. But Philoponus gives the example of the separation of an alloy of

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[8] Boyle, *Sceptical Chymist,* 18.

[9] Boyle, *Sceptical Chymist,* 20.

[10] Boyle, *Sceptical Chymist,* 21.

lead and gold; "can any man doubt that sees these two so differing substances separated from the mass, that they were existent in it before it was committed to the fire?"[11] Carneades replies that he might find the example persuasive if the peripatetics would show nature combining the fire with "the other three elements" as the refiners mix the lead and the gold. After all, Carneades continues,

> it must be first proved, that the fire does only take the elementary ingredient asunder, without otherwise altering them. For else 'tis obvious that bodies may afford substances which were not pre-existent in them; as flesh too long kept produced maggots, and old cheese mites, which I suppose you will not affirm to be ingredients of those bodies.[12]

Implicit in Boyle's argument here is that the apparent composition of any body is best confirmed by the cycle of analysis and synthesis, i.e., that products of analysis should be rejoined to produce the original body. That he did not feel compelled to state such a principle directly suggests that its validity was generally recognized. The difficulty was in applying it, for there was still no recognition of which material bodies were the simple ones in terms of which composition could be expressed. Here Boyle was utilizing the analysis/synthesis cycle to criticize and challenge the traditional claims, rather than to support a compositional scheme of his own, for he had none.

Throughout the book Boyle applies these basic arguments to ever more specific claims of his opponents. He criticizes the peripatetics for their lack of experimentation, their refusal to treat directly with Nature. They claim to know the truth *a priori,* but they are just playing with words. He praises the chymists for treating directly with Nature, but criticizes them for too frequently simply finding what they expect to find.

Boyle was not the first to challenge the validity of the four elements and the *tria prima;* many of his arguments date back at least a century before, and many of them come right out of the writings of van Helmont, for whom Boyle had great respect.[13] But his sustained attack on these

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[11] Boyle, *Sceptical Chymist,* 24.

[12] Boyle, *Sceptical Chymist,* 24-25.

[13] Charles Webster, "Water as the Ultimate Principle of Nature: The Background to

doctrines and his great reputation served as a caution for later chemists.

Boyle was extremely skeptical that chemistry was on the right track at all. However, though clearly expressing a strong preference for a mechanical chemistry, he had no effective system to offer in the place of the philosophies he attacked. In his mechanical view there was only one kind of matter, though it came in particles of various sizes and shapes. Any particular body owed its properties to the arrangement of these particles of which it consisted. Real bodies which showed themselves to be stable and frequently met with in experimentation, obviously had stable arrangements, but this was an argument *ex posteriore,* and the mechanical view provided no way to predict this or any other behavior of real bodies.

The transformation of one substance into another was a matter of rearrangement of the particles. In principle this would permit the transformation of one metal into another just as properly as any other more familiar chemical change. Indeed it might be said it permitted the transformation of anything into anything else, and Boyle at one time claimed to have converted a little gold into silver, a claim only a rich man might feel free to make.[14]

On a more explicit chemical consideration, this view raises the question of whether there are any such things as elements. As Boyle writes near the end of the *Sceptical Chymist,*

> [T]hough it may seem extravagant, yet it is not absurd to doubt, whether, for ought has been proved, there be a necessity to admit any elements, or hypostatical principles, at all....
>
> And to prevent mistakes, I must advertise you, that I now mean by elements, as those chymists, that speak plainest, do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved; now whether

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Boyle's *Sceptical Chymist," Ambix* 13 (1966): 96-107; Alan G. Debus, "Fire Analysis and the Elements in the Sixteenth and Seventeenth Centuries," *Ann. Sci.* 23 (1967): 127-147.

[14] See Lawrence M. Principe, *The Aspiring Adept. Robert Boyle and his Alchemical Quest* (Princeton, New Jersey: Princeton University Press, 1998). This provides a reading of *The Sceptical Chymist* that is distinctly sympathetic toward alchemy.

> there be any one such body to be constantly met with in all, and each, and those that are said to be elemented bodies, is the thing I now question.[15]

Parts of this passage have often been quoted to support a claim for Boyle as the first to give a modern definition of an element. Yet it is perfectly clear from Boyle's own words that he saw this definition not as original, but as the commonly accepted one. It is ironic that Boyle, who doubted the existence of *any* elements, has so often been given the credit for the modern definition of that concept.

It is difficult to assess accurately the significance of Boyle's criticism of the chymical philosophy of his day, for in fact his contemporaries were already focusing increasingly on operational concepts. His own contribution to chemical experimentation was both extensive and competent, but the mechanical philosophy within which it was often "explained" never produced more than *ad hoc* explanations. His most significant discovery, for the theme of this study, is the use of vegetable colors as a test for acid and alkali.[16] Though he clearly recognized the usefulness of such tests, the application of "indicators" did not become at all systematic until about the middle of the eighteenth century. Boyle also utilized specific tests for the presence of specific ingredients, e.g., oak galls for the presence of iron. Boyle's chemical writings contain a wealth of specific information and his experiments and discoveries are frequently cited by chemists of the next century.

Boyle's Philosophical Caution

Boyle became known and admired for his philosophical temperance, his freedom from what in the next century came to be called "spirit of system," that commitment to a particular philosophy into which everything was made to fit. It is worth including here a quotation from the Introduction:

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[15] Boyle, *Sceptical Chymist,* 186, 187.

[16] William Eamon, "New Light on Robert Boyle and the Discovery of Color Indicators," *Ambix* 27 (1980): 204-209; A. Albert Baker, "A History of Indicators," *Chymia* 9 (1964): 147-167.

> [I]t has long seemed to me none of the least impediments of the real advancement of true natural philosophy, that men have been so forward to write systems of it, and have thought themselves obliged either to be altogether silent, or not to write less than an entire body of physiology ... it not unfrequently happens, that ... a writer, to vent some few peculiar notions or discoveries of his own, presumes to write a whole body of philosophy.[17]

Boyle was consistent with this cautious position even with regard to the mechanical philosophy which he so obviously preferred. He avoided the logical fallacy so common in the argumentation of his time, that of assuming that *any* explanation is *the* explanation, an attitude that might be called the "rational imperative." His attitude is very clear in the following passage:

> If I took upon me to demonstrate, that the qualities of bodies cannot proceed from (what the schools call) substantial forms, or from any other causes but mechanical, it might be reasonably enough expected, that my argument should directly exclude them all. But since, in my explications of qualities, I pretend only, that they may be explicated by mechanical principles, without enquiring, whether they are explicable by any other; that, which I need to prove, is, not that mechanical principles are the necessary and only things, whereby qualities may be explained, but that probably they will be found sufficient for their explication.[18]

In the *Sceptical Chymist* Boyle points out that in nature there are always many possible explanations, and it is fallacious to argue the case for one explanation by the exclusion of another. He could present the mechanical view only as one possibility among many. It is, he says,

> a very common mistake amongst most disputants, who argue as if there could be but two opinions concerning the difficulty about which

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[17] Robert Boyle, *Certain Physiological Essays* (London, 1661), 3-4.

[18] From the "Advertisement" to Robert Boyle, *Mechanical Origin and Production of Qualities,* as given in the source-book, Marie Boas, *Robert Boyle on Natural Philosophy* (Bloomington, Indiana: Indiana University Press, 1965), 234.

> they contend; and consequently they inferr, that if their adversaries opinion be erroneous, their's must needs be the truth; whereas many questions, and especially in matters physiological, may admit of so many differing hypotheses, that 'twill be very inconsiderate and fallacious to conclude (except where the opinions are precisely contradictory) the truth of one from the falsity of another. And in our particular case 'tis no way necessary, that the properties of mixt bodies must be explicable either by the hermetical, or the Aristotelian hypothesis; there being divers other and more plausible waies of explaining them, and especially that, which deduces qualities from the motion, figure, and contrivance of the small parts of bodies; as I think might be shewn, if the attempt were as seasonable, as I fear it would be tedious.[19]

Because his mechanical philosophy provided no adequate intellectual basis by which chemistry could be restructured, Boyle was compelled when discussing specific chemical bodies to use the familiar vocabulary and attendant concepts of the Paracelsian chymists:

> [S]uspecting the common oyle of vitrioll not to be altogether such a simple liquor as chymists presume it, I mingled it with an equal or a double quantity (for I tryed the experiment more than once) of common oyle of turpentine, such as together with the other liquor I bought at the drugsters. And having carefully (for the experiment is nice, and somewhat dangerous) distilled the mixture in a small glass retort, I obtained according to my desire (besides, the two liquors I had put in) a pretty quantity of a certaine substance, which sticking all about the neck of the retort discovered itself to be sulphur, not only by a very strong sulphureous smell, and by the colour of brimstone; but also by this, that being put upon a coal, it was immediately kindled, and burned like common sulphur. And of this substance I have yet by me some little parcells, which you may command and examine when you please. So that from this experiment I may deduce either one, or both of these propositions, that a real sulphur may be made by the conjunction of two such substances as chymists take for elementary, and which did not either of them apart appear to have any such body in it; or that oyle of vitrioll though a distilled liquor, and taken for part of the saline

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[19] Boyle, *Sceptical Chymist*, 175.

> principle of the concrete that yeelds it, may yet be so compounded a body as to contain, besides its saline part, a sulphur like common brimstone, which would hardly be itself a simple or uncompounded body.[20]

Boyle calls oil of vitriol and oil of turpentine simple bodies by the standards of the contemporary chymists because they are distilled from solids, distillation being but a form of analysis by fire. Note that he identifies sulfur as a distinct body by smell, color, and flammability. Note also that he dismisses without explanation the idea that sulfur itself might be a *simple* body. Is he here speaking only for the chymists whose views he is refuting, or does he share this assumption? He seems to include himself in this dismissal of such a thought. How surprised Boyle would be to learn that the sulfur is indeed a simple body and the central ingredient of the oil of vitriol! The passage illustrates the state of thinking available at that time concerning elements and simple bodies, the component bodies of "mixts."

The Absence of Air from Chemistry

By the end of the seventeenth century, the old traditional elements from Aristotle had been either abandoned by the new Paracelsian iatrochymists or absorbed under new terminology. Paracelsus' *tria prima* of MERCURY, SULPHUR, and SALT became the new set of elements or principles, each more narrowly focused on a single property than had been the four elements of Aristotle. Yet the *tria prima* clearly derived from the older tradition. SALT assumed the role of the Aristotelian EARTH, while SULPHUR took that of FIRE. The MERCURY of Paracelsus rather absorbed the characteristics of both AIR and WATER, becoming the carrier of all spiritual, i.e., volatile qualities of the products of fire analysis. MERCURY also carried the basic metallic properties from the mercury/sulphur theory of metals brought to the Latin West from Arabic alchemy.

With the attention of the seventeenth-century chemists increasingly given to material bodies, AIR seems to have dropped out, as an "airy nothing" not worthy of further consideration. It might not have been missed

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[20] Boyle, *Sceptical Chymist,* 122.

except for the discovery of what nothing was really like, that is, the vacuum: the total absence of air above the mercury in a Torricellian barometer, a device developed earlier in the century. The Aristotelian tradition denied the possibility of a vacuum, though the ancient atomic philosophy made it an absolute necessity. René Descartes (1596–1650), the epitome of the mechanical philosophers of the seventeenth century, was a thorough corpuscularian who nonetheless denied the existence of space without matter. Matter's only intrinsic property was extension, and extension without matter (a true vacuum) was inconceivable. But in the Torricellian barometer, there it was, a space above the mercury column previously filled with the liquid mercury itself. There was no way any material substance could be in that space. Yet for the convinced Aristotelian there had to be something there, though the problem of its materiality remained.

To the growing number of materially minded experimentalists, here was a new opportunity for investigation. Chief among these was Robert Boyle, who with Robert Hooke (1635–1703) created improved versions of Otto von Guericke's air pump, with which they were able to produce vacuums in spaces more convenient than the small tubes above columns of mercury.

Boyle's first publication resulting from his experiments on air appeared in 1660, *New Experiments Physico-Mechanical Touching the Spring of the Air and Its Effects*. This was quickly followed by *A Defense of the Doctrine Touching the Spring and Weight of the Air* in 1662. Additional publications followed throughout his life, though these first two contain nearly all of his fundamental discoveries. Boyle, alone of all the experimenters who quickly capitalized on this new opportunity, made truly original discoveries in pneumatics.[21]

Boyle easily confirmed the widely accepted hypothesis that it was the weight of the atmosphere that held up the column of mercury in the Torricellian barometer. This theory dated from an experiment by Blaise Pascal, who had sent his brother-in-law to carry a mercury barometer up a mountain to observe what happened. Indeed, the mercury stood at a lower level in the tube when measured on top of the mountain than it did at the

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[21] Boas, *Boyle on Natural Philosophy*, 99.

mountain's base. This was just as it should if it was the weight of the atmosphere that supported the mercury column.

Boyle's experiment was much more spectacular and convincing. He enclosed the mercury reservoir in a glass container through which the barometer tube extended. As he drew the air from the enclosing container by use of his air pump, the mercury level in the barometer tube fell with each stroke of the pump. This observation led Boyle to suggest that there ought to be a quantitative relationship between the height of the column (the pressure) and the volume of the air in the container. This hypothesis was confirmed by additional experiments designed to demonstrate conclusively that an Aristotelian critic, Franciscus Linus, was wrong in claiming that air was too tenuous a body to hold up something as heavy as mercury. There must be, Linus said, some invisible threads in the space above the mercury that were responsible for holding up the heavy column of mercury. Boyle's response was the famous "J" tube experiment, in which he poured mercury into the end of the long arm after sealing the end of the short. The air trapped in the short arm of the "J" tube was increasingly compressed by addition of mercury into the end of the long arm. By measuring the various lengths of the shrinking volume of air so trapped, and comparing those volumes with the differences in the mercury levels in the two arms of the tubes, the inverse relationship between the pressure and the volume was immediately visible; thus Boyle's law, $PV = k$.[22]

Boyle was also able to settle a number of other questions about the role of air. A ticking watch was suspended by a thread inside a glass container; it was noted by all observers that the sound became fainter with each stroke of the pump that was removing the air. In other experiments, it was noted that the transmissions of light and of the magnetic influence were not affected by the removal of the air. Thus Boyle in the space of a few years established the foundations of the science of pneumatics.

Boyle's view of the atmosphere is fundamentally physical, its composition being a mixture of three kinds of particles. The first came from the many extraneous exhalations "from the earth, water, minerals, vegetables, and animals, &c," but these made up only a very small part of the atmo-

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[22] Boas, *Boyle on Natural Philosophy,* 336ff.

sphere itself. The second sort of particles, even more subtle than the first, consist of "the magnetical steams ... and the innumerable particles" of light from the sun and other stars. But the third set of particles "are those, which are not only for a while, by manifest outward agents, made elastical, but are permanently so, and on that account may be styled perennial air."[23] In short, Boyle's concept of the atmosphere is that of an intrinsically elastic air which carries in it the various "steams and smoakes" from a variety of sources. It is these adventitious ingredients that are responsible for any seemingly chemical involvement of the atmosphere. The air itself is characterized by its elasticity and has no chemical function.

The successful establishment of a science of pneumatics that provided a detailed mechanical understanding of air as a physical body undoubtedly helps explain the chymists' neglect of air as a chemical body. Also the contrast between the elusive etherial nature of the air and the growing sense of reality of the more material bodies, the salts, acids, alkalies, metals, cinnabar, saltpeter, and other specific items, also made it easy to ignore air as a chemical ingredient. For whatever reasons, hardly anyone at the beginning of the eighteenth century included air among the elements or principles in a chemical discussion.

In this account I have emphasized Boyle's critical role in refuting the philosophical chemical systems of his time. As we shall see shortly in the work of Nicholas Lemery, Boyle was not totally successful in eliminating either the concepts or their vocabulary of the chemical systems he criticized. Indeed, many of the most traditional concepts survived to the end of the next century.

Boyle's motivation in attacking the prevailing philosophies of his time was to clear the way for a mechanical explanation of chemical behavior. Though he managed to present a persuasive rationale for the possibility of such a system, he failed to provide the kind of detail that might make such a system functional. Mechanical views, like those Boyle sought to replace, remained *a posteriore* in their explanatory power and infinitely adaptable to whatever facts needed explaining, lacking any predictive power.

Like his chemical philosophy, Boyle's experimental investigations were

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[23] Boas, *Boyle on Natural Philosophy,* 380-381.

not typically within the iatrochymical tradition of drug preparation, but his experimental chemical investigations gave him a much-respected reputation in the next century. Nevertheless, in spite of the wide range of this work and his experimental skills in carrying them out, his investigations did not lead to a coherent empirically based system of chemistry. Like the alchemists of antiquity who imposed an Aristotelian philosophy on a limited chemical practice, the seventeenth-century natural philosopher tried to impose a mechanical philosophy on the chemical practice of that time, but similarly failed to produce a progressive chemical system. Chemistry's magical qualities so obscured the essential evidence upon which a compositional organization of chemical behavior was eventually based, that another century was required before that goal was successfully achieved.

3

THE STAGNATION OF CHEMICAL THEORY: 1675–1750

ROBERT BOYLE's devastating attack on the four elements and the *tria prima* did not result in their disappearance from chemical writing, for he had not offered a persuasive alternative for rationalizing the growing knowledge of chemical behavior. Experimentalists, that is, those still doing chemical preparations, writing texts, and publishing in academy journals, had perforce to continue to use most of the familiar language and concepts in spite of their inability to promote higher organization. But during the next two or three generations they used that language more cautiously, in ways that no longer so firmly implied a system behind the vocabulary. EARTH came to refer more and more to the material stuff left behind after a fire analysis, WATER to the actual phlegm distilled from such a process, and SALT the soluble material extracted from the residual earthy material. AIR had effectively disappeared from the chemical language in the seventeenth century, but FIRE continued as the most important chemical agent in whatever form. MERCURY and SULPHUR remained common terms in both metaphysical and experimental contexts.

Though the mechanical philosophy became widely received, there was no successful effort to create a mechanical chemistry. But mechanical language explanations for certain kinds of chemical observations became increasingly common. In short, toward the end of the seventeenth century and early in the eighteenth, the chemical literature became increasingly descriptive in its style and eclectic in its explanations. The vocabulary utilized terms from both the older traditions and the new mechanical philosophy, but the theoretical implications associated with either seem much looser. Explanations or theoretical descriptions were offered only when the evidence clearly allowed. In most cases no explanation suggested itself and the event was simply described. Chemical theory had become essentially stagnant and remained so well into the eighteenth century.

The first edition of Nicholas Lemery's *Cours de chymie,* published in 1675, can be viewed as the culmination of the seventeenth-century textbook tradition in France. The slim first edition was quickly followed by a much enlarged second edition in 1677 and many subsequent editions, eleven in all before the author's death in 1715. The book remained popular well into the 1720s, with translations into Latin, Dutch, German, English, Italian, and Spanish appearing during the author's life. Most of the changes in the later editions were simply expansions of the descriptive material of medical preparations and related procedures, with no essential changes in the early chapters on chemical principles. New empirical knowledge was absorbed without either conflict with, or correction of, its mixed and loose theoretical content.[1]

The persistent popularity of this book strongly suggests two significant things. First and most obvious, the book accurately represented a way of organizing chemical knowledge satisfactory to the chemical and pharmaceutical communities.[2] Second, the continued popularity of a book that changed relatively little between 1675 and 1715 suggests that the state of chemical understanding was little changed by the accumulation of chemical detail, that there was no dramatic breakthrough either in discovery or in theoretical invention during that time. It seems appropriate to view Lemery's text as a representative picture of the state of chemical attitude in the early decades of the eighteenth century.

The first half of the century was a time of accumulation and reassessment without serious change of attitudes or direction. Two events of this

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[1] For extended accounts of this important chemist, see Hélène Metzger, *Les doctrines chimiques en France du début du XVII à la fin du XVIII siècle* (Paris, 1923); Michel Bougard, *La chimie de Nicolas Lemery* (Turnhout: Brepols Publishers, 1999); and Owen Hannaway's life story of Lemery in *Dictionary of Scientific Biography* (New York: Charles Scribner's Sons, 1981), vol. 8, 172-175.

[2] Jonathan Simon, "The Chemical Revolution and Pharmacy: a Disciplinary Perspective," *Ambix* 45 (1998): 1-13, especially 2-3.

time had great significance later, but generated little effect at the times of their appearance. About 1700 the phlogiston concept, which became the center of vigorous controversy near the end of the century, was introduced by the German Georg Ernst Stahl (1660–1734). In 1727, the Englishman Stephen Hales (1677–1761) conclusively demonstrated that air was materially involved in chemical reactions and must become a part of the chemists' concern. But it was not until the 1760s that pneumatic chemistry and phlogiston were joined in a mutually reinforcing relationship; together they became the intense focus of attention that eventually led to a chemical revolution.

Lemery's COURS DE CHYMIE *(1675–1715)*

Although Lemery's *Cours de chymie* contains nothing like Paracelsus' religious spiritualism, the English translator of the book, Walter Harris, had attended Lemery's lectures in Paris and was probably reflecting something more than his own feelings when he wrote in the preface that "Chymistry is of a nature so exalted, and so purified a being, that it bears some proportion to the Soul itself, and activates inanimate things into different Motions as the Soul doth the Body."[3]

Chemistry, in other words, is claimed by some of its practitioners to have a close connection with ultimate, spiritual reality. This purpose is much more subdued in Lemery's than it was in Paracelsus' writings, but something of that attitude occasionally surfaces in later writings as well when chemists, trying to establish their distinction from mechanical philosophy, were self-consciously claiming a deeper understanding of the natural world.

Writing in the seventeenth-century textbook tradition, Lemery's book opens with a brief introductory section offering comments on chymistry in general, its definition and descriptions of its apparatus and basic procedures. The rest of the book is divided into three parts dealing with recipes for drugs derived from the mineral, vegetable, and animal kingdoms. The

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[3] Nicolas Lemery, *A Course of Chymistry,* translated by Walter Harris (London, 1677), unpaginated Preface.

discussion of mineral drugs is by far the largest, occupying nearly two thirds of the whole book. The writing is generally clear, providing easily followed descriptions of the processes by which various chemical changes are brought about. Only occasionally does he add comments on how a preparation might be used medically.

Lemery's definition of chemistry places him squarely in the iatrochemical tradition that combined practice with teaching. "Chymistry is an Art that teaches how to separate the different substances which are found in Mixt Bodies: I mean by a Mixt Body those things that naturally grow and increase, such as Minerals, Vegetables, and Animals."[4] Here Lemery is retaining the ancient conception of a world of natural history, the things that grow in Nature. It is the chemists' challenge to hasten the natural processes to accomplish their own purposes. Since Lemery's chief concern in the preparation of drugs is with those from the mineral world, the implication of their growth in nature is particularly interesting. Their presence in the earth is owing to the First Principle, "an universal Spirit, which being diffused over all the World, produces different things according to the different Matrixes, or Pores of the Earth into which it settles." Lemery suggests that the universal spirit "is a little Metaphysical" and hastens "to establish sensible ones."[5] Chymists, he claims, meet with five sorts of substances in their analyses, by which he always means fire analysis, from which they "conclude that there were five Principles of Natural things, Water, Spirit, Oil, Salt, and Earth." These five are the "sensible Principles" whose properties can be invoked to explain the particular properties of whatever material the chymist is working with. These five had become the popular ones during the seventeenth century and remained so pretty much until the middle of the eighteenth century.

WATER and EARTH are passive principles, the other three being active. The Spirit of Mercury is the most active, "a subtile, piercing, light substance, that is more in motion than either of the others." It causes bodies to grow; hence it is found in vegetables and animals, though little in minerals.

"The Oyl which is called Sulphur by reason of its inflammability, is a

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[4] Lemery, *Course,* 2.

[5] Lemery, *Course,* 2.

sweet, subtile, unctuous substance," said to "cause the diversity of Colours and Smells...."[6] As we shall see, this sulphur principle has its own independent history, though it later merges with the phlogistic tradition that comes to France from Germany in the early eighteenth century.

"Salt is the last of the Active Principles, which remains disguised in the Earth, after the other Principles are extracted.... It is a fixt, incombustible substance, that gives Bodies their consistence, and preserves them from corruption."[7]

All these principles are easily found in animals and vegetables, but not so easily in minerals. Fire analysis does not separate gold and silver into their principles at all, yet he believes that these metals contain them. Lemery suggests that in these metals the principles are so tightly bound that they cannot be separated except by "breaking their Figures" by which the principles are themselves characterized.[8] Lemery does not say what would result if indeed the particle shapes of the principles were broken.[9]

Apart from occasional *ad hoc* mechanical explanations, Lemery's theoretical comments are chiefly concerned with the traditional principles. The presence of one of the principles in a mixt body can be inferred from the correspondence between the properties of the mixt and those of the principle. Thus a body which is hard and stable to heat is presumed to owe those properties to the presence of the earthy principle in its composition with little or no oyl or sulphur. The combustibility of a body clearly indicated the presence of the sulphur or oyly principle in its make up. In spite of the compositional language, the function of these principles was rather to rationalize the properties observed than to define the material composition of the various mixts with which the chymist dealt in the laboratory.

Lemery uses the names of the principles in ambiguous ways, sometimes to refer to the material products of fire analysis, other times as names for metaphysical causes of observed properties. The focus on properties independent of substance may seem perverse to us today, but we can better understand that kind of thinking if we recognize that, strictly speaking, it is

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[6] Lemery, *Course,* 2. [7] Lemery, *Course,* 4. [8] Lemery, *Course,* 5.

[9] Note Lemery's reference to mechanical concepts which he does not systematically develop in a separate section of the book.

the properties that we experience directly, and from those properties we infer the underlying materiality. It is the hardness and other properties of a stone that we experience directly, not the stone itself. In the intellectual world of the seventeenth century that still required a cause for every effect, the traditional earthy principle still served as the cause of the perceived solidity. In this sense the hardness of the stone was the experiential reality, for which the material stone was invented as a carrier of the property.

Lemery utilizes the five principles very little in the body of the text. The mercurial spirit, which was presented so prominently in the first section, never comes up for discussion in the text, nor does water as a principle. Salt is used as a generic material term, referring to all those bodies soluble in water and conveying a saline taste. Chief among these are the acid salts, derived from the First Principle as a universal acid liquor that percolates through the earth and, by long fermentation and concoction,

> perfectly unites the acid with stoney parts, for the making of Salt.... Vitriols, Alums, and all other Salts that are naturally found in the Earth, may be explicated upon the same principle; for according as Acid Liquors do meet with different earths, they produce different Salts.[10]

This process, incorporating both the Salt principle and the Earth principle, illustrates the implicit concept of neutral salt that becomes increasingly explicit through the early decades of the eighteenth century when it becomes the most important concept in the materialization of chemical composition.

Having completed a discussion of the five principles, Lemery devotes the rest of the book to the descriptive chemistry of real material bodies. The centuries of alchemical manipulation had generated a good deal of empirical information about a few bodies of particular importance. In the absence of a truly useful theoretical structure, seventeenth-century textbooks were organized around the bodies we might call "privileged." Each formed the center of a lot of related chemical behavior, which after undergoing a variety of chemical changes were generally easily retrieved in their original

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[10] Lemery, *Course*, 7.

form. This operational pattern can be seen as an unconscious anticipation of the modern concept of substance.

In the largest section of Lemery's book, the mineral bodies provide the chapter headings, beginning with ten metals. To the seven metals of antiquity three of more recent distinction were added: bismuth, antimony, and arsenick (*sic*). Another eleven chapters follow, each focused on such important substances as quicklime, common salt, niter or saltpeter, sal armoniac (*sic*), vitriol, and sulphur. These are in a sense the privileged bodies, each serving as the starting material from which useful pharmaceutical preparations could be made, or interesting chemical manipulations could be reliably described.

In general the information is quite specific to its own chapter, and little effort is made to describe parallel behavior between one metal and another, for example. Occasional excursions into descriptions of principles or mechanical explanations give what little sense of philosophical unity there is. A closer look at some of his descriptions will give us a truer feeling for the state of chemical understanding and what concepts were there and what were still lacking before the art could become more truly a science.

Illustrative Privileged Bodies

MERCURY, for example, could be dissolved in acid or converted to a calx, and from either the mercury could be obtained again in metallic form. It could be combined with mineral sulphur to make cinnabar (mercuric sulfide), a more convenient form for transportation than the heavy liquid metal.[11] To get the metallic mercury back, the artificial cinnabar was heated with lime; thirteen and half ounces of mercury can be obtained from a pound of artificial cinnabar. Lemery speaks of "the cause of this disguise of *Mercury* in *Cinnabar*":

> Cinnabar then is nothing but a mixture of *Acid spirits* and *Mercury* together; thus if you mix it with some Alkali, and drive it upwards by fire, the Acids ... must leave the Bodies they were joined to before, for

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[11] Lemery, *Course*, 83.

> to enter into the Alkali; and this is what is happening here, for the Acids finding the Quicklime very porous, do leave the *Mercury*, and adhere to the Quicklime; so that this *Mercury* being disengaged from what held it fixed before, and driven by the fire, comes forth of the Retort in form of spirit, but the coolness of the Water that is in the Recipient, condenses it, and resolves it into Quicksilver.[12]

Two points are particularly worth noting. Lemery speaks of mercury being "disguised," a word that Boyle also used to describe gold in a chemically combined form.[13] It seems to mean that the mercury is present *as mercury* and not transformed into another substance, but only hidden in some way. This interpretation is strengthened by speaking of cinnabar as a "form" of mercury. These verbalisms suggest that mercury metal is conceived to be a kind of primary body, that when undergoing chemical changes the different forms it takes are all spoken of as being still mercury in the same way that bricks in a wall are still bricks. It seems appropriate to designate mercury as a privileged body on which a number of familiar transformations can be carried out, knowing that the mercury is always there whatever disguise it might wear. From our point of view the language is ambiguous. Lemery is not making a clear distinction between what we would call chemical and physical changes. We would prefer to describe such forms of mercury as being distinct chemical substances (compounds) having an identity just as distinct as that of mercury itself. The ambiguity is further reinforced by the fact that cinnabar was a naturally occurring body, had its own name, even though it was also a form of mercury, or mercury in disguise.

Second, note that Lemery here shows awareness of what is later called affinity, or elective attraction: the pattern of behavior where one substance shows a particular chemical preference by leaving its combination with one body to attach itself to another. In this case the acid has a greater affinity for the quicklime than for the mercury, hence joins the lime and leaves the mercury to be volatized and driven forth as a spirit. You may ask, Where was the acid that Lemery speaks of? It is a component part of the mineral

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[12] Lemery, *Course,* 84-85.

[13] Robert Boyle, *The Sceptical Chymist* (New York: Everyman, 1949), 31.

sulfur, but more of that later. Note also Lemery's *ad hoc* mechanical explanation of why the acid joins the quicklime, the lime is very porous and accepts the acid points, which Lemery does not mention here.

In a later passage Lemery observes the odd fact that the acid of sea salt (hydrochloric) will precipitate mercury previously dissolved by another acid, the spirit of niter (nitric acid):

$$Hg(NO_3)_2 + 2HCl = HgCl_2 + 2HNO_3$$

Here again Lemery resorts to a mechanical explanation; though all acids have sharp points that "prick and penetrate," they differ "in the figure of their points" as is evidenced by the different crystal shapes a body takes when dissolved in different acids. In this case the acid with grosser points (HCl) "falling on this dissolution [of mercury in nitric acid] do move, jostle, and easily break the points impregnated with the spirit of *Niter*, and so make them let go their hold, whence it comes that *Mercury* precipitates down by its own gravity." Again Lemery speaks of a compound of mercury, the precipitated mercuric chloride, as mercury itself, illustrating again a lack of verbal distinction between one substance and another. Mercury in these reactions is a privileged body that takes on different forms.[14]

Note that almost any chemical change might be "explained" in terms of mechanical action of imaginary jostling of points and pores. But such an explanation has no predictive power at all; it is all made up after the event. How does he know that the acid of sea salt has grosser points than the acid of niter? In his mind it would have to have grosser points in order to precipitate the mercury. The circular reasoning is implicit, but obvious to us.

Lemery describes the preparation of the "red precipitate" of mercury by first dissolving metallic mercury in spirit of niter (nitric acid). The product is dried, then heated further to form the red precipitate (mercuric oxide):

> This preparation is improperly called Precipitate, there being no pre-

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[14] Lemery, *Course*, 100-101.

> cipitation at all.... That which causes the Corrosion [of the mercury] is the more fixt part of the Spirit of *Niter*, that closely adhered to the *Mercury*, and this is that which encreases its weight.
>
> All these preparations are nothing but so many Disguises of *Mercury* by Acid Spirits, which according to their different adhesions, do cause such different effects.[15]

Sulphur

In the following passages, Lemery is speaking of mineral sulfur (brimstone), not the sulphur principle which of course has similar properties:

> Some think that *Sulphur* is a *Vitriol* sublimed in the Earth, because these mixts are very often found near each other; that there is a great deal of *Sulphur* in the mass of *Mineral Vitriol*, and that the *Acid Spirits* which are drawn from them both are wholly alike.[16]

That mineral sulfur contained the acid of sulphur was an unchallenged fact to chymists of that time, a natural conclusion to draw from the application of analysis by fire. Lemery here points out that the acid spirit from mineral sulfur is the same as that obtained from vitriol.

The next two passages illustrate the difficulty and/or reluctance the chymists of that time had in confidently identifying bodies from different sources as being the same body. This is particularly hard to do in a system that emphasizes the reality of properties, for these properties had no measurability and are easily blended or gradually increased or decreased, and it is hard to say when the properties of two different samples are really alike and that the two bodies are identical. "Flowers of sulphur" and "magistry of sulphur" provide an illustration.

When mineral sulfur is sublimed, the condensed sublimate is called flowers of sulphur, which in those days had medicinal uses. "This operation is intended only to rarifie the *Sulphur*, that being rendered more open, it may work the better." Note again the mechanical explanation.

To make the magistry of sulphur requires a more complicated proced-

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[15] Lemery, *Course*, 102-104.

[16] Lemery, *Course*, 210.

ure, but one that had been known for a long time. Sulfur is added to salt of tartar (potassium carbonate, the standard alkali of the time) and heated. The product (potassium polysulfide) was called liver of sulphur because of its color and consistency, a kind of pâté. Dissolve the liver of sulphur in water and add any acid, the resulting precipitate was called the magistry of sulphur (finely divided sulfur).

> Water all alone is not able to dissolve such a gross body as *Sulphur;* wherefore an Alkali Salt is added to divide it into small imperceptible particles.
>
> The Acid Liquor pierces the Alkali, and by separating its parts makes it let go its hold, so that the *Sulphur* gathers itself together, and falls down to the bottom in a white powder.... Fifteen grains of this Powder will do as much as double the quantity of *Flowers of Sulphur* for Diseases of the Breast, and it doth not heat so much.[17]

Although Lemery sees these two products as similar, there is a difference of degree in their medical efficacy. We are left wondering if he thought they were really the same thing. Many other examples of this kind of ambiguity could be given.

Saltpeter

Niter or saltpeter is an important material and has its own chapter (Chapter Four). Its importance lies chiefly as the source of the spirit of niter (nitric acid), and quite a lot of its chemical behavior was known.

> Niter is a Salt impregnated with abundance of Spirits out of the Air, which do render it Volatile, it is taken from among the Stones and Earths of old ruined buildings.... *Saltpeter* is not at all inflammable as the greatest parts of Chymists do believe; but where it finds some *Sulphur* in the fire, it unites with it, and promotes its flagration by its Volatile part; so that it serves for a Vehicle to it.[18]

"Salt-peter makes no flame," Lemery adds elsewhere, "except in the

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[17] Lemery, *Course,* 212.

[18] Lemery, *Course,* 171.

presence of some sulphurous matter, and Coals, 'tis known, are full of such parts."[19] Alcohol, too, is a sulphur. In this context, Lemery is speaking of sulphur as a principle.

Saltpeter plus charcoal yields an alkali salt which "hath a taste like that of the Salt of Tartar [potassium carbonate], and they differ but little in virtue."[20] He does not say they are identical, though they would both be impure potassium carbonate. There simply did not exist at this time a clear conception of the idea of chemical substance, defined by material composition. The chief means of identifying an artificially prepared body was by its method of preparation. The inevitable presence of impurities made precise identification by explicit properties uncertain in any case, and here Lemery exhibits proper caution in indicating only the similarity rather than the identity of salt of tartar and the product of charcoal in molten saltpeter.

But his unwillingness to claim identity owes much to the continuing practice of seeing chemical change as the blending of properties rather than the formation of distinctly different bodies. Lemery states a little later that the product of the above reaction is alkaline, "by reason that the Salt of Coal, which is an Alkali, is intimately mixed with the parts of Salt-peter."[21] The language of this statement strongly suggests that for Lemery the product retains the properties of the bodies from which it was made. This habit of seeing chemical change as a continuous blending of properties is one of the most difficult for eighteenth-century chemists to abandon.

Sal Armoniac

Sal ammoniac (ammonium chloride) had been known from antiquity, it being easily obtained by sublimation from animal refuse (urine) and from coal soot, chimney sweepings, etc. Its virtues seemed to lie in its volatility, that is its spirituality. Here are a few remarks from Lemery's book.

If the Sal Armoniack be Calcined in a Crucible, it flies all away into

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[19] Lemery, *Course,* 184.

[20] Lemery, *Course,* 183-184.

[21] Lemery, *Course,* 185.

> the Air, by reason the Volatile Salts predominating do carry along with them the fixt."[22]

Here the implicit view is that the properties of the ingredients are also those of the combination, a concept of blending of properties rather than a discontinuous chemical transformation. The sal ammoniac can be decomposed by treating it with quicklime. His explanation is based on the familiar idea that acids and alkalies attract and destroy each other's properties:

> *Quicklime* which is an Alkali, destroys the power of the Acid Sea Salt, by which it in a manner chained up the Volatile Salts in the *Sal Armoniack* whence it comes to pass, that as soon as the *Lime* and *Sal Armoniack* are mixed together, there exhales an unsufferable smell of Urine.... This spirit is an excellent *Menstruum* to make Precipitations with, it destroys Acids mighty well, and so all other Volatile Alkalis; it is used to Precipitate Gold, after it is dissolved.[23]

Lemery offers another way to prepare the Volatile Spirit of Sal Armoniack using in place of the lime the Salt of Tartar (potassium carbonate) which he says is "a more powerful Alkali than *Lime*." The Salt of Tartar "serves in this Operation, as the *Lime* did in the other."

It is apparent from what has been so far presented that Lemery is in effect using the concept of a neutral salt as the combination of an acid with an alkali, though he nowhere in this book uses the term nor explicitly defines it. We will see in the next chapter something of the origin and subsequent significance of this concept. The idea of neutral salt is implicit here, though it had not yet been so identified.

The residue of the reaction above with sal ammoniac and salt of tartar was significant to Lemery for it was a source of febrifugous salt, which

> is nothing else but a mixture of the *Salt of Tartar*, and the Fixt Acid part of *Sal Armoniack*, it works by Urine, and very seldom by sweat, by reason that being a fixed body, it Precipitates downward more easily

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[22] Lemery, *Course*, 185.

[23] Lemery, *Course*, 192-193.

> than rarifies; and by this means it comes to open Obstructions, which are most commonly the cause of Agues.[24]

In an extension of these experiments Lemery points out that the acid spirit of the febrifugous salt can be obtained by the same method used "to make the *Spirit of Salt.*" That method is to mix sea salt thoroughly with potter's earth and heat vigorously.

> You'l find in the Receiver an Acid Spirit, which is a very good Diuretic. It is esteemed to be specifick for Malignant Diseases: the Dose is to an agreeable acidity in Juleps, and Broths.[25]

Here again we can wonder if Lemery recognizes that the products of different procedures are identical. The two products are given different medical applications which suggests, but does not demonstrate, that he did not recognize the two spirits as being chemically the same, i.e., hydrochloric acid.[26]

> [The Spirit of Salt] is an Aperitive and it is used in Juleps to an agreeable acidity for such as are subject to the Gravel. It is likewise used for cleansing the Teeth, being tempered with a little water, and to consume the rottenness of bones.[27]

Lemery adds the recipe for making a "Dulcified Spirit of Salt of Basilius Valentinus": take equal parts of Spirit of Salt and wine and digest for two or three days in a gentle sand heat.[28]

Note his use of "dulcifie"; that is, the spirit of wine dulcifies the sharpness of the spirit of salt, it does not make a new compound. The property has been modified, a linguistic residue of the older view of chemical change as modification or blending of properties rather than the discontinuity of change that we perceive by describing as change in material composition. He uses the same vocabulary in dulcifying the spirit of niter.

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[24] Lemery, *Course,* 195.

[25] Lemery, *Course,* 195.

[26] Lemery, *Course,* 167.

[27] Lemery, *Course,* 167-168.

[28] Lemery, *Course,* 168.

> The *Spirit of Wine* doth very well serve to dulcifie the *Spirit of Niter;* for being a *Sulphur*, it easily joyns with the acid points, and renders them uncapable of corroding as they did before.[29]

On the Preparation of Acid Spirits

Acids were among the most significant agents at the chymists' disposal at the end of the seventeenth century, the chief one being what we call sulfuric. They called it vitriolic because it was made from the distillation of vitriol, usually the green variety (ferrous sulfate) because it was the cheapest. Three vitriols were generally recognized, the blue of copper and the white of zinc in addition to the green of iron. All are sulfates and any one of them could be used to produce vitriolic acid. Here is a paraphrased account of Lemery's description of the heating of green vitriol:

The first water that comes over is called *Phlegm of Vitriol.* [Since ferrous sulfate is hydrated, this would be simply the water of hydration.]

Next with gentle heat still comes the *Sulphurous Spirit of Vitriol.* [This would be sulfur dioxide gas, detected only by its odor.]

Further distillation yields *Acid Spirit of Vitriol* [i.e., dilute sulfuric acid], and finally, *Oyl of Vitriol* [a more concentrated form].[30]

To make the other acids, the appropriate salt, sea salt (sodium chloride), or niter (potassium nitrate), was ground fine and thoroughly mixed with potter's clay, rolled into balls, and placed in a proper container for distillation. The function of the clay is to "divide the parts of the salt"[31] and make it easier for the acids to be distilled off, which combining with moisture in the air form the solution called the acid spirit of sea salt or of niter, as the case might be. If the apparatus is properly arranged, the solution can be collected in a receiver. The reason why the clay is unnecessary in the production of Acid spirit of vitriol is that "Vitriol contains earth enough."[32]

Analysis / Synthesis

Early in the eighteenth century it became a widely recognized procedure that the synthesis of a body from the products of its analysis was a strong

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[29] Lemery, *Course*, 181-182. [30] Lemery, *Course*, 199-200. [31] Lemery, *Course*, 168.
[32] Lemery, *Course*, 202.

confirmation of the body's composition. As with so many other important concepts, this is already implicitly visible in Lemery's book, although not specifically recognized. The following brief account is typical of many others in this work, where a casual description contains implicitly and unconsciously a fundamental procedure of later great significance for the establishment of material composition.

> Acid spirits are Salts turned fluid by the force of fire, which hath disengaged them from their more terrestrious part, and they be revived again by pouring them upon some Alkali; for example, the *Spirit of Vitriol* remaining some time upon *Iron*, doth reincorporate into *Vitriol,* and the *Spirit of Niter,* poured upon the *Salt of Tartar* makes a Saltpeter.[33]

Discontinuity and Identity

The lack of verbal distinction between mercury and its compounds, that the latter are all forms of mercury, indicates the absence of the concept of chemical identity that today we call substance—the clear awareness that the red precipitate is not mercury even though we can get mercury from it. The verbal ambiguity seems to be a residue of the philosophical tradition that bodies are distinguished from one another by the forms imposed on the basic matter, rather than by their material composition. In these representative cases of the times, there appears to be more than one kind of matter, at least at the level the chemist can reach. There are certain bodies which show up enough, are important enough, that they constitute a class of "mixts" stable enough to become what I have called "privileged bodies." It is these bodies, though not ultimately simple, on which different forms and disguises can be imposed to give bodies of different qualities or properties and hence identity.

By focusing on properties rather than composition, chemical change appears as a continuous process, rather more like the continuous changes of a physical mixture, a solution of an acid, for example, or a little black paint added to a bucket of white paint. The result of such mixing would

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[33] Lemery, *Course,* 202.

be expected to have the same properties as the ingredients, though in a diluted or blended combination.

Since all bodies have properties, it is easy to conceive of change as merely the change of properties, their dilution or blending. It is much more sophisticated to conceive of the properties as derived from changes of composition that cannot be directly perceived. It was not until the end of the eighteenth century that chemistry acquired the necessary concepts for a compositional organization.

The first edition of Lemery's famous *Cours de chymie* provides us with an excellent summary of contemporary chemical knowledge of that date, 1675. In this study of the development of chemical composition, what important points should we take with us into the eighteenth century?

1. The centuries-long practice of describing bodies in terms of the metaphysical four-element style, or one or another of its latter day successors, had only the appearance of a compositional expression. The four elements and the five of the iatrochymists, were only *words* representing the qualities perceived in a body resembling the qualities of one or another of the presumed elements. This approach carried with it the implication that the qualities of the mixt were a mix of the qualities of the elements involved.

2. The concept of chemical substance or species is hardly visible. Composition is a continuum and the language of chemical change is one of the blending or shifting of properties. More WATER makes things more fluid, more EARTH makes things more solid, more resistant to fire. The whole support for the four elements or the five principles was derived from fire analysis; there was no way to confirm such an analysis by synthesis, as Boyle had said in the *Sceptical Chymist.* The description of chemical change in terms of change in composition had not yet even begun to become clear. Change was more apt to be described as dilution or blending of properties than as change of composition. A product of a chemical reaction possesses the properties of the bodies used to make it in a diluted, modified, or blended form. The identification of a body by its material

composition is limited to a few long-familiar materials, such as cinnabar, and more generally the natural neutral salts such as alum or the vitriols.

3. The idea that the composition of a body could be confirmed by the cycle of analysis and synthesis is visible in practice, especially with neutral salts, but again the idea is only implicit through practice, but not explicitly stated.

4. The theoretical expressions in the beginning of the book are given very little application in the main body of the text. Lemery provides an unintegrated mixture of mechanical and traditional explanations, both infinitely adaptable to whatever event he wishes to "explain." Neither has any predictive value.

5. Of the modern ideas implicit in this book, the most important ones that become explicit in the next few decades are the concept of neutral salt as a combination of an acid with a base, that is, an alkali, an earth, or a metal. Neutral salts also provide the best examples of material composition as confirmed by analysis and synthesis.

6. AIR has all but disappeared from chemical consideration. When mentioned at all, the atmosphere is seen as an intermediary between some kind of reservoir for the universal acid, the cosmic influence from the heavens that trickles through the earth to form salts and ore bodies.

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THE DEVELOPMENT OF THE IDEA OF NEUTRAL SALT

ONE OF THE CENTRAL THEMES of this book is to show how the development of the concept of neutral salt in the eighteenth century made possible the creation of a compositional nomenclature by L.-B. Guyton de Morveau in 1782, which when adapted to the new chemistry of Lavoisier led to the creation of a definition of "simple body" the material element. The second major theme then describes how this new chemistry led to the final development of modern chemical composition in its atomic structure introduced by John Dalton. His atomic theory contained the symbolic operators that furnished the most convenient representation of the material composition of bodies that had become available by the end of the eighteenth century. The idea of an individual atomic weight unique to each element depended most immediately upon the concept of "simple body," introduced by the authors of the *Méthode de nomenclature chimique* in 1787. The new nomenclature was itself based on the principle that a name of a body ought to correspond to its composition.

As we have seen in the previous chapter, the experiential knowledge of neutral salts had become fairly well established toward the end of the seventeenth century. By the end of the eighteenth century the neutral salts represented the largest class of chemicals whose composition in terms of other material bodies had been established. Historians have generally credited G.-F. Rouelle with providing the first explicit definition about mid-century and thus bringing this concept into conscious utilization.[1]

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[1] For detailed accounts of Rouelle, see Rhoda Rappaport, "G.-F. Rouelle: An Eighteenth-

In 1744 Rouelle wrote:

> I call a neutral salt every salt formed by the union of whatever acid, whether vegetable or mineral, with a fixed or a volatile alkali, an absorbant earth, a metallic substance, or an oil.[2]

Although the explicit definition was new, the term had been around for some years, and ten years later in another *mémoire* on the same topic, Rouelle provided a brief history of the concept.[3]

In 1782 Guyton de Morveau proposed a systematic nomenclature for the salts. The simple bodies were the acids and the bases which in combination made up the large class of neutral salts. He proudly pointed out that by combining the names of the twenty-four bases (alkalies, earths, and metals) with each of the eighteen acids then known, 324 different salts could be systematically named, and from those names any chemist could also know their composition.[4]

A History of SALT *to 1750*

My version of this history of salt is based entirely on the writings of the seventeenth- and eighteenth-century chemists. But the reader of this book can gain further insights and examples of this topic by reading contemporary monographs written by Frederic Holmes and Ursula Klein.[5] Their accounts can be seen as basically parallel to this one.

Century Chemist and Teacher," *Chymia* 6 (1960): 68-101; and her "Rouelle and Stahl: the Phlogistic Revolution in France," *Chymia* 7 (1961): 73-102.

[2] G.-F. Rouelle, "Mémoire sur les sels neutres," *Mémoires de l'Académie Royale des Sciences* (Paris) [herinafter *Mémoires* (Paris)] 1744: 353-364, at 353.

[3] G.-F. Rouelle, *Mémoires* (Paris) 1754: 572-588.

[4] L.-B. Guyton de Morveau, "Mémoire sur les dénominations chymiques, la nécessité d'en perfectionner le système, & les règles pour y parvenir," *Observations sur le physique* 1782: 370-382.

[5] Frederic Lawrence Holmes, *Eighteenth-Century Chemistry as an Investigative Enterprise* (Berkeley, California: Office for History of Science & Technology, University of California, 1989. Ursula Klein, "Origin of the Concept of Chemical Compound," *Science in Context,* 7 (1994): 163-204. Ursula Klein, "E.F. Geoffroy's Table of Different 'Rapports' Observed Between Different Chemical Substances – A Reinterpretation," *Ambix* 42 (1995):

SALT was one of Paracelsus' *tria prima.* Like the other principles and the four elements of the alchemists, SALT as principle took its qualities as well as its name from the material bodies with the same properties. In a fire analysis, SALT was to be found in the non-volatile residue and extracted from the non-soluble EARTH by water. This real salt demonstrated the more or less universal presence of the salt principle in all such bodies. The presence of SALT as principle accounted for the body's solidity and resistance to fire. In its material manifestation, it was recognized by its solubility and its saline taste.

Both the material and the philosophical meanings of the word salt were in constant use, the context usually making clear the meaning intended. The real salt obtained by water extraction from the residue of fire analysis, like common salt, had taste; solubility and taste came to be the chief properties by which salts were identified. By these criteria, liquid acids also came to be classed as salts.

By the middle of the seventeenth century, many chemists, Johann Glauber being perhaps the first, had recognized the mutual destruction of acids and alkalies in what he called their mutual "killing and nullification." In 1688, Pierre Borel proposed "an essay to judge the mortification of acids by alkalies."[6] The characteristic effervescence of this reaction became the standard way of characterizing the acid or alkaline quality of a body; if it effervesced with an acid, it was an alkali, and vice versa. But effervescence was not recognized as being the result of the liberation of a gas, but rather the manifestation of the vigorous "strife," the intestine motion resulting from the violent reaction. Most often such reactions produced heat and the bubbling was easily identified with boiling.

Van Helmont, the most prominent of the seventeenth-century iatrochemists, made the acid-alkali reaction the chemical model for a theory of animal digestion. One of his pupils, Sylvius by name, carried this idea into a total system by claiming that *all* bodily functions were acid-alkali reactions, and that all body fluids were either acidic or alkaline. This theory

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79-100. Both here, and in her *Verbindung und Affinität* (Basel: Birkhauser, 1994), Klein argues that it was Geoffroy who first articulated the concept of composition.

[6] Robert P. Multhauf, *The Origins of Chemistry* (New York: Franklin Watts, 1966), 306.

was vigorously attacked by Robert Boyle, who demonstrated its inadequacies by showing numerous and common exceptions. One of the specifics that he refutes was the idea that anything that acids attack and dissolve must contain an alkali. As an illustration, the solution of copper in *aqua fortis* (nitric acid) was held to be caused by the fundamental reaction between the acid and the alkali in the copper. Boyle pointed out that this was an "unsafe way of arguing," for a good spirit of urine (an alkali) will also dissolve the copper filings.[7] Other explicit counter-examples left the acid-alkali hypothesis pretty well untenable as a comprehensive organization of either chemistry or physiology. Yet the reaction between acids and alkalies remained the most familiar among real laboratory materials. Lemery described so many such reactions, giving them mechanical explanations, that in 1723 Senac dismissed his book by saying that "Lemery speaks only of the combat of acid and alkali."[8]

At the end of the seventeenth century, three mineral acids were well known, the spirit of niter (nitric), spirit of salt (hydrochloric), and vitriolic acid or spirit of sulphur (sulfuric). There is no historical study that identifies the first report of acid-alkali interaction. In the seventeenth century the term alkali, Arabic in origin, meant the vegetable alkali, named according to common agreement in books of that time for the plant *kali* (otherwise unidentified) which contained an abundance of it. This product would have been potassium carbonate obtained by leaching the ashes of the burnt plant. The alkali of tartar made from the deposits found in wine barrels, was also potassium carbonate, and the two were often recognized as being alike, though the different names reflecting their respective origins were usually retained.

Alkalies were identified by the effervescence they produced with acids. Some chemists thought there might be a single alkaline salt present in all bodies that effervesced with acids, that salt being a counterpart to the universal acid responsible for all the particular acids. Lemery rejected that view and claimed that anything that effervesced with an acid was itself an alkali

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[7] Robert Boyle, "Reflections upon the Hypothesis of Alkali and Acidum," *Works* vol. 3, 603-608 at 603.

[8] J.-B. Senac, *Nouveau cours de chymie, suivant les Principes de Newton et Sthall* (*sic*) (Paris, 1723), liij.

in its own right. When acid was added to an alkali, the saturation point was recognized by the cessation of the effervescence. The effervescence itself was thought to be the result of the vigorous strife between the acid and alkali, something akin to ebullition and boiling. There was no recognition that it was caused by the liberation of air or a gas. Air as a chemical entity just did not exist at the end of the seventeenth century.

Boyle's work with the color changes of various vegetable pigments added a new way to determine the point of saturation. The ability of acids to turn blue vegetable colors red was well known in his time, but he believed himself to be the first to discover that an alkali, any alkali, would turn the color to green. Boyle recognized the potential use of such colors for the independent identification of the acidity or alkalinity of an unknown body and so used them himself; syrup of violets was his favorite. Though Boyle's writings were well known and admired throughout the continent as well as in Britain, systematic use of color indicators does not appear to be common until nearly 1750.

As Marie Boas has pointed out, the acid-alkali theory had a surprisingly short life.[9] But its brief existence highlighted and made explicit a long familiar reaction, and by the beginning of the eighteenth century neutral salts produced by the reactions between acids and alkalies had become a generally recognized class of bodies, known to be composed of an acid and an alkali and identified by the failure to effervesce with either a known acid or a known alkali. It was not far into the eighteenth century before the category was easily expanded to include combinations of an acid with earths and metals as well as with alkalies.[10]

In the first edition of his textbook, Nicholas Lemery used the Paracelsian idea that salts were formed in the various matrices of the earth where the universal acid found them when trickling down from above. This idea was made more specific in later editions:

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[9] Marie Boas, "Acid and Alkali in Seventeenth-Century Chemistry," *Arch. Int. d'Hist. Sci.* 9 (1956): 13-28.

[10] For an excellent general account of this topic, see Frederic Lawrence Holmes, "The Chemistry of Salts" in *Eighteenth-Century Chemistry as an Investigative Enterprise* (Berkeley, California: Office for the History of Science & Technology, University of California, 1989), chapter 2.

> As for *Salt,* I am apt to think that there is one chief, of which all the rest are compounded, and to conceive it to be made of an Acid liquor sliding through the Veins of the Earth, which doth insensibly insinuate and incorporate in the Pores of stones, which it does dilate and attenuate afterwards by a long fermentation and concoction of several years, a salt comes to be formed, that is called fossile; and this Opinion is the more likely to be true, because from the mixture of *Acids* and some *Alkali* matter, we always draw a substance very like unto Salt. Now stones are an *Alkali.* I add that the long fermentation, and concoction which is made in the stone, serves to digest, and perfectly to unite the *Acid* with the stony parts, for the making of *Salt.*[11]

Here Lemery is not only reflecting a continuing tradition from the Paracelsian cosmology, he has also moved along the road toward the conception of the neutral salt. His ambiguous use of the term salt illustrates this. In its first appearance the term refers to a principle of transcendent, non-isolatable existence, the generator of *all* salts, but later in the passage, "salt" refers to the particular material bodies found in nature. This ambiguity takes a long time to disappear from the chemical literature. It is not until the end of the century and the assimilation of the new nomenclature and the conscious utilization of its attendant concept of "simple body" that the transcendent principles of composition disappeared, taking the ambiguities of their names with them. Ambiguity of language is a mark of the exploratory, creative period of scientific progress, as well as indicating a period of confusion.

We see a slow and largely unconscious increase in the expression of chemical composition in terms of real, that is, material component bodies. Nowhere is this more visible than in the experimental work being done on materials now identifiable as salts. The climax, as previously indicated, is Rouelle's explicit definition of neutral salts as combinations of any acid with any base, that is, anything that would fix the acid into a solid state; an alkali, an earth, or a metal. A brief review of the earlier history will give us a better understanding of how these chemists thought of neutral salt.

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[11] Nicolas Lemery, *A Course of Chymistry,* 4th English edition translated from the 11th French edition of 1715 (London, 1720), 7.

From Matrix to Base

Though it is often implied by modern historians that the term "base" was first used in its modern sense by Rouelle in his mid-century definition of neutral salt, the term has a previously unwritten history going back at least as far as Paracelsus himself. A rough version of that history is given next.

According to the medical historian Walter Pagel, Paracelsus conceived a matrix as a place where things were generated.

> [T]he elements earth, water, air and fire are also called "*Matrices*"—the "wombs" in which objects are generated, in which they dwell, and from which they receive their "signature" and ultimate destination. Already the alchemists had compared the elements with hermetic vessels, not only as mere containers, but in the sense that the shape and kind of vessel used essentially and specifically influenced the nature of its contents. This idea may have inspired Paracelsus' concept of elementary "matrices."[12]

As described by Pagel, "matrix" appears to function as a device for retaining the distinction of bodies one from another, even while finding enough similarities to classify them in groups; the species within a genus, so to speak. The term was still used by Lemery, Homberg, and many other chymists well into the eighteenth century.

By the beginning of the eighteenth century, WATER and EARTH had become the two passive elements; in a way they were the old Aristotelian matter onto which various properties were impressed by the active elements, SPIRIT, FIRE, and SALT. Surely EARTH is the more passive, indeed, its recognition depends upon its extreme passivity. It is the otherwise undistinguished material that remains after a fire analysis, it's what doesn't distill off, called the *caput mortuum*. Later, some time in the late sixteenth or early seventeenth century, it was recognized that the solid residue of fire analysis had to be divided because it often contained salt, which could be

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[12] Walter Pagel, *Paracelsus. An Introduction to Philosophical Medicine in the Era of the Renaissance* (Basel and New York: S. Karger, 1958), 82.

removed by solution in water. The name of EARTH was retained for the insoluble material still remaining.

In the sixteenth century, the correspondence between the heavens and the earth, the macrocosm-microcosm pattern, was very close. "As above, so below" was the saying, and in Paracelsus' writings this was important. One of the heavenly influences most common in that time was that which induced the seed of things to grow in the earth. Chemically, those heavenly influences were responsible for the growth and development of metallic ores towards their more perfect forms. Though Nicholas Lemery did not rely heavily on this association, he did make casual reference to the alchemical correspondence between the planets and the metals. In speaking of tin, he writes: "The name of the planet *Jupiter* is given unto it, and it is thought to receive its particular influence from it." He does not, however, state what the influence might be or attempt to utilize it. By this time the influence had become more generalized. The universal acid which resided in its atmospheric reservoir, had its origin in heavenly influences. It slowly trickled its way through the earth's porosities, finding here and there, in some cavity, a propitious place for combination and growth. These were the wombs of the earth; the particular qualities of each were impressed on the universal acid, solidifying it in ways determined by the particular womb, or matrix, in which it was solidified.

It was well known that the acids were generated in the laboratory by distillation of a salt, and that the salt contained the acid as a constituent. The earthy residue remaining after that distillation became identified with, or at least corresponded to, the matrix in the larger earth where the salt was originally prepared by nature. Remember that the chemical tradition had long been of imitating in the laboratory what nature did naturally.

What we see in the early eighteenth century is the gradual transition of matrix as womb first into earth, and then into base, as Roulle used it at mid-century. Some illustration of this follow and illustrate the origin of the concept of base from the Renaissance concept of matrix.

One of the fundamental problems of natural history (in general and chemistry in particular) at this time was that of organizing a rapidly increasing number of factual details. Even as the botanist was receiving a flood of new species from around the world being deliberately explored, so the chemist was becoming aware of the differences between bodies or materials that bore large scale similarities yet could increasingly be distinguished from one another. The concept of matrix being familiar to seventeenth-century chemists, *could* have been used to "explain" how things might seem roughly the same yet be different, especially when the method of preparation was the chief means of identifying a drug; that and the starting material. The idea of matrix could account for differences caused by impurities when starting materials from different sources might have been used.

Wilhelm Homberg, in a 1702 memoir on the general principles of chemistry, describes the sulphur principle as always active in its nature. On the other hand, the EARTH never acts but "serves only as a recepticle or matrix for the other principles."[13] Here very clearly expressed is the verbal connection between the matrix as womb in the earth (as instrument), and EARTH as an element or principle. There is a continuous linguistic and conceptual connection between the matrix of Paracelsus and the base of Rouelle. As Louis Lemery, a son of Nicholas Lemery, put it in 1706:

> As a vitriol is made similar to common vitriol with iron and several acid spirits, I wish to know if some evidence can be found of iron in common vitriol, to convince me still further than I now am that natural vitriol is formed in the bowels of the earth with the same materials and in the same manner that we fashion it in our laboratories.[14]

In 1703, Homberg, after identifying the acid of common sulfur and the acid of vitriol as exactly the same thing (*parfaitement la même chose*), adds his fourth and principal evidence for that identification: that common sulfur and vitriol can be obtained from the same mineral source; "specifically, common sulphur and vitriol can be obtained ... from the same matrix or mineral rock, having, however, only the same acid salt which gives form to these two different materials."[15]

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[13] Wilhelm Homberg, "Essais de chimie; Article première, Des principes de la chimie général," *Mémoires* (Paris), 1702: 33-52 at 34.

[14] Lemery le fils, "Sur le fer & sur l'aimant," *Mémoires* (Paris), 1706: 120.

[15] Wilhelm Homberg, "Essay de l'analyse du souffre commun," *Mémoires* (Paris), 1703: 31-40 at 39.

The author of the *Histoires* of the Paris Academy in 1711, made a useful summary of Louis Lemery's "Mémoire sur les precipitations chimiques...." The final paragraph follows.

> He [Lemery] is surprised that a solution having been made by one acid, the precipitation is made by another acid. Mercury dissolved by spirit of nitre is precipitated by the spirit of salt. It appears that the entire system of acids and alkalies is turned upside down, but M. Lemery saves it by showing that the acids are never pure, but always accompanied by some sulphurous or earthy particles drawn from the matrices where they are formed, that the difference of these particles makes that of the acids, which from their [own] nature may be perfectly alike; that the acid of nitre is purer, and that of salt more enveloped by sulphur or of earth, that these foreign matters are the reason that the acid of salt is a species of alkali with regard to that of nitre which is absorbed by it, and from this comes the great facility they have of uniting together as it appears with aqua regia composed of these two acids.[16]

In another paper of 1713, Lemery *le cadet* is concerned to find out why saltpeter enhances the inflammation of combustibles, and other salts do not. When saltpeter and vitriol are heated together in a crucible to make *aqua fortis,* "the saltpeter is found deprived of its acids, which are evolved, while those of the vitriol remain at the bottom of the crucible with the matrix of the saltpeter."[17] Lemery here is using "matrix" almost as we would use base. It is also clear that he has a fairly well developed idea of the pattern of exchange of partners, or what later is called affinity. Later, Lemery explains why alum and vitriol do not cause an increase in the inflammation of a combustible oil:

> In a word, if when an oil burns it does not cause a sufficient decomposition of the alum and the vitriol, the flame ought not to be increased, for in our hypothesis the acid of the salt ought to leave its terrestrial matrix and carry its action on to the sulphurous vapor, and

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[16] "Mémoire sur les precipitations chimiques," *Mémoires* (Paris), 1711: 56-78. *Histoire de l'Académie Royale des Sciences* [herinafter *Histoires*] 1711: 31-34.

[17] Lemery *le cadet,* "De l'action des sels sur différentes matières inflammables," *Mémoires* (Paris), 1713: 97-108 at 104.

> the acid of the oil ought to abandon it, to unite to the terrestrial matrix of the salt, which becomes ready to receive it only in so far as it has previously lost its own acid.[18]

The historian should note three points. (1) Lemery is again using "matrix" very nearly as we would use "base." (2) Lemery is seeing a double decomposition type of reaction, in which the oil is seen as a combination of the sulphurous vapor and a sulhpurous acid, while the salt is a combination of a terrestrial matrix and an acid. He expects the two acids to change partners, but only if the acid of the salt is more volatile, as is true with the acidic vapor of the saltpeter, but not of alum and the vitriol. (3) It is also interesting that Lemery is very consciously using the hypothetico-deductive argument here to frame and justify his procedures and his explanation.

In 1717 Louis Lemery wrote two papers on niter, following up his earlier work just cited above.[19]

> With regard to what we have spoken of, in order to have an idea clear and precise, and to avoid all contention on what should be meant by the word *Nitre,* we remark first, and if one doubt of it, it will be clearly seen by the following that there is a large number of bodies which contain a particular acid such as that of saltpeter, and consequently different in its nature and in its effects from all the other acids that we know, from those for example of alum, of vitriol, of sulphur, and of common salt. That this acid is the true nitrous principle, or the true principle of Nitre; but as it is only by the aid of art, that is to say, by distillation, that this acid is found free and developed up to a certain point, and that in its natural state it is found in several sorts of terrestrial, saline, sulphureous materials which serve it as *base or the matrix,* it forms by that, different species of nitrous bodies which are all alike by their acid, and are different from one another by the nature of the materials which enclose the acid."[20]

Here Lemery uses matrix and base as linguistically as well as conceptually

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[18] Lemery *le cadet,* "De l'action des sels," 105.

[19] Lemery *le cadet,* "Premier mémoire sur le nitre," *Mémoires* (Paris), 1717: 31-51; and "Second mémoire sur le nitre," 122-146.

[20] Lemery *le cadet,* "Premier mémoire sur le nitre," 31, my emphasis.

equivalent. But the matrix concept still dominates when he speaks of the materials enclosing the acid. Note also that he is using the word "species" [*espèce*], a linguistic step toward what later becomes the genus/species language for the naming of neutral salts.

By the 1730s, the use of the word "matrix" has largely disappeared, though as late as 1735 Jean-Baptiste du Hamel uses it as equivalent to base.

> If it is wished to obtain the marine acid from sal ammoniac, vitriolic acid is employed, known to have greater power than that of marine acid; it removes by its superiority of force, the alkali which was its base or its matrix and takes it for its own, and the marine acid, thus disengaged and free, passes off in distillation.[21]

Thus we see how in the space of a few years, an ancient rather transcendental idea of the *matrix* is transformed into the modern idea of *base.* Let us now look at some other "modern" ideas as they appeared in embryonic form between 1700 and 1750.

Chemistry in the Paris Academy Mémoires

The tendency toward material realism we see in the early years of the eighteenth century suggests a growing impatience with the intangible principles that by definition lay beyond direct experience. One senses a sort of "let's get on with it" spirit, rarely expressed directly, but manifest by the willingness to accept reality on both the transcendent and the experiential levels, rather than pausing to decide which was meant. As patterns of material relationships and composition appeared through endless repetitions of their experimentation, the philosophical principles were ignored rather than abandoned or challenged. Let us follow these developments through the pages of the *Mémoires* of the Paris Académie des Sciences from the beginning of the eighteenth century.

Wilhelm Homberg (1652–1713), though born in Batavia of German ancestry in what was then the Dutch East Indies, spent his adult career in

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[21] Jean-Baptiste du Hamel, "Sur le sel ammoniac," *Mémoires* (Paris), 1735: 106-116, 414-434, 483-544. Quotation from *Histoires,* 1735, 23-26.

Paris, becoming the outstanding chemist of the Paris Academy at the end of the seventeenth century. His work was focused on the behavior and composition of neutral salts, an investigation derived from the recently popular medical theory of acid/alkali. Earlier experience in the century had established the pattern of neutralization of an acid by an alkali, a pattern of mutual destruction of properties. The available acids were the vitriolic or spirit of sulphur, spirit of nitre, spirit of sea salt, and acid of vinegar. The only alkali was salt of tartar (potassium carbonate). Lime was known but possessed a separate identity, not clearly classed as either alkali or earth.

Homberg called chemistry "the art of reducing compound bodies into their principles by means of fire, and of composing new bodies in the fire by mixing of different materials." He points out that the word *principle* has two significations, the first being the more philosophical and referring to the ultimate mechanical nature of things that we know little about:

> [F]or we have still determined nothing certain of the figure, or the arrangement, and of the movement of the primary materials; and as chemical physics, which consists only in the experience and exposition of facts, searches only for certain truth, has determined this second kind of principle more material and more sensible, by means of which it claims to explicate easily, and to assign to its matter its proper operation, and identify by that more distinctly the bodies that we examine by its analysis.[22]

Firmly in the iatrochemical tradition, Homberg believed that the analysis by fire revealed the familiar five principles, SALT, SULPHUR, MERCURY, WATER, and EARTH. SULPHUR was the active and EARTH the passive principle, the others having an intermediate nature. EARTH never acts, but "serves only as a receptacle or matrix for the other principles."[23] These, of course, were the philosophical principles, and he spent some time describ-

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[22] W. Homberg, "Essais de chimie. Article premier. Des principes de la chimie en général," *Mémoires* (Paris), 1702: 33-52 at 33. On Homberg generally see M. Gyung Kim, "Chemical analysis and the domains of reality: Wilhelm Homberg's Essais de chimie, 1702–1709," *Sudites in History & Philosophy of Science,* 31A (2000): 37-69.

[23] Homberg, "Essais de chimie," 34.

ing the composition of various classes of natural bodies in terms of the presumed content of these principles. In his work on salts, however, his descriptions were generally in terms of the acid and the alkali from which they were made. The composition of a salt prepared in this way was of course known, but not its quantitative composition, for the strength of the acid was not known.

In 1699 Homberg attempted to determine the quantity of volatile acid salts contained in their solutions. He added the acid to a weighed quantity of the alkali until the alkali was saturated, presumably judging that point by the cessation of effervescence. The resulting salt was then dried as thoroughly as possible and weighed. The increase in weight Homberg took to represent the weight of the real acid in the solution used. He carried out this procedure using spirit of nitre, oil of vitriol, *aqua regia,* and distilled vinegar, compiling tables of his results. He took no account of the loss of the carbon dioxide that escaped from the alkali, of course, for he knew nothing of it. The implicit principle upon which Homberg's efforts were based is that of the conservation of weight, and we can see how futile all such efforts at quantitative composition were until gases were recognized as a part of chemistry, and techniques were developed for measuring and isolating the different kinds of air.[24]

It will be seen a little later that Homberg was not alone in his awareness of the conservation of weight principle. But it was not until nearly the end of the century, after adequate techniques for handling aeriform matter were developed, that Lavoisier verbalized it as a fundamental principle and utilized it systematically as a rigorous way of establishing quantitative composition.

The use of the analysis/synthesis cycle as a way of confirming the qualitative composition of a body becomes a conscious and deliberate method about this time, made possible by the growing knowledge of the composition of neutral salts. If a body analyzed by fire could be reformed from the elements obtained, it would constitute a convincing demonstration of the validity of the analytical results. The reader may recall that Robert Boyle

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[24] W. Homberg, "Observations sur la quantité exacte des sels volatiles acides contenus dans les différens esprits acides," *Mémoires* (Paris), 1699: 44f.

had challenged the Aristotelians on this principle. Like so many other principles and concepts in the chemistry of this period, this one was used implicitly for many years before a deliberate definitive statement of the principle was given.

One of the earliest deliberate efforts to carry through the analysis/synthesis cycle on a significant scale is that attempted in the early eighteenth century. In 1703 Homberg published his "Essay de l'Analyse du Souffre Commun,"[25] followed the next year by Geoffroy's synthesis of the same material. Sulphur, Homberg pointed out, is the most considerable principle of chemistry, hence any gain in our understanding of that principle will aid in the understanding of all. He carried out the analysis by burning ordinary sulfur and concluded that it is composed of EARTH, SALT, a material purely fat and inflammable (i.e. SULPHUR), and a little metal, the first three being there in nearly equal proportions, while the metallic presence is negligible. The acid spirit produced in the burning is a volatile salt that has been deprived of its oily spirit, which along with the earthy matter were dissipated into the air and lost to the worker. The presence of the acid-salt and the inflammable material were traditional ingredients of ordinary sulfur, but it is not so clear how he arrived at the others.

In spite of the seeming obscurity of this event, Homburg is quite clear in recognizing that the acid of common sulfur and the oil of vitriol "sont parfaitement la même chose," because "everything that can be made by the spirit of vitriol can be made the same by the spirit of sulphur and vice versa."[26] Also, the vitriols can be recompounded with either of these acids with a selected metal to give the true vitriols of the metal involved. Additional evidence comes from the fact that when salt of tartar is treated with either of the two acids, salts with identical crystals are formed. To us, all of this sounds very clear and convincing as demonstrating unambiguous chemical identity. But what Homberg calls the principle argument is that sulfur and vitriol can be obtained separately from the "same matrix or mineral rock," from which he concluded that they have in common "only the same acid salt."[27]

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[25] W. Homberg, "Essai de l'analyse du souffre commun," *Mémoires* (Paris), 1703: 31-40.

[26] Homberg, "Souffre commun," 39.

[27] Homberg, "Souffre commun," 35.

It is historically significant that Homberg found it appropriate to state so emphatically that acid of common sulfur and the oil of vitriol "are exactly the same thing," and offer such elaborate evidence to justify that identity. Acid of sulfur and oil of vitriol were first prepared long ago and given names derived from their origin without any initial awareness that they were the same thing. In Homberg's time, and even much later, these were kept in separate bottles with separate labels. This is only one example of many deliberate efforts to show the identity of materials, chiefly salts, prepared in different ways. This illustrates the unconscious movement toward what today we call a substance, having a somewhat more explicit evidence than those "privileged bodies" in Lemery's *Cours de chymie.*

Oil of vitriol was prepared by heating a natural vitriol, most typically green (iron) vitriol. This yielded sulfur trioxide which combined with the moisture of the air to give a fairly concentrated sulfuric acid. The name, oil of vitriol, was derived from its source, and from its viscous nature. Acid (or spirit) of sulfur was made by the combustion of common sulfur, the sulfur dioxide produced reacted with the moisture and the oxygen of the atmosphere to give a much more dilute solution of the same acid, mixed with some unoxidized sulfur dioxide.

Homberg is not the first to recognize their identity, but that he feels compelled to elaborate the reasons for declaring their identity strongly indicates how recently that recognition had come to the chemical community.

A year later Etienne-François Geoffroy (1672–1731) attempted the synthesis of sulphur, for though fire separates the true principles, "they are so altered that they cannot lead us to the true knowledge of the nature of the bodies that compose it."[28] But we can be assured of success if we can recompose the body. Geoffroy's experiment was a long-familiar one that had already appeared in many forms and would appear many times again. The addition of spirit of sulphur (dilute sulfuric acid) to the oil of tartar (potassium carbonate) gave the salt of tartar (potassium sulfate). This, when heated with the addition of hot charcoal, produced what was known as liver

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[28] E.-F. Geoffroy, "Mémoire de recomposer le souffre commun par réunion de ses principes," *Mémoires* (Paris), 1704: 278-286 at 278.

of sulphur (potassium polysulfide). When distilled vinegar was added to a solution of this material, a white powder is precipitated, recognized as a very purified form of sulfur, called magistry of sulphur. Thus Geoffroy has produced the sulfur by combining an earth (in the oil of tartar), a salt (the spirit of sulphur), and a fatty inflammable material (charcoal). The Permanent Secretary of the Academy, whose duties included the writing of summaries of the worthy articles in the *Mémoires,* commented that "One is never so sure of having decomposed a mixt into its true principles as when with the same principles one can recompose it."[29] Clearly the strategy for establishing chemical composition is recognized in the analysis/synthesis procedure. But much essential knowledge still was lacking, and many improved concepts had to be conceived and refined before it could be put into reliable and systematic practice.

Salts in Nature

Only a few naturally occurring salts were known to the chemists of the early eighteenth century; chief among them were the vitriols, alum, and saltpeter. Borax was another that gained some attention in the early decades of the eighteenth century, though no one seemed to know how to relate it to familiar forms of matter. Nicholas Lemery in 1703 recognized it as a neutral salt by its failure to produce any fermentation when treated with several acids and different alkali salts. From these the inference was clear that borax itself was neither acid nor alkali and was therefore a neutral salt.[30] But Lemery was not able to identify either the alkali or the acid that made up this curious salt. The alkali was identified shortly thereafter, but it was not until the early nineteenth century that the nature of the acid component of borax was identified.

The vitriols, blue, green, and white, were especially important because it was from them that vitriolic acid was prepared. The natural vitriols, copper, iron, and zinc sulfates respectively, were so named presumably because of the glassy surfaces of their crystals (from the Latin *vitreus* "like glass").

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[29] Bernard de Fontenelle (1656–1756) in *Histoires, 1704:* 37.

[30] "Sel salé ou moyen composé," as it was called in *Histoires,* 1702: 49.

The acid was prepared chiefly from the green vitriol (the cheapest) simply by heating and condensing the sulfur oxides driven off. The solid "colcathar" (an iron oxide) remaining in the crucible had its own medicinal uses and the yield of acid was known to be higher when the humidity was also high.

Homberg's concern to establish the identity of acid of sulphur and oil of vitriol (see above) was not unique. Others of the chemical community recognized the importance of establishing the identity of chemical composition. This pattern is most visible among the neutral salts. Louis Lemery showed the identity of the artificial iron vitriol and the natural green variety. In his paper "Sur le fer & sur l'aimant," he expressed his purpose explicitly:

> As a vitriol similar to common vitriol is made with iron and several acid spirits, I wish to know if some evidence can be found of iron in common vitriol, to convince me still further than I now am that natural vitriol is formed in the bowels of the earth with the same materials, and in the same manner that we fashion it in our laboratories.[31]

Having synthesized a vitriol by dissolving iron in vitriolic acid and found that it did not respond to the magnet, he then heated it strongly, producing the odor of common sulphur leaving a solid residue which he called a true colcathar. After being heated intensely, this residue responded to the magnet as had the residue of natural English vitriol when similarly treated. "This last operation certainly proves to us that common vitriol is not different from that we make; and it teaches us the particular nature of colcathar, which is a remedy of much use in medicine."[32]

Geoffroy in 1713 also made some "Observations on Vitriol and Iron." All three of the vitriols found in shops are composed of an acid like that in alum and in sulfur, "with the exception that with alum the acid is mixed with an absorbant earth or a species of chalk, and that in sulphur it is united with bituminous or fatty parts, and that in vitriols it is joined with

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[31] Lemery *le cadet,* "Sur le fer et sur l'aimant," *Mémoires* (Paris), 1706: 119-135 at 120.

[32] Lemery *le cadet,* "Sur le fer," 121.

metallic parts."[33] This requires some explaining! Common mineral sulfur was thought to be a compound of an acid spirit identical with vitriolic acid, and a fatty bituminous inflammable matter, the traditional sulphur principle, later called phlogiston. The base of alum had not yet been clearly distinguished from other so-called earths, hence Geoffroy's expressed uncertainty. He knew that it was like lime in being only slightly soluble and therefore unlike the alkaline salt, but it was not the same as lime.

In this view common sulfur, alum, and the vitriols are products of that universal acid trickling down through the earth to form various bodies in the many matrices or wombs to be found there. In a sense, common sulfur has the same compositional structure as the neutral salts, viz., an acid joined to an oily body that gives it solid form. This pattern survives in Rouelle's classic definition of neutral salt in 1744, when he said: "I call a neutral salt every salt formed by the union of whatever acid, whether vegetable or mineral, with a fixed or a volatile alkali, an absorbant earth, a metallic substance, or an oil."[34]

Geoffroy went on to describe how he distilled green vitriol in a cracked crucible so that the "volatile sulphureous acid spirit of vitriol" [sulfur dioxide] could escape, all this "following the procedure of Stahl." Geoffroy advised his readers who wanted this explained to consult Stahl's original paper in the Journal of Halle in Saxony.[35] Georg Ernst Stahl (1660–1734) is the inventor of the phlogiston theory that we will be centrally concerned with a little later. This reference to Stahl in 1713 is the earliest that I have found in the Paris Academy *Mémoires.*

Geoffroy, in a paper of 1717, describes an experiment where he adds powdered charcoal to molten saltpeter, after which there is an alkaline salt remaining in the crucible. This was a familiar reaction, one of the standard methods of preparing the alkali salt (potassium carbonate). But Geoffroy called attention to the fact that the saltpeter, a body essentially acid in

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[33] E.-F. Geoffroy, "Observations sur le vitriol & sur le fer," *Mémoires* (Paris), 1713: 168-186 at 168.

[34] G.-F. Rouelle, "Mémoire dur les sels neutres," *Mémoires* (Paris), 1744: 353-364 at 353.

[35] Geoffroy, "Observations sur le vitriol," 172.

nature, is transformed in this reaction into an alkaline body.[36] This seemed to puzzle him. The author of the *Histoire* expressed it nicely when he wrote: "The opposition of acids and alkalies, so celebrated in chemistry, and which produces or explains so many phenomena, is not, however, so great that these two species of hostile salts do not change into one another."[37]

We would not be puzzled by this change, as Geoffroy obviously was. We see that the *composition* of the final product is very different from that of the starting materials, and as a consequence we expect its properties to be different. For us it is composition that determines the identity of a body and its properties. It is easier to understand Geoffroy's puzzlement if we recognize that he is looking at the properties themselves as having the true reality, acidity and alkalinity, and he is puzzled to see acidity become alkalinity.

Geoffroy's attempt to quantify this procedure is noteworthy. The fixed alkaline salt cannot have come from the charcoal, he thought, for sometimes only 3 or 4 ounces of charcoal were used on a pound of saltpeter. Now, a pound of saltpeter gives 12 to 14 ounces of good spirit of nitre containing about 4 ounces of the acid salt, the rest being water. (Recall Homberg's 1699 paper measuring the amount of real acid in the solution.) One ounce of acid salt poured onto an ounce of salt of tartar and dried yields a product weighing only two and a half dragms more than the original alkaline salt of tartar. The saltpeter itself is half water, he says, so how can a pound of saltpeter furnish 10 to 14 ounces of fixed alkali salt, if the saltpeter has only 4 to 5 ounces of fixed alkali and if the carbon gives only a few grains? "It is necessary, I say, that a good part of the acid portion of the saltpeter remains concentrated in this earth along with the earth of carbon and some portion of its sulphur, to compose this saline mass by the intervention of the matter of fire."[38]

It is clear from this that Geoffroy was fully cognizant of the principle of the conservation of weight, for his argument is based upon it. Because

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[36] E.-F. Geoffroy, "Du changement des sels acides en sels alkalies volatiles urineux," *Mémoires* (Paris), 1717: 226-238.

[37] *Histoires,* 1717: 34.

[38] Geoffroy, "Observations sur le vitriol," 231.

the weights he has measured do not add up, he is forced to explain the extra weight in terms of an incomplete analysis of the saltpeter and the fixing of the particles of the fire in order to preserve the conservation principle. With the advantage of nearly three more centuries of progress, we can deeply sympathize with Geoffroy in his futile effort to apply quantitative principles when the qualitative information was not complete.[39] There was no knowledge of the chemical involvement of gases and in these reactions where gases were either fixed or liberated, no quantitative accounts could possibly be made to balance.

Affinity Becomes Explicit

We have seen already in Lemery's *Cours de chymie* of 1675 examples demonstrating his implicit use of elective attraction. Others have traced the replacement of one metal by another at least as far back as Glauber before the middle of the 17th century.[40] Chymists were aware of this elective behavior for a long time, and used it as a kind of explanation long before Geoffroy systemized the phenomena in 1718 in a truly functional way.

The appearance of Geoffroy's "Table des différens rapports observés en chymie entre différentes substances" in 1718 provided the most important summary of chemical behavior in the early eighteenth century. Geoffroy's purpose in this table (Fig. 1) was to enable chemists to determine what reactions take place in many of their operations, "and to predict what should result when they mix different bodies."[41]

In any column, the bodies lined up below the heading "reference substance" are arranged in the order of increasing ease of replacement. Thus in the first column headed by *Esprits acides,* the *Sel alcali fixe* (carbonates

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[39] This illustrates the point made by J.B. Gough in his analysis of eighteenth-century chemical composition: "Before one can effectively quantify, one must have effectively qualified." See his "Lavoisier and the Fulfillment of the Stahlian Revolution," *Osiris* 4 (1988): 15-33 at 21.

[40] See Multhauf, *Origins of Chemistry,* chapter 14, and Alistair M. Duncan, *Laws and order in Eighteenth-Century Chemistry* (Oxford: Clarendon Press, 1996).

[41] Henry M. Leicester and Herbert S. Klickstein, eds., *Source Book in Chemistry* (New York: McGraw Hill, 1952), 67-75 at 67. This is a complete translation of this important document

of potassium and sodium) is at the top of the list of bodies that will combine with the acid spirits generally. That is, it has a stronger "rapport" with the acid spirits than any of the bodies that lie below it in that column. The second, third, and fourth columns provide the similar relationships for the specific acids, the marine, nitrous, and vitriolic acids.

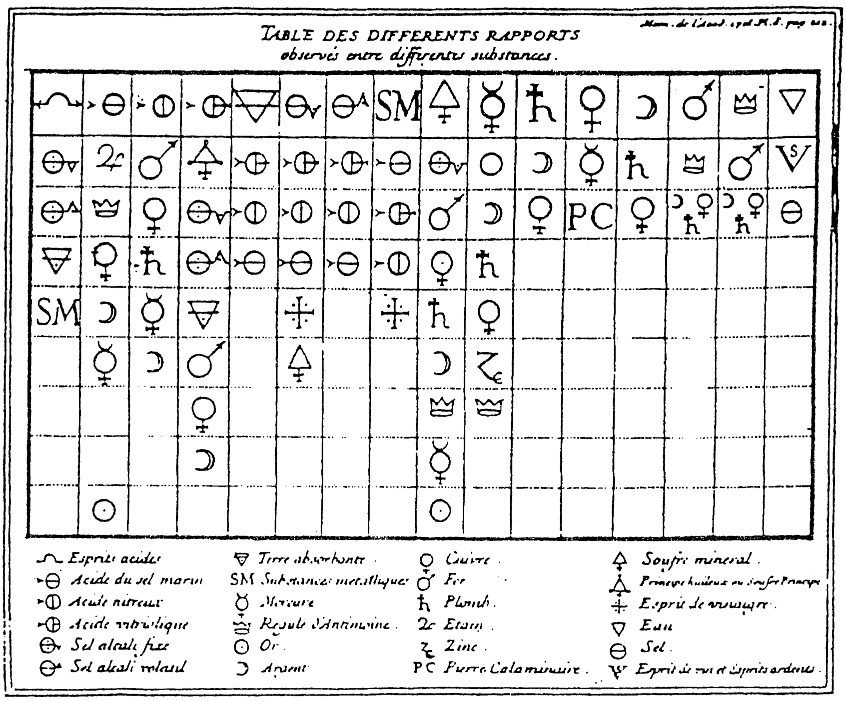

Fig. 1. E.-F. Geffroy's Table of the Different "Rapports."

Esprits acides: acids
Acide du sel marin: hydrochloric acid
Acide nitreux: nitric acid
Acide vitriolique: sulfuric acid
Sel alcali fixe: carbonates of potassium and sodium
Sel alcali volatil: ammonium carbonate
Terre absorbante: alkaline oxygen compounds, calcium carbonate, etc.

Regule d'Antimoine: antimony
Pierre Calaminaire: zinc carbonate
Soufre mineral: common sulfur
Principe huileux ou Soufre Principe: SULPHUR
Esprit de vinaigre: acetic acid
Esprit de vin et Esprits ardents: combustible organic compounds (alcohols, etc.)

Note that each of these entries can be thought of as representing a different chemical reaction. In column two, for example, the tin at the top of the list (indicated by ♃, the traditional astrological sign for the planet Jupiter) will replace the mercury (☿) or any of the other metals from their combination with the "marine acid" that heads the column. When looked at this way, well over half of all the reactions implied in the table involve the neutral salts, typically the replacement of one metal by another, or one absorbent earth by an alkali, or one acid by another, etc. If the column headed by SM (*Substances metalliques*) were replaced by eight columns each headed by one of the eight metals, then an even higher proportion of the total reactions summarized would involve neutral salts than in the table as it stands. Note also that with the exception of the sulphur principle, every substance represented is materially real, chiefly acids, alkalies, earths, or metals, the components of neutral salts.

There is no evidence to suggest that Geoffroy himself saw his table as a summary of the acid-base-salt relationship. Recent studies by Ursula Klein have gone into much greater detail, and about far more aspects of chemical composition in Geoffroy's table, than just the acid, base, salt that has been emphasized here.[42] Another study by Klein has greatly enlarged our perspective on the development of chemical composition, and her work is in very positive resonance with this story. She credits Geoffroy with first generalizing "the basic concept of modern chemistry—that of the chemical compounds and its related notions of chemical analysis, chemical synthesis, and chemical affinity." She stresses that this generalization was closely related to chemical operations and experiments and not to traditional metaphysical theory.[43]

Geoffroy's table is a very convenient way of summarizing a large proportion of the available chemical knowledge of the early eighteenth century. Later versions of the table became very popular as they were brought up to date and expanded to accommodate the rapidly growing knowledge of chemical change. The acid-base-salt relationship remained the basic organizational structure of them all, and later became the basis for the new nomenclature as well.

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[42] Klein, "Geoffroy's Table of Different 'Rapports'," *Ambix* 42 (1995): 79-100.

[43] Klein, "Origin of the Concept of Chemical Compound," *Science in Context* 7 (1994): 200.

From 1720 on, the pages of the Paris Academy *Mémoires* reveal an ever-growing practice of describing neutral salts in terms of the acid and the base they contain. In Homberg's work at the beginning of the century, the alkalies were almost the only base mentioned. Slowly the earths become important, as they took over the role of the Renaissance concept of "matrix," the womb in which salts grow in the earth. The vitriols are recognized as neutral salts with a metallic base.

Though the concept of neutral salt received its first explicit definition only in 1744 by G.-F. Rouelle, two examples from the Paris Academy *Mémoires* in the 1720s provide excellent evidence that its operational maturity had been reached long before that. M. Boulduc, le Fils, (1675–1742), one time demonstrator at the Jardin du Roi before Rouelle, published a paper in which he systematically demonstrated that a newly discovered mineral in Spain was identical with the long-known Glauber's salt (sodium sulfate). In the following passage from the introductory section, he summarizes the nature of a neutral salt:

> It has not been difficult to judge right away, by the crystallization that the salt consistently assumes, that it is a neutral salt [*sel moyen*], that is to say, a salt composed of an acid and an alkaline base, either saline or earthy, which cause it to be crystallized under a certain form; knowing by different operations that we do in chemistry that the fluid acids named *Sal-fluor,* and disengaged from all other mixtures, on encountering a material either *saline alkaline* or earthy, or metallic, with which it can be bound, they insinuate into it, are corporified, and take a solid form with it, and that then this material which serves as base and body causes this mixture to be crystallized in such and such a fashion, according to the differences among the materials that have been unified to different acids.[44]

By an extended series of experiments he demonstrates that the acid in the new salt gives the same results as the acid in Glauber's salt, and that

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[44] Giles François Boulduc, "Mémoire sur la qualité & les propriétés d'un sel découvert en Espagne, qu'une source produit naturellement; & sur le conformité & l'identité qu'il a avec un sel artificiel que Glauber, qui en est l'auteur, appelle SEL ADMIRABLE," *Mémoires* (Paris), 1724: 118-137 at 118.

the acid is that of vitriol. He then establishes that the bases of the two salts are identical not only with each other, but also with the base of sea salt. He concludes that the newly discovered salt from Spain is a natural variety of Glauber's salt. Although Boulduc provides no new discovery nor new insight into the chemistry he describes, his work shows the contemporary knowledge of neutral salts at its confident best, the analysis and synthesis of Glauber's salt and its composition in terms of the acid and the base it contains.

Louis Lemery in 1727 made an investigation of Borax, in an attempt to determine its composition. Borax is an example of a mineral salt whose makeup was little known, in contrast with other mineral salts such as the vitriols, alum, and niter. Soon after its discovery it had been identified as a neutral salt, but its acid and base had not yet been determined.

> It can even be said that of several of the salts just named, that what analysis that has been made of them, tells of their natural and internal composition, is newly confirmed and justified by means of recomposition, which reassembles and reunites the materials which analysis has separated, or from similar materials reforms the same saline compounds, or at least some compounds that resemble them enough to dare be flattered that one has discovered a little of the mystery of the composition of the salts that we act upon.
>
> It is known, for example, that iron and the spirit of vitriol, mixed together, make a true vitriol; it is known that spirit of nitre poured on some niter fixed by charcoal, or on salt of tartar, reforms a true saltpeter; but neither the analytical way nor that of recomposition offers us anything similar to anything approaching that for borax.[45]

These two papers by Boulduc and Lemery demonstrate a level of empirical knowledge about the neutral salts that is confident and mature. It is the empirical nature of that knowledge that should be stressed here, for the composition of neutral salts is always expressed in terms of other material bodies, the acids and the bases of which they are composed, the

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[45] Lemery *le cadet*, "Expériences et réflexions sur le borax," *Mémoires* (Paris), 1727: 273-288.

acids and bases from which they can be made, the acids and bases into which they can be decomposed.

By 1750 the realm of the neutral salts had become the most secure, the most explicitly empirical of all chemical knowledge. It has provided the evidence which most securely demonstrates the doctrine of affinities, the operating concept of proximate analysis, the confirmation of composition by the cycle of analysis and synthesis. The chemistry of neutral salts was to become the empirical core of the new nomenclature that organized the new chemistry of the chemical revolution.

5

AN HISTORIOGRAPHIC DIGRESSION: PHLOGISTON

THE HISTORY of eighteenth-century chemistry has been dominated for the last two hundred years by the elaboration of the so-called chemical revolution, focused on the overthrow of the phlogiston theory of combustion by Lavoisier's antiphlogistic chemistry in the 1780s. In the reigning phlogistic view, metals and other combustibles contained an inflammable principle called phlogiston, whose presence was directly responsible for its combustibility. When the body burned, the flame manifested the departure of the phlogiston, which was lost in the atmosphere or perhaps combined with a part of it. The same explanation was applied to the calcination of metals, a chemical change which turned them into a powdery calx. This calx could be restored to its metallic state simply by heating it with phlogiston-rich charcoal, thus confirming by analysis and synthesis the composition of the metal as calx plus phlogiston.

The basis of Lavoisier's arguments against phlogiston was his assumption of the conservation of weight in chemical reactions. He was able to show by careful attention to the weights involved that the phlogistic view had events just backwards; instead of phlogiston leaving the metal, it was oxygen of the air that combined with it. This inversion of the composition of metals and combustibles gained for the new view the title of "antiphlogistic chemistry." Two centuries of scholarship have reinforced Lavoisier's own view of the revolutionary nature of these events.

The drama of the 1780s has so fascinated historians that they have generally neglected the first half of the century, selectively retrieving from it only what is essential to the narrowly conceived notion of the chemical revolution as represented by the title of James B. Conant's book, *The Overthrow of the Phlogiston Theory, The Chemical Revolution of 1775-1789.*[1] As a result of this restricted view, two misleading assumptions that can be identified have become implicit in the traditional literature on the eighteenth century. These are, first, that the nature of combustion was a problem of long standing; and second, that the phlogistic doctrine was a well developed system that dominated chemical thought from the time of its introduction about 1720. Since these assumptions are only implicit, it is impossible to attack their foundations rigorously. But what I have found concerning the use of phlogiston in this period clearly does not support these traditional assumptions.

The Problem of Combustion

Because the chemical revolution was largely fought over the details of combustion and calcination, historians have usually presented the history of phlogiston as an early and erroneous effort to solve the same problem. J.H. White's early effort at a serious history of phlogiston essentially builds the story on the problem of combustion, offering two chapters titled "The Problem of Combustion" with two more titled "The Problem of Calcination."[2] What White offers are examples of slightly differing ways early chemists described combustion. All these had one thing in common: something escaped during combustion, and whether they *called* it fire, sulphur, the inflammable principle, or finally phlogiston, the basic *explanation* was essentially the same: combustion was a decomposition process characteristic of those bodies that contained an adequate amount of the inflammable principle, whatever it might be called. No one at the time suggested that there was a problem. The "problem" White sees is the fact that the products of combustion were heavier than the original combustible, but he offers no examples to illustrate that this bothered any of the early workers. That is, this is a problem (and it is a problem) from his own viewpoint, not from that of seventeenth and eighteenth century chemists, even though they did know that the products of combustion and calcination weighed

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[1] Cambridge, Massachusetts: Harvard University Press, 1960.

[2] J.H. White, *The History of the Phlogiston Theory* (London: Edward Arnold, 1932).

more than the original materials. The conservation of weight was simply not a standard principle for chemists before the mid-eighteenth century.

Other modern writers similarly assume the existence of a problem of combustion, but generally do not focus on it, still less demonstrate what was problematic for early eighteenth-century chemistry. Merely assuming a problem of combustion gives intensity to the confrontation between the old and the new that historians of science have come to love as defining a scientific revolution. Thus Lavoisier's successful attack on the "problem of combustion" is given additional drama when it is seen as the efforts of a single chemist to solve a problem of long standing. In historical reality, there was no problem about combustion until Lavoisier challenged the traditional view that combustion and calcination were decomposition processes. I am in agreement with Tenney L. Davis' insight, printed over sixty years ago, that "phlogiston became of importance only when it became an object of attack."[3]

From antiquity, combustion and the heat it produced had been the principal agent of chemical change. Both combustion and analysis by fire decomposed the body in question, and it was commonly demonstrated that the traditional four elements or Paracelsus' *tria prima* were produced by that process. For the iatrochemists following Paracelsus, the same burning of the green stick produced the MERCURY, SULPHUR, and SALT principles instead of the four elements. It is true that Boyle and some others recognized the probability that some of the products of fire analysis were created by the fire, but whatever the products of combustion, the process itself was universally accepted as being one principally of decomposition, more easily accomplished (as a late eighteenth-century chemist would put it) with bodies rich in the sulphur principle. Nicholas Lemery could say that only SULPHUR is inflammable. No chemical process was more widely familiar and no explanation more unchallenged than that of combustion. A body capable of burning was made so by the sulphur principle it contained, or later in the eighteenth century, by phlogiston, the indirect descendant, through *terra pinguis,* of Paracelsian SULPHUR.

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[3] Tenney L. Davis, "Boyle's Conception of Element Compared with That of Lavoisier," *Isis* 16 (1931): 82-91, at 82.

The Reception of Phlogiston in France

Georg Ernst Stahl, who introduced phlogiston into the vocabulary of eighteenth century chemistry, took his immediate inspiration from the work of J.J. Becher (1635–1682). Becher's own experience in the mining activities of Germany and later in England perhaps influenced him to emphasize earths in his presentation of chemical principles.[4] In his major work, *Physica Subterranea,* first published in 1669, Becher offered AIR, WATER, and EARTH as the elementary principles, though AIR was assigned only a mechanical role. There were three kinds of EARTHS, *terra vitrescible* [sic], *terra fluida,* and *terra pinguis,* whose characteristics correspond very closely with the Paracelsian principles of SALT, MERCURY, and SULPHUR respectively. When Georg Ernst Stahl republished Becher's *Physica Subterranea* in 1703, the qualities associated with the *terra pinguis,* the fatty earth, were transferred to ***phlogiston,*** making that concept an intellectual grandchild of the Paracelsian sulphur principle. In 1718 Stahl published his *Treatise on Sulphur* in which he gave his reasons for introducing and preferring the word phlogiston to that of sulphur or sulphur principle. Since this inflammable principle cannot be found in isolation, he said, it cannot be denominated by its directly observed properties:

> I have felt that it is most fitting to name it from its general action, which it customarily shows in all its compounds. And therefore I have chosen the Greek name phlogiston, in German, *Brennlich.*

He goes on to state that this principle is found in all three of the kingdoms, especially in the vegetable and animal ones, where it is chiefly found in the fatty materials.

> In the mineral kingdom there is nothing but water, common salt, pure vitriolic salts, and light sand and stones in which the substance is little or not at all found. On the other hand, coal and bitumen are full of

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[4] Becher's amazing career is the subject of Pamela H. Smith's book, *The Business of Alchemy: Science and Culture in the Holy Roman Empire* (Princeton, New Jersey: Princeton University Press, 1994).

> it; sulphur, not indeed in weight, but in the number of its finest particles, is completely possessed with it. Not less is it found in all inflammable, incomplete, and so-called "un-ripe" metals.[5]

But even in this *Treatise on Sulphur,* his fullest account of the phlogiston concept, Stahl himself does not use the term exclusively, but continues to use the old terms more or less interchangeably with phlogiston.

Stahl also published a number of papers in the various journals of the time, hence his views on phlogiston were available in France to those who could read the German and Latin, often mixed, in which they were written. Let us now look to see how these ideas appeared among the chemists of the Paris Academy of Science.

We have already seen that the idea of an inflammable principle whose presence is required for a body to be combustible had been around for a long time. Thus in a sense, the phlogiston concept did not have to come to France, it was already there and had only to be renamed. Every scholar who has read in the literature of eighteenth-century chemistry must recognize or suspect that the ancestral roots of the phlogiston theory go back to the fiery element that came to the West as a part of the Aristotelian tradition. In the sixteenth century this elementary role became transferred to Paracelsus' SULPHUR, one of the *tria prima* which also included philosophical MERCURY and SALT. Lemery in 1675 had identified as a SULPHUR every body that would burn. Becher's *terra pinguis* and Stahl's phlogiston are variations of Paracelsian sulphur. The "sulphureous principle" is used by Lemery (1675) as a principle of inflammability in very much the same way that phlogiston was used a century later in the great debates of the chemical revolution.

Lemery's successors in France—his son Louis, Wilhelm Homberg, and Etienne-François Geoffroy, who were the chief authors of chemical papers

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[5] Georg Ernst Stahl, *Zufällige Gedanken und nützliche Bedenken über den Streit von dem sogenannten Sulphure* (Halle, 1766); translated into French by Baron d'Holback (*sic*) as *Traité de soufre* (Paris, 1766). English version taken from *A Source Book in Chemistry 1400–1900,* Henry M. Leicester and Herbert S. Klickstein, eds. (Cambridge, Massachusetts: Harvard University Press, 1952), 61. See David R. Oldroyd, "An Examination of G.E. Stahl's *Philosophical Principles of Universal Chemistry,*" *Ambix* 20 (1973): 36-52.

in the *Mémoires* of the Academy during the first twenty years of the eighteenth century—all used the denomination of "sulphureous principle" or one of its equivalent traditional terms in a manner any later phlogistonist would recognize as his own.

The first mention of Stahl I have found in the *Mémoirs* of the academy is in Geoffrey's 1713 paper, "Observations sur le vitriol & sur le fer."[6] But phlogiston is not mentioned. Nor is it mentioned in L. Lemery's "Second mémoire sur le nitre," where Stahl is next mentioned in the *Mémoires.*[7] I find the word "Phlogiston" first used in the *Mémoires* only in 1720, in a paper by Geoffroy defending his paper on "Rapports" of 1718 against a few criticisms. He explains why he has placed "the oily principle, or as Stahl names it, the phlogistic principle, the inflammable principle or the principle of inflammability, above the alkali salt."[8] Geoffroy in this passage clearly sees these terms as equivalent, with perhaps a hint that Stahl's phlogiston term is idiosyncratic.

Homberg

In 1705, Wilhelm Homberg wrote that all rigorously analyzed mixts lose their sulphur principle and, the more carefully the artist attempts to obtain it, the less he will find. Somewhere along the line he concludes that this elusive principle is the same as light.[9]

In a somewhat more materialistic mood in 1710, Homberg published "Observations sur les matières sulphureuses & sur la facilité de les changes d'une espèce de soufre en une autre."[10] He divides sulphureous matters into three classes: (1) when the sulphur principle is held in an earthy matter, e.g. common sulfur, *charbon de terre,* jet, asphalt, yellow amber, etc. (2) When it is held in an aqueous matter, e.g. animal & vegetable oils or bituminous matter. (3) When it is held in a mercurial matter, it produces metallic sulphur.

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[6] *Mémoires* (Paris, 1713): 168-186. See chapter 4.

[7] *Mémoires* (Paris, 1717): 126-146.

[8] "Eclairissements sur le table inserée dans les mémoires de 1718, concernant les rapports observés entre différent substances," *Mémoires* (Paris, 1720): 20-34, at 29.

[9] Wilhelm Homberg, "Du souphre principe," *Mémoires* (Paris, 1705): 88-96.

[10] *Mémoires* (Paris, 1710): 225-234.

He sees the true sulphur principle in all the sulphureous materials, for example "metals dried by calcination to the point that they cannot be melted, or that they are vitrified into a scorious matter." When oil is added to these destroyed metals and heated, they regain their original form. "The reason is that the vegetable oil takes the place of the oily or sulphureous matter of the mineral that the fire of calcination had evaporated; we see this in all the calxes [*les chaux*] of the lesser metals; but most clearly in those made of tin in the *verre ardent.*"[11]

In drying a metal, he cautions, it is necessary to avoid a support which has any oil in it, otherwise it will prevent the calcination by supplying the sulphur as fast as the metals loses it. There is no difference evident here between Homberg's sulphureous principle and Stahl's phlogiston as it is generally presented in the secondary literature of the chemical revolution. Does Homberg get it from Stahl? It is possible, but seems unlikely.

Geoffroy

In 1704, just the year before, Étienne-François Geoffroy had published a paper describing the heating of metals by means of a powerful burning lens which concentrated the sun's rays on several different metals, iron, copper, tin, and lead.[12] Without any apparent need to say so explicitly, Geoffroy takes it for granted in this paper that such heating is a decomposition process. The chief technical difficulty was in finding something to hold the metal that would not itself be destroyed by the heat. Charcoal does not work because it is "penetrated by oily or suphureous parts" and the first effect of the fire is to liberate the oily part of the charcoal which replaces that liberated from the metal. He settled on stoneware as cheap and convenient.

In conclusion he says that "It results from all the experiences that I have reported that the metals called imperfect, namely iron, copper, tin, and lead, are composed of a sulphur or an oily substance and of matter capable

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[11] *Mémoires* (Paris, 1710): 226.

[12] "Expériences sur les métaux, faites avec le verre ardent du Palais Royal," *Mémoires* (Paris, 1709): 162-176.

of being vitrified."[13] It is from this sulphur or this oil that the opacity, the brilliance, and the malleability of the metals derives. He further draws the following conclusions:

–that this metallic sulphur does not appear at all different from the oil of vegetables or of animals;
–that it is the same in all the imperfect metals and even in mercury;
–that these four metals have for a base a material susceptible of vitrification;
–that this material is different in each of the four metals, for they vitrify differently;
–that it is from this difference in the base that the differences of the metals derive.

It is a clear case of Geoffroy's already knowing the composition of the metals, for he offers no evidence of any kind to support his view that metals contain an oily matter or a sulphur. He weighs nothing, he collects nothing of the fumes, etc.

In 1704 Geoffroy had attempted to synthesize common sulfur (see the previous chapter) by first reacting spirit of sulphur (dilute sulfuric acid) with salt of tartar (potassium carbonate). This material was dried and heated with charcoal to produce the liver of sulphur, which precipitated ordinary sulfur in a white powder when vinegar was added to its aqueous solution. After indicating a similar production of sulfur by other mixes and digestions, such as oil of vitriol and oil of terpentine, he sums up the procedures by saying, "All the other inflammable matters, such as wood, charcoal, mineral coal (*le charbon de terre*), or others united with some one of these salts, will not fail to produce sulphur in the same manner."[14] Geoffroy's method in the synthesis of sulfur is far from new, but his recognition that any of these inflammable materials will serve represents an interesting generality and raises an unanswered question. Does he arrive at this generality on his own, or has he been influenced by reading Stahl's ideas on phlogiston? We have already seen that he does not mention Stahl in any of his papers in the Academy *Mémoires* until some years later.

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[13] *Mémoires* (Paris, 1709): 175.

[14] *Mémoires* (Paris, 1704): 280-282.

James Partington says that "Geoffroy was one of the first French chemists to adopt the phlogiston theory."[15] But Partington does not say what distinguishes a follower of Stahl's phlogiston theory from a traditional chemist who never uses the word phlogiston and continues to speak of the "oily principle" and the "sulphur principle" (*Principe huileux & soufre principe*). The evidence strongly suggests that Geoffroy is reflecting a tradition older than what he might have got directly from Stahl.

With the appearance of Jean-Baptiste Senac's book in 1723, the French chemical community had available a clear direct source of knowledge about the chemistry of Stahl.[16] This book has not been given much attention by modern historians, nor have they examined the faithfulness of its doctrines to those of Stahl. But like Stahl himself, Senac continued to use the old terms without any very obvious preference for phlogiston. In a discussion of the calcination of tin, for example, Senac writes,

> The sulphureous or phlogistic parts on which the metallic form depends are dissipated by the action of the fiery parts; it follows then that the metallic parts are no longer bound as before, for their union depends on the oily matter.[17]

Senac's explanation of the weight gained by metals when calcined is fairly typical of those who remarked on the phenomenon before the discovery of oxygen in 1774. It is a simple confusion of weight and density:

> Calcined tin weighs more than before the calcination. We have said that the igneous parts which are introduced into the substance produce that increase, and it is possible that they do contribute to it. But as the light matter is driven off by the fire, the metallic corpuscles contract. Thus it happens that if tin loses some matter, it occupies less space,

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[15] James R. Partington, *A History of Chemistry,* 4 vols. (London: Macmillan, 1962-1970), vol. 3, 52.

[16] J.-B. Senac, *Nouveau cours de chymie, suivant les principes de Newton & de Sthall* [*sic*], 2 vols. (Paris, 1723). The book was published anonymously, but was usually attributed to Senac. See Partington, *A History of Chemistry,* vol. 3, 58.

[17] Senac, *Nouveau cours,* vol. 1, 318. Three different names for the same thing in a single sentence!

> and consequently it will not have any diminution in the weight. The fabric of the metal is not softened, its parts are only contracted in proportion as the sulphureous parts are evaporated. But because the metal yields more easily, the approach of its parts is not proportional to the volume of the corpuscles which are exhaled, it is thus necessary that the weight increase.[18]

Senac's admiration for Stahl is great; he sees "the celebrated Sthall" (*sic*) as "the reformer of chemistry,"[19] a science obviously much in need of reform, as is evident in his opening of the main part of the book:

> Chemistry offers vast material, little light, much work; Philosophy has not provided any clarity; the principles that are followed are obscure or uncertain; the books are presented in terms more appropriate to hide the ignorance of their authors than to enlighten the mind. To these shadows the chemists often join fairy tales; finally they are always in dispute with one another, they accord neither with themselves nor with nature.[20]

His discussion of the composition of common sulfur will be familiar:

> Sulphur is composed of an acid and the principle of inflammability combined. Take some vitriolic acid, a little nitre or salt of tartar, toss them all into a crucible, put the matter in fusion with some charcoal. With an acid precipitate the resulting mass, and you will have a true sulphur.
>
> It is a true sulphur because it does all the things sulphur does; inflames with nitre, dissolves metals, blackens silver, etc.
>
> It is composed of an acid salt and the inflammable principle because the vitriolic acid is either changed into an alkali, or evaporated, or remains in the sulphur. It is not changed into an alkali, since the weight of the alkali is not very different from what it was before; it is not evaporated, since it can be obtained from the new compound. Moreover by deflagration it produced a bitter salt formed of an acid and an alkali. It lacks for the formation of the sulphur only the inflam-

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[18] Senac, *Nouveau cours,* vol. 1, 318-319.

[19] Senac, *Nouveau cours,* vol. 1, liv.

[20] Senac, *Nouveau cours,* vol. 1, 3.

> mable matter, for if you give back to it the phlogiston contained in the carbon you will find again the same matter you have destroyed with the flame. The sulphur does not come from the carbon, for carbon plus the alkali will not produce it.[21]

The reader will recognize this clear description as a brief summary of the analysis and synthesis of sulfur carried out by Homberg and Geoffroy early in the century. Metals also contain the inflammable principle, though his demonstration of their composition is not so elaborately illustrated as it is for sulfur.

> The analysis of metals shows them to be bitumins cooked by a long digestive heat and brought to a certain degree of fixity; for deprived of the sulphureous principle they are reduced to cinders and glass.[22]

Although Senac's book claims to be a presentation of the views of Newton and Stahl, the continuity it exhibits with the views of French chemists earlier in the century is strong and clear. It is hard to see that what he has offered would change things very much. Nonetheless, his book may be regarded as the vehicle that brings Stahl's central doctrine into France in a direct and well-focused form. Common sulfur and the metals all owe their particular form to the presence of an inflammable principle, as had been demonstrated repeatedly by experimentation. Most of this had been done many times by chemists in the iatrochemical tradition, but here it is consolidated and clarified, for Stahl's writing style was notoriously obscure. Yet Stahl, Senac, and the writers who follow, continue to use sulphureous principle, sulphur, the inflammable principle, the oily principle, and phlogiston interchangeably, without any indication of general preference for phlogiston.

It is important to note that in all these uses, phlogiston or the inflammable principle is used merely as a name when describing ordinary (and familiar) chemical behavior. There is no apparent effort to organize larger blocks of chemical knowledge around a phlogistic doctrine, nor to extend it beyond the bounds of its traditional application to metals and sulfur. I

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[21] Senac, *Nouveau cours,* vol. 1, 36-37.

[22] Senac, *Nouveau cours,* vol. 1, 41.

have found no evidence to indicate the existence of what might be called a phlogiston *theory* in the early decades of the eighteenth century.

Senac's book could be seen as organized more on the mechanical doctrine of affinity than on a phlogistic viewpoint. It provides a most explicitly clear statement how the concept of differential affinity can be applied in the design of experimental procedures.

> To separate mercury from sulphur, it is necessary to seek among our elements a material which has more affinity with the sulphureous acid than mercury has; lime is such a species, as it will detach the acid from the mercury by its alkali salt, but as the alkali salt is there in small quantity, it requires three parts of chalk for one of cinnabar, if one operates with tartar or another alkali salt, only equal parts are required.[23]

The evidence up to about mid-century suggests strongly that though the French chemical community is aware of Stahl, the word phlogiston is seen as little more than a neologism for concepts already familiar. It is hard to convince oneself that the introduction of phlogiston into France created any significant changes in the way chemistry was conceived, or that the organization of chemical knowledge was significantly altered.

In spite of the fact that Senac's book had not produced the fundamental changes in chemistry that he had claimed for the principles of Newton and Stahl, the latter's reputation was somehow established and survived as the chemist with the greatest reputation in the French community. As late as 1766, the Baron d'Holbach found it appropriate to translate into French two major works of Stahl, finding them after forty years sufficiently current that contemporary chemists would find them profitable. The translation of the *Traité du soufre,* d'Holbach claimed, would allow "French Chymists ... to profit from numerous discoveries, and the luminous views with which this work is filled." This work, he wrote, is the one that has been best received by knowledgeable chymists, and where Stahl has best presented his doctrine for effective dissemination.

D'Holbach admits that the followers of Paracelsus before Stahl had utilized a "Sulphureous Principle, or of Sulphur, but the idea that they

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[23] Senac, *Nouveau cours,* vol. 1, 395.

made of it was so little exact, that there was reason to say that they gave that name to everything that they did not comprehend." He credits Becher with demonstrating that the sulphur principle is a simple body of an earthy nature, and not "as Paracelsus and his disciples appeared to have believed, a compound body like common sulphur that we find in the bowels of the earth, with which they confounded it most often." Stahl, in turn, is credited with

> [making] known to us the different states where this principle is found in the three kingdoms of nature, its passage from each of these kingdoms into the others; it is he who has demonstrated for us that it is the principle of colors and of odors, that it gives to metals their malleability, and finally that is the coloring body, the fixed sulphur, etc., of the ancient Chymists.[24]

Coincidentally, it was just at this time in the late 1760s that phlogiston became re-invigorated through its extension to the belatedly discovered importance of air in chemical change, and for the first time it began to take on the attributes of a good theory. Almost immediately phlogiston came under attack on these very points, and the chemical revolution had begun.

In conclusion, it is apparent that the evidence from the early eighteenth century does not support two unstated but widely held assumptions about phlogiston and combustion in that period. First, that combustion was a significant problem of long standing. The traditional view at the time held that combustion was a decomposition process in which the fiery principle, by whatever name, escaped and was lost in the atmosphere. This view had been utilized without complaint or comment for centuries. Combustion was not a problem until Lavoisier challenged the traditional view in the 1780s.

Second, it has been tacitly assumed that Stahl's "phlogiston theory" quickly became a well-developed theoretical structure, and achieved almost

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[24] From the "Avertissement du Traducteur" of Stahl's *Traité du soufre* (Paris, 1766) translated by Baron d'Holbach from the German edition of 1718. In the copy I used, the translator's remarks are found shuffled into the Table of Contents at the end of the volume. It consists of two sheets, four pages, found between 386 & 387, and 390 & 391.

universal acceptance until the 1780s. In the eighteenth century, chemistry scarcely possessed anything like what we would today call a theoretical structure, with a coherent central core of axioms, assumption, or principles from which a significant body of derivative truths could be found consonant with experience. In its earliest appearance, what modern historians call the "phlogiston theory" was hardly more than a neologism for the traditional sulphur principle, variously denominated also as the oily principle, the inflammable principle, or just plain sulphur. Before 1750, its most coherent application was with the analysis and synthesis of the metals, and of sulfur itself. As we shall see, it was only its application to pneumatic chemistry beginning in the 1760s that gave phlogiston theoretical status.

The history of science has accorded Stahl a larger significance for eighteenth-century chemistry than I verify in my own studies. J.B. Gough, for instance, has offered a story of the compositional development of chemistry before Lavoisier (which seems to have been stimulated by my paper with Betty Jo Dobbs in 1968) in which he credits Stahl with the origin of an eighteenth-century chemical focus on composition. This influenced French chemists, including Lavoisier, who in effect fulfilled and completed a revolution actually begun by Stahl.[25] I do not find his evidence or presentation persuasive, so I prefer my current view of an *evolutionary* development of composition that begins in the seventeenth century, before Stahl appeared, and grew almost without conscious focus until Lavoisier's systematic application of the conservation of weight principle brought about the chemical revolution.

However, before we can provide a full summary of chemistry in France prior to the chemical revolution of the 1770s, we need to present two other topics in early eighteenth century chemistry: the return of air, and the revival of the four element theory that had been largely invisible among French chemical writers for more than a century.

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[25] J.B. Gough, "Lavoisier and the Fulfillment of the Stahlian Revolution," *Osiris* 4 (1988): 15-33. I will discuss Rhoda Rappaport's work on Rouelle and Stahl in Chapter Seven. See Robert Siegfried and Betty Jo Dobbs, "Composition: A Neglected Aspect of the Chemical Revolution," *Ann. Sci.* 24 (1968): 275-293.

6

HOW AIR RETURNED TO CHEMISTRY: A BRIEF HISTORY OF AIR 1600–1750

IN THE SEVENTEENTH CENTURY, the growth of iatrochemistry carried an increased focus on material bodies concerned for drug development, leaving AIR with no role for those focused on the practicality of drug preparations. But even as chemists largely ignored it, there was a rapid growth in the physical understanding of the air of the atmosphere. That success may well have partly served to justify the iatrochemists' implicit belief that AIR had no significant chemical role to play. Yet even in that marvellous century it was easy to overlook a number of observations that clearly connected the atmosphere with chemical change. The earliest of these was made by the French doctor of medicine, Jean Rey, who in 1630 published his account of heating lead and tin in the open air. He noted as many others had before him, that the calx produced was heavier than the metal he had heated. The air particles, he said, insinuated themselves into the pores of the metals expanded by the heat and remained there after cooling, providing a purely mechanical explanation for the gain in weight.[1]

It had been long known that candles burning in confined spaces soon went out, and that small animals quickly expired when similarly confined. The cause of these effects, however, was not certain. Was it that the air was somehow used up, or was the air poisoned by something produced by the flame or the animal's breathing? Robert Boyle, with the advantage of his improved air pump, was able to determine the role of air in combustion

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[1] Jean Rey, *The Increase in Weight of Tin and Lead on Calcination* (Edinburgh: Alembic Club Reprint, no. 11, 1904).

and respiration. Candles placed in containers from which some of the air was then removed went out in a much shorter time than in the same container whence the air was not removed. Sparrows, mice, and kittens expired quickly when placed in similar circumstances. It was immediately clear that both combustion and respiration required the air or something in it. Not a new idea certainly, but now demonstrated in dramatic and convincing fashion. These experiments seemed pretty conclusive in showing that it was the *lack* of air that caused the deaths, and not a poisoning by the accumulation of "fuliginous steams" produced by the breathing animal itself.

Boyle's famous experiments on the heating of metals in closed containers provide further information about the chemical role of air. He had previously carried out experiments consisting of heating metals in furnaces, where the flames themselves were in close proximity to the metal. From the gain in weight he concluded that he had thus shown "that either flame, or the analogous effluxions of fire, will be, what chymists would call corporated with metals and minerals exposed to its naked action."[2] He wanted later to determine if such subtle parts of the flame could penetrate the walls of a sealed container and be "corporated," as evidenced by a gain in weight of the product. These experiments again conducted in furnaces fueled by common charcoal gave affirmative results; the gain in weight, though smaller than when the metals were more exposed, supported his belief that the flame had penetrated the walls of the sealed crucibles. He resolved now to conduct the experiment with the most refined fuel, "a spirit of wine, or some such liquor as will totally flame away without affording soot, or leaving any drop of phlegm behind it." Thus the gain in weight could only come from the flame. An ounce of tin filings was sealed in a glass retort with a long drawn out neck and heated with an alcohol lamp. After two hours, the retort was cooled and broken to obtain and weigh the calx of tin produced. The gain in weight was reckoned to be five grains; "so that of so fine and pure a flame, as of this totally ardent spirit, enough ... was arrested, and in good measure fixed by its operation on the tin it had wrought upon."[3]

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[2] Quoted from Marie Boas, *Robert Boyle on Natural Philosophy* (Bloomington: Indiana University Press, 1965), 266.

[3] Hall, *Boyle on Natural Philosophy*, 268 and 269.

The experiment was repeated with an ounce of lead in place of the tin, and the neck of the retort was sealed. When after two hours of heating with the alcohol lamp, the neck of the retort was broken off, Boyle noted that the "air rushed in with a noise (which showed the vessel to have been very tight)" and again found that there was a considerable gain in weight.[4] For Boyle these two experiments confirmed his initial hypothesis that there was some subtle part of flame that was able to penetrate even the walls of a glass container and add its weight to that of the metal by combination with it. It may be worth noting here that Boyle made no speculations about the composition of the product; he did not say, for example, that the calx was a combination of the metal with the particles of fire.

The experiment was repeated a century later by Lavoisier, who recognized that the gain in weight was owing to the oxygen which combined with the metal. Being more knowledgeable of the chemical behavior of the air, Lavoisier carefully weighed the sealed retort both before and after the experiment and noted that there was no gain in weight; when the seal was broken, the air rushing in replaced the oxygen fixed with the lead.

We have seen that Boyle's conception of chemistry was a very mechanical one and this attitude is nowhere more evident than in his view on the composition of the atmosphere. He was much impressed by the presence of many extraneous exhalations "from the earth, water, minerals, vegetables, and animals, &c," but these made up only a very small part of the atmosphere itself. The second sort of particles, even more subtle than the first, consist of "the magnetical steams ... and the innumerable particles" of light from the sun and other stars. But the third set of particles "are those, which are not only for a while, by manifest outward agents, made elastical, but are permanently so, and on that account may be styled perennial air."[5] In short, Boyle's concept of the atmosphere is that of an intrinsically elastic AIR which carries in it the various "steams and smoakes" from a variety of sources. It is these adventitious ingredients that are responsible for any seemingly chemical involvement of the atmosphere. For Boyle, the air itself is characterized by its elasticity and has no chemical function.

The successful establishment of a science of pneumatics that provided

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[4] Hall, *Boyle on Natural Philosophy*, 269-270. [5] Hall, *Boyle on Natural Philosophy*, 380-381.

a detailed mechanical understanding of air as a physical body undoubtedly helped justify the chemists' neglect of AIR as a chemical body. By the beginning of the eighteenth century, hardly anyone included AIR among the elements or principles in a chemical discussion.

There is another factor to be considered in explaining the chemists' continued neglect of air. Its elusive and etherial nature, its ubiquitous presence served a convenient function for the chemist as an infinite reservoir of all things spirituous and etherial, which chemistry was still utilizing. Lemery in the 1690s made just such a use of the atmosphere when he wrote, "the Air contains a Spirit which forms diverse things according to the different dispositions of the subjects that it enters into."[6] This was his explanation of the alleged recharging of a specially prepared common salt that yielded its "spirit of sea salt" (hydrogen chloride) nine times, in between times resting in the air. Two points to be added here: first, the recharging probably came from the air all right, but from its moisture rather than some "Spirit." This explanation is of the same structure as that given for the "certain Universal Spirit" he describes in the first edition (p. 2) that took various forms as determined by which matrix in the earth it settled in.

On the other hand, the contrast between the elusive etherial nature of the air and the growing sense of reality of the more material bodies, the salts, acids, alkalies, metals, cinnabar, saltpeter, and other specific items, must have made it easy to neglect air as a chemical ingredient.

Robert Hooke and John Mayow, English contemporaries of Boyle, also conducted many experiments and devoted much writing on the role of air in combustion and calcination of metals. In some ways their ideas were closer to modern views than those of Boyle, yet the fact remains that neither their work nor Boyle's caused chemists generally to bring AIR back into chemistry. The science still lacked the clear principles of organization by which the value of these experiments might have been judged, and so they remained isolated bits of curious information awaiting later developments.

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[6] Nicholas Lemery, *A Course of Chemistry,* 3rd English ed. (London, 1698), 357.

Stephen Hales: *Air Returns to Chemistry*

What introduced air into chemistry was some hard, unarguable evidence that air did indeed enter into the apparent composition of solid bodies.[7] The evidence could hardly have appeared under a more unlikely title than *Vegetable Staticks,* published by Stephen Hales (1677–1761) in 1727. The book was in most respects exactly what the title implied, an account of a number of ingenious experiments in the investigation of the flow of the juices within plants. But by far the largest chapter is devoted to "Experiments, whereby to prove, that a considerable quantity of air is inspired by Plants."

Hales' method was to heat a wide variety of materials and to measure the volume of "air" given off. His quantitative approach was itself inspired by the example of Isaac Newton, whose Queries in the *Opticks* he frequently referred to in the text. But his ultimate justification went slightly beyond Newton's authority, to that of God.

> The farther researches we make into this admirable scene of things, the more beauty and harmony we see in them: And the stronger and clearer convictions they give us, of the being, power and wisdom of the divine Architect, who has made all things to concur with a wonderful conformity, in carrying on, by various and innumerable combinations of matter, such a circulation of causes, and effects, as was necessary to the great ends of nature.
>
> And since we are assured that the all-wise Creator has observed the most exact proportions, *of number, weight and measure,* in the make of all things; the most likely way therefore, to get any insight into the nature of those parts of the creation, which come within our observations, must in all reason be to number, weigh and measure. And we have much encouragement to pursue this method, of searching into the nature of things, from the great success that has attended any attempts of this kind.[8]

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[7] For an excellent account of Hales' influence, see Henry Guerlac, "The Continental Reputation of Stephen Hales," *Arch. Int. Hist. Sci.* 4 (1951): 393-404.

[8] Stephen Hales, *Vegetable Staticks* (London: Oldbourne Reprint, 1961), Introduction, xxxi, emphasis in the original.

Armed with this highest of all possible justification, Hales proceeds to heat a wide variety of bodies and to measure the volume of the air produced. Newton is credited for this attention to air:

> It appears by many chymio-statical Experiments, that there is diffused thro' all natural, mutually attracting bodies, a large proportion of particles, which, as the first great Author of this important discovery, Sir *Isaac Newton,* observes, are capable of being thrown off from dense bodies by heat or fermentation into a vigorously elastick and permanently repelling state: And also of returning by fermentation, and sometimes without it, into dense bodies: It is by this amphibious property of the air, that the main and principal operations of Nature are carried on; for a mass of mutually attracting particles, without being blended with a due proportion of elastick repelling ones, would in many cases soon coalesce into a sluggish lump.[9]

Hales then refers to John Freind who "has from the same principles given a very ingenious *Rationale* of the chief operations in Chymistry."[10] Freind was one of the Englishman who in the late seventeenth and early eighteenth centuries were trying to apply mechanical principles to chemical phenomena.[11] But, Hales added, it is important to gain more information from experience.

> And it is with satisfaction that we see them more and more confirmed to us, by every farther enquiry we make; as the following Experiments will plainly prove, by shewing how great the power of the attraction of acid sulphureous particles must be at some little distance from the point of contact, to be able most readily to subdue and fix elastick aereal particles, which repel with a force superior to vast incumbent pressures: Which particles we find are thereby changed from a strongly repelling, to as strongly an attracting state: And that elasticity is no immutable property of air, is further evident from these Experiments; because it were impossible for such great quantities of it to be confined

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[9] Hales, *Vegetable Staticks,* Preface, xxvii.

[10] Hales, *Vegetable Staticks,* xxvii.

[11] Arnold Thackray, *Atoms and Powers. An Essay on Newtonian Matter-Theory and the Development of Chemistry* (Cambridge, Massachusetts: Harvard University Press, 1970).

> in the substances of Animals and Vegetables, in an elastick state, without rending their constituent parts with a vast explosion.[12]

Although he is not at all discriminating, ignoring as he does the possibility that the airs he obtains are not all alike, the quantity of the air Hales obtains, and the wide range of materials from which he gets it, was impressive to those chemists who previously had almost totally neglected it. Others of course had previously noted that particles are thrown off by heat or fermentation, but none could have been fully appreciative of the quantity of it until such time as it was measured. It is very much to Hales' credit that he was able to devise ways to make quantitative measurements, for he was the first to collect gases by bubbling them through water into a water filled receiver. This will be explained a little later.

What kind of things did Hales obtain air (gases) from? Hog's blood, deer's horn, oyster shell, dried oak, wheat, pease, mustard seed, amber, and tobacco all yielded copious quantities of air. The volume of air collected was converted into weight through the estimate of its density (all airs were assumed without comment to have the same density), which yielded for the above materials the range of about one third part of air as measured by weight. Honey, beeswax, and sugar produced much less than one third part by weight. Mineral substances such as coal, earth, antimony, pyrites, salt plus calx of bones, nitre, vitriol, and sal tartar, all yielded various quantities of air, some copious, some not.

Some of Hales' most significant work derived from his admiration of Isaac Newton, especially ideas found in the *Opticks.* It is an amusing irony in the history of science to see how reasoning later proved to be wrong or totally inappropriate to some particular application nonetheless led to important results. Such is the case with Hales and some ideas he obtained from Newton's *Opticks.*

Newton states in Prop. X of the *Opticks,* Book Two, Part III, that "the Forces of the Bodies to reflect and refract Light, are very nearly proportional to the densities of the same Bodies; excepting that unctious and sulphureous Bodies refract more than others of this same density."[13] Two

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[12] Hales, *Vegetable Staticks,* Preface, xxvii-xxviii.

[13] Isaac Newton, *Opticks,* 4th ed. [1730] (New York: Dover Reprint, 1952), 270.

pages later he supplies a table indicating the power of refraction, the densities, and the ratios of these two values for a number of different bodies; in the constancy of the ratios in this last column the general validity of the proposition is evident. From this relationship Newton suggests that the diamond, with its very high refractive power, is "probably ... an unctuous Substance coagulated,"[14] that is, a combustible substance, a conjecture confirmed by chemists near the end of the eighteenth century.

Newton's theory of refraction was based on the presumed attraction of the particles of transparent bodies for the particles of light passing near them. Since objects containing sulphurous particles (combustibles) have greater power of refraction than other bodies, they must have a greater force of attraction, a proposition Newton supports by citing the fact that the concentrated rays of sunlight attract the sulphurous particles from combustible bodies as flame.

Hales extended these considerations to make the sulphurous acid particles the active agent in holding the particles of air fixed in solid bodies. Many of his experiments showed that after air had been produced by strong heating, the air was reabsorbed when it was allowed to cool and stand for some time in contact with the solid residue. This was owing, said Hales, to the strong attraction the acid sulphurous particles had for air, both of which then somehow recombined with the solid.

In order to prevent reabsorption, which made it difficult to measure the true quantities of air produced, Hales rearranged the apparatus so that the air was bubbled through water before being collected in a container above. A consequence of this new arrangement, equivalent to the familiar pneumatic trough of the beginning chemistry lab,[15] was the ability of later workers not only to measure the quantity of air produced in a variety of other kinds of reactions than direct heating, but also to isolate a particular air and characterize it by properties that distinguished it from other airs. Hales, however, dominated by Newtonian mechanical views, treated all the airs he produced as if they were one and the same; he assumed, for exam-

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[14] Newton, *Opticks,* 274.

[15] John Parascandola and Aaron J. Ihde, "History of the Pneumatic Trough," *Isis* 60 (1969): 351-361.

ple, that they all had the same density, from which he calculated the weight of air produced by multiplying by its volume.

Inflammable bodies contain not only sulphurous acid particles, equivalent to the traditional SULPHUR of the Chymists, but they also contain air. As Hales expressed it, fire and especially flame, consist of

> the action and re-action of the acid sulphurous particles of the fuel, and the elastick ones which arise and enter the Fire, either from the fuel in which they abound, or from the circumambient air: For by Experiment 103, and many others, acid sulphureous particles act vigorously on air; and since action and re-action are reciprocal, so must air on sulphur; and there is we see, plenty of both, as well in mineral as vegetable fuel, as also in animal substances, for which reason they will burn.[16]

Air is able to enter and be maintained in a solid state because it is so strongly attracted by the acid sulphureous particles,

> which arise either from fire or from fermentation: And therefore elasticity is not an essential immutable property of air particles; but they are, we see, easily changed from an elastick to a fixt state, by the strong atraction of the acid, sulphureous and saline particles which abound in the air. Whence it is reasonable to conclude, that our atmosphere is a *Chaos,* consisting not only of elastick, but also of unelastick air particles, which in great plenty float in it, as well as the sulphureous, saline, watry and earthy particles, which are no ways capable of being thrown off into a permanently elastick state, like those particles which constitute true permanent air.
>
> Since then air is found so manifestly to abound in almost all natural bodies ... may we not with good reason adopt this now fixt, now volatile *Proteus* among the chemical principles, and that a very active one, as well as acid sulphur; notwithstanding it has hitherto been overlooked and rejected by Chymists, as no way intitled to that denomination?[17]

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[16] Hales, *Vegetable Staticks,* 159.

[17] Hales, *Vegetable Staticks,* 179-180.

It is evident that Hales' picture of the composition of combustibles and the rationale for their combustion is neither clear nor complete, but his evidence created the inescapable necessity that chemists take seriously the reality of air in chemical composition. This was based on the impressive variety of things that yield air upon heating, and the equally impressive quantity of air produced, often approaching or exceeding one third of the original weight of the body heated. We must also acknowledge the fundamental importance of the techniques he developed that allowed the isolation and manipulations of gases.

Of particular interest to our story is the translation of Hales' *Vegetable Staticks* into French in 1735. Prior to this time it is hard to find in any of the *Mémoires* of the Paris Academy any reference to air at all. Functionally, air had simply disappeared from the chemical tradition of Lemery that characterizes French chemistry of the period. Hales' translator was le conte de Buffon (1707–1788), just then beginning his own career. Buffon was then, even as he has become known to historians, primarily a natural historian rather than a chemist, and his interest in the *Vegetable Staticks* no doubt originally came from that devotion. Yet what Buffon emphasizes in his *Préface du Traducteur* is the novelty and importance of Hales work on air. Even the title has been modified to make the work on air more prominently displayed. The full English title is reproduced on p. 124 (Fig. 2).

In giving the French title as *La statique des végétaux et l'analyse de l'air,* Buffon not only shortened it, but also promoted the analysis of air to equal status with the primary subject. In the translator's preface, he praises Hales for avoiding all "spirit of system" and relying on experimentation, the method of the "great Newton, that Messrs Verulam, Galileo, Boyle, and Stahl have recommended and embraced." Hales' book is not made merely to be read, he says, but to be studied:

> The initiation of the analysis of air is the best part of his book, and the one he has least developed: I have tried to supplement it in adding to the figures: everything is new in this part of his work; it is a fruitful idea from which follows an infinity of discoveries on the nature of different bodies which he submits to a new kind of test: there are surprising facts that he has hardly deigned to announce. Had it been imagined that air could become a solid body? Had it been believed that its

springiness could be removed and restored? Had it been thought possible that certain bodies, such as the bladder-stone and tartar are more than two thirds air, solid and transformed?[18]

VEGETABLE STATICKS:
Or, An Account of ſome
Statical Experiments
ON THE
SAP in VEGETABLES:
Being an ESSAY towards a
Natural Hiſtory of Vegetation.
Alſo, a SPECIMEN of
An Attempt to Analyſe the Air,
By a great Variety of
Chymio-Statical Experiments;
Which were read at ſeveral Meetings before
the ROYAL SOCIETY.

Fig. 2. Stephen Hales' Title Page (in Part).

The significance of Buffon's emphasis on Hales' experiments on the air cannot be overstated, for Buffon was the man of influence who certainly assisted Rouelle in obtaining his position at the Jardin des Plantes. Of Rouelle, more in the next chapter.

Buffon's perception of the significance of Hales' work on air was not apparently typical of the French scientific community. In the years between

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[18] Stephen Hales, *La statique des végétaux et l'analyse de l'air,* traduit de l'Anglois par M. de Buffon (Paris, 1735), vii.

1735 (when the *Vegetable Staticks* was translated) and about 1770, the *Mémoires* of the Academy show no significant attention to the role of air in chemistry. Nor does Diderot's *Encyclopédie* reflect a significant 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 showed air to be obtainable from a wide variety of substances. Two brief examples are given with no hint of the chemical importance of Hales' discovery.

Herman Boerhaave was a professor of the medical school of Leiden whose chemical textbook became a very important contributor to the early eighteenth-century organization of chemistry, as will be seen in the next chapter. But he seems to have vacillated on the role of air as a chemical component of bodies. Initially he considered air in essentially the same way as Boyle, a chaos of various smokes and effluvia which accounted for its particular chemical actions, but whose elastic parts were entirely without chemical behavior. After the appearance of *Vegetable Staticks,* however, he seems to have accepted Hales' evidence without really abandoning his earlier view. When Lavoisier in 1774 summarized the earlier literature on the chemical fixing and liberation of air, he wrote of Boerhaave's views thus:

> The celebrated Boerhaave, to whom we are indebted for an excellent Treatise on the Elements, does not seem to have been always of one uniform opinion, as to the combination and fixation of air. Sometimes he appears to deny that air can be combined with bodies so as to contribute to the formation of their solid parts; sometimes he seems to adopt the contrary opinion, and to inlist under the banner of Dr. Hales. In short, on reviewing what this author has said in different passages of his works, one may plainly discern, that the publication of Dr. Hales' experiments had induced him to change his opinion, and that he adopted, to a certain degree, the system of the fixation of air in bodies; but it is also evident, that this theory did not appear to him sufficiently proved to oblige him to retract, from his works, what he had said on the contrary side of the question.[19]

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[19] A.-L. Lavoisier, *Essays Physical and Chemical,* translated from the French *Opuscules physique et chimiques* [1774] by Thomas Henry (London, 1776; London: Cass Reprint, 1970), 27-28.

In the next chapter we encounter a revival of the four-element ordering of chemistry through the work of Boerhaave and Rouelle. The latter, especially, by assigning distinct chemical and physical roles for each of these traditional concepts, helped re-introduce air (gases) into the mainstream of French chemical thought.

7

THE RETURN OF THE FOUR ELEMENTS

FROM JEAN BEGUIN early in the seventeenth century through Nicholas Lemery and his successors publishing in the Paris Academy *Mémoires* in the eighteenth century, French chemical literature makes virtually no reference to the Aristsotelian four elements, which had long before been supplanted by the somewhat more materially based five principles. Lemery's *Cours de chymie* that climaxed the seventeenth-century textbook tradition was not superceded in France until the appearance of P.-J. Macquer's *Elémens de chymie théorique* in 1749. Lemery's book had sustained the iatrochemical tradition of the five principles throughout nearly three quarters of a century, during which period there was no sign in the French chymical literature of loyalty to the four-element pattern of the peripatetic world of academia. Then, with the appearance of Macquer's texts in 1749–51, a newly materialized doctrine of the four elements was introduced.

Macquer found in the four elements a convenient way to organize the great gains in the empirical knowledge of chemical behavior that had accumulated in the previous fifty years. Macquer's definition of chemistry is consonant with the iatrochemical tradition, but his constituent elements are different, and even though the four elements have names identical with the Aristotelian tradition, they were given an identity that was more operational than metaphysical.

> The Object ... of Chymistry is to separate different substances that enter into the composition of bodies.... But this Analysis, or Decomposition, of Bodies is finite.... In whatever ways we attempt to go further, we are always stopped by substances in which we can produce no

> change, which are incapable of being resolved into others.... To these substances we may ... give the title of Principles or Elements.... Of this kind the principal are Earth, Water, Air, and Fire.[1]

As we shall see, the materiality that Macquer assigned to the revived four elements derived largely from the French iatrochemical studies of the previous fifty years. His new conception derives from the influence of his teacher, G.-F. Rouelle, and the Dutch chemist Herman Boerhaave.

Boerhaave

Until the publication of P.-J. Macquer's textbooks about the middle of the eighteenth century, the only major text to appear that gave Lemery's *Cours de chymie* significant competition was that of Herman Boerhaave (1668–1738) which first appeared in 1724 as an unauthorized publication of his chemical lectures at the University of Leyden. Boerhaave had by this time gained an outstanding reputation for his teaching skills and had drawn students to the University medical school from all over Europe. Though he might have been flattered by the implied compliment in the publication of his teaching, he was angry and felt obliged to prepare and publish his own accurate account of his lectures. It may have been the burden of this extra work that made him petulant; in any case, he undertook the task reluctantly and perhaps with false modesty: "With what confidence could I, conscious of my own insufficiency, and full of admiration for other authors, enter the list of writers in chemistry? At length, however, I undertook the disgustful work, which I now publish; and which I openly declare was extorted from me."[2]

Boerhaave, the son of a protestant clergyman, was brought up with the expectation of following in his father's profession and indeed obtained a doctorate in philosophy from the University of Leyden in 1690. For reasons

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[1] P.-J. Macquer, *Elements of the Theory and Practice of Chemistry,* translated by A. Reid, 2 vols. (London, 1758), vol. 1, 1-2.

[2] Boerhaave's Latin version, *Elementa Chimiae,* appeared in 1732. English quotations are from Herman Boerhaave, *A New Method of Chemistry,* translated from the Latin by Peter Shaw, MD, 2 vols. (London, 1741), vi.

not entirely clear he embarked on a study of medicine at Leyden, where he did not attend the lectures but pursued his studies vigorously on his own while employed at the university library. He took his medical doctorate at Harderwijk in 1693. Chemistry was not taught at Leyden during those years, but he became thoroughly familiar with the available literature, making himself a follower of the iatrophysical traditions originating in Italy, a pattern that dominated his later medical thought and writings and which left no place for the iatrochemical doctrines, especially the acid-alkali theory of Sylvius and Tachenius. Thanks to his early classical education, he was comfortably familiar with the Aristotelian four-element pattern of metaphysical components which formed the organizational basis of his chemical presentations.[3]

After receiving his medical degree, Boerhaave practiced medicine in Leyden for the rest of the century while still contemplating a career as a clergyman. In 1701 he received a lectureship in medicine at the University of Leyden, and his lectures became so popular that he received a professorship of botany and medicine in 1709. It was not until 1718, after receiving the professorship in chemistry, that Boerhaave began teaching that subject.

The bulk of Boerhaave's book resembles Lemery's by showing a mixture of the traditional iatrochemical recipes heavily spiced with *ad hoc* mechanical explanations. Boerhaave's mechanical views never achieved a real synthesis with the traditional chemical recipes, for the mechanical views so dominated his conceptions that the chemistry as such was left without any real identity. Indeed it is difficult at times to discern any chemistry at all in his conceptualization of the traditional four elements, which were assigned roles under the rubric of "instruments," the agents by which chemical change is initiated and accomplished. That had long been the role of fire; but Boerhaave, by placing his emphasis on the agents of change rather than on the nature of the change, was taking a much more physicalist view of chemistry than the iatrochemists of France. Boerhaave found the four

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[3] See G.A. Lindeboom's biography of Boerhaave, *Dictionary of Scientific Biography,* vol. 1, 224-228; and his *Herman Boerhaave: The Man and his Work* (London: Methuen, 1968); Hélène Metzger, *Newton, Stahl, Boerhaave et le doctrine chimique* (Paris: Albert Blanchard, 1930); Rina Knoeff, "the Making of a Calvinist Chemist: Herman Boerhaave, God, Fire and Truth," *Ambix* 48 (2001): 102-111.

traditional bodies insufficient and added two more instruments, *Menstrua* and *Vessels,* that is, the solvents and the containers in which experimentally-initiated changes of the chemist take place. The mechanical nature of his definition of chemistry is worth noting:

> Chemistry is an art which teaches the manner of performing certain physical operations, whereby bodies cognizable to the senses, or capable of being render'd cognizable, and of being contain'd in vessels, are so chang'd, by means of proper instruments, as to produce certain determined effects; and at the same time discover the causes thereof; for the service of various arts.[4]

His mechanistic approach is further illustrated by the way he organized his treatment of the metals, arranging them in a sequence of decreasing densities rather than according to some chemical property, or some traditional sequence. Metals are defined entirely in terms of their physical properties, as the "heaviest of fossils, fusible by fire, but cohering again in the cold, so as to become ductile and distendable under the hammer."[5]

When he discusses the chemical aspects of metals, Boerhaave resorts to alchemical descriptions, which still utilize the MERCURY-SULPHUR conception that had largely been abandoned even if not refuted nor completely superceded. There are only six simple metals, he says, gold, silver, copper, tin, iron, and lead:

> The ancients indeed added quicksilver to the number; but this as wanting hardness, ductility and fixity, has no pretensions to be a metal. However, the great affinity it bears to the rest, in respect to weight, simplicity, the place where it is found, and its easy uniting with other metals, has given rise to a very ancient opinion, which prevails much today, that mercury is the chief basis of matter of all the metals.[6]

Boerhaave then goes on to give brief accounts of the metallic-astrological symbols, finding justifications for each of them in the particular properties of the metals themselves. After a whole page of this, the translator

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[4] Boerhaave, *New Method,* vol. 1, 65.

[5] Boerhaave, *New Method,* 67.

[6] Boerhaave, *New Method,* 67.

cannot resist commenting, "The elements of chemistry, perhaps, should rather be kept clear of these caballistic conceits, for fear of giving a wrong turn to the mind at its first setting out in this practical science; tho' they may have their use in reading the alchemical literature."[7]

In speaking of mercury Boerhaave states:

> It unites the most readily with gold of all metals, next with lead, next with silver, and next with tin; more difficultly with copper, and scarce at all with iron. May we not hence argue that it readily unites with the mercury which makes the basis of metals, by some affinity of nature therewith; and this the readier where there is a greater quantity of mercury, and less of a foreign matter in the metal?

Here Boerhaave has provided a kind of mechanical "explanation" of the varying order of affinities of mercury for the other metals through the principle of like attracts like. The alikeness is found in the heaviness of the metal, which is owing to the quantity of the philosophical MERCURY contained in each metal.

Among the concluding corollaries at the end of his discussion of the metals, he includes the following.

> 6. Gold therefore consists of a pure, simple matter, like mercury fixed by another pure, simple, subtile principle, diffused thro' its minutest parts, and intimately uniting them to one another, and to it self. This the chemists mean when they say it consists of mercury and sulphur.
>
> 7. The other metals consist of the same principles [along with another] lighter matter which is different in the different metals, and is called earth. [Some say there is also crude sulphur.]

He adds that "It is wrong to say metals can be easily converted one into another, except regarding the mercurial parts;... the quantity of gold obtained in a transmutation is limited by the amount of mercury in the original metal." Nowhere in his discussion of the metals does he attempt to express

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[7] Boerhaave, *New Method,* 68.

their composition in terms of the four elements, but relies instead on the alchemists' MERCURY and SULPHUR.[8]

Boerhaave apparently conducted a great deal of chemical experimentation with much patience and care. Yet he seems out of the main stream of the thinking of chemical practitioners. He tacitly admitted this in the Author's Preface, where he states that he little imagined that he should do anything in chemistry:

> [T]here are already so many books extant on it, and several of them well written. I scarce saw room for me, either to do better, or to produce any thing new upon the subject. The duty of my professorship, indeed, required me to give annual lectures in chemistry; but I had no farther aim in this, than to teach the first rudiments, and exhibit a few examples of the art, to those under my care. And to this end, the order wherein I digested matters, and the openness and simplicity wherewith I delivered them might perhaps be of service. In both these respects, indeed, my endeavours still seem'd wanting to raise chemistry, at length, into a rank with the other academical sciences.

At this point, the translator interjects, "Hence may appear the reason of our title; *A New Method of Chemistry;* for the author's aim is not to improve the matter, but only the manner of the science...."[9]

Boerhaave need not concern us further in our quest for the history of the conceptualization of chemical composition, for unlike Stahl and the other chemists discussed in previous chapters, he seems hardly to be concerned with composition at all. He fits best into the sequence of mechanical philosophers who were trying to subsume chemistry under the dominance of mechanics, to make chemistry a derivative science. In England especially there was a prestigious group of followers of the philosophy of Isaac Newton who fit this pattern.[10]

The use of the four elements becomes more significant through the

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[8] Boerhaave, *New Method,* 103.

[9] Boerhaave, *New Method,* v.

[10] See Arnold Thackray, *Atoms and Powers* (Cambridge, Massachusets: Harvard University Press, 1970).

work of Guilleaume-François Rouelle, who in the middle of the century utilized the same pattern for his own presentations. Rouelle became the central figure in gathering French chemical thought into a loose synthesis that also incorporated the Stahlian doctrine of phlogiston. By combining the elemental role of the four elements with Boerhaave's instrumental role, he created a pattern that gave each of them a double function, one physical and the other chemical. This distinction proved to be highly important in freeing the chemical tradition from the domination of the much-admired mechanical philosophy, and allowed chemistry to find its compositional foundations in its own internal experience.

Rouelle and the Consolidation of French Chemistry

G.-F. Rouelle has long been recognized as one of the really important intellectual ancestors of the chemical revolution attributed to Lavoisier. This is not because he in any way anticipated Lavoisier's work, but rather because he more than anyone else in mid-eighteenth century defined the chemistry that Lavoisier inherited and eventually replaced.

Guilleaume-François Rouelle (1703–1770) was apprenticed in pharmacy in Paris between 1730 and 1737. He began giving private lectures in chemistry in 1737, gaining enough notoriety that he received the appointment as Demonstrator and Professor in Chemistry at the Jardin des Plantes, where L.-C. Bourdelin (1696–1777) was the Professor. This was in 1742. Rouelle retained both these titles as well as continuing his private lessons until 1768 when ill health forced his retirement. The public lectures at the Jardin were aimed toward a public audience of widely mixed backgrounds, so he kept his private lectures for more sophisticated and serious students of chemistry.[11]

Rouelle's private lectures were attended by nearly everyone who later became chemically significant in France, including Lavoisier. Rouelle's views which incorporated a modified form of the phlogistic doctrine from Germany, were spread by a small group of men to whom Martin Fichman

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[11] Rhoda Rappaport, "G.-F. Rouelle: An Eighteenth-century Chemist and Teacher," *Chymia* 6 (1960): 68-101.

has given the name of French Stahlists.[12] These men generated the mainstream of French chemistry from about 1750 up through the 1780s, when Lavoisier's revolution was completed. Of these, Pierre-Joseph Macquer (1718–1784) was probably the most influential in spreading Rouellean views; his textbooks published at mid-century were widely used and almost universally praised, and his *Dictionary* in 1766 also became a widely admired and utilized standard of chemical knowledge. Rappaport says:

> The publication of Macquer's *Elémens de chymie théorique* (1749) ... was in all likelihood the most important single event in the spread of Rouelle's chemical theories. While Rouelle was not acknowledged as the source of Macquer's theories, the debt to Rouelle is so marked that Macquer's textbook and his own private courses in chemistry can be considered two of the principal channels through which Rouelle's teaching reached a still wider audience.[13]

Another of the French Stahlists, Gabriel-François Venel (1723–1775), wrote most of the chemical articles in Diderot's *Encyclopédie,* thus providing further influential expression of his teacher's views. The last of the French Stahlists of significance, though less well-known today, was the prominent experimenter and writer, Antoine Baumé (1728-1804).

Rouelle's Element/Instrument Theory

Rhoda Rappaport has provided an analysis of Rouelle's overall structure into what she has denominated his Element/Instrument theory.[14] In Rouelle's design, happily laid out more clearly by Rappaport than Rouelle ever expressed it himself, each of the four elements, EARTH, WATER, AIR and FIRE, occurred either fixed in a chemical combination, or free in an uncombined state.

Rouelle's chemistry can be seen as a loose synthesis of two lines of in-

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[12] Martin Fichman, "French Stahlism and the Chemical Studies of air," *Ambix* 18 (1971): 94-122.

[13] Rappaport, "G.-F. Rouelle," 77.

[14] Rhoda Rappaport, "Rouelle and Stahl: the Phlogistic Revolution in France," *Chymia* 7 (1961): 73-102.

fluence. The first is from Boerhaave whose use of the four traditional elements chiefly as physical instruments provides a pretty clear anticipation of one part of Rouelle's Element/Instrument theory as described by Rappaport. The other source is the more diffuse one of the French *chymistes,* the tradition of Lemery, Geoffroy, Homberg and their successors in the Paris Academy, as has been presented here in earlier chapters. From this tradition Rouelle obtained the knowledge of phlogiston which the earlier French chemists had variously called the sulphur principle, the oily principle, etc. From them he also got the concept of earth-as-matrix, the captor of the spirit of acid, the base which gave fixity to the acid in the form of a neutral salt, whose definition Rouelle himself perfected in the two papers of 1744 and 1754.

Rouelle deliberately and persistently emphasized the distinction between physical and chemical behavior, and related this distinction to a qualitative mechanical view of matter. Specifically, he believed that the properties of the bodies in the aggregate state were not necessarily the same as the properties of the individual particles making up the aggregate. By this distinction he avoided the problem faced by the Boylean philosophers who saw elasticity as an intrinsic property of air, even down to the individual particle. For those who, like Boyle, hypothesized an elastic particle of air, the presence of air in chemical combination required a considerable force to hold the elastic particle in its combination. Rouelle, however, assigned elasticity only to the aggregate association of air particles, though he offered no explanation for the distinction, and thus had no problem in conceiving of individual air particles combined with the particles of other materials. The presence of heat or free fire could cause further expansion by generating motion of aggregate particles of air.

This distinction between the singular or aggregate states of particles was codified through the conception of the two forms for each of the four elements. Each could exist either free from combination, that is, in an aggregate state where only similar particles were together, or in a fixed state, that is, combined with particles of a different kind. Thus we can generate the pattern in Fig. 3.

The last items in each column are those emphasized by Rappaport in her interpretation of Rouelle's Element/Instrument theory. On the other

Physical	**Chemical**
aggregate	singular
free	fixed
Instrument	**Element**

Fig. 3. States of Particles.

hand, Fichman emphasizes the physical/chemical distinction.[15] These interpretations are not in conflict, however, for either of the binaries used carries with it the other in the same column above or below. J.B. Gough sees Stahl as the originator of this chemical/physical distinction.[16] If he is correct, that would perhaps explain Rouelle's views, for as Rappaport has shown, Rouelle was indeed influenced by Stahl.[17] In my view, however, Rouelle gained his chemical aspects from the French chemical patterns of experimentations and may have derived the physical views from Boerhaave.

The above arrangement is more of a simple ordering than a true system with strong interlocking relationships, yet the importance of Rouelle's explicit distinction between chemical and physical associations or combinations cannot be overemphasized. Chemistry at this time still had not established its clear independence, and one of its fundamental struggles of this century can be seen as that of independence from the mechanical philosophy.

Rouelle also retained in his organization the hierarchical concept found in the mechanical philosophy of chemistry, as well as in the writings of Becher and Stahl. In the increasing order of complexity, the categories of combination were *element* or *principle* as the simplest, *mixt* (made up of two elements), *compound* (made of a mixt plus another element), and *supercompound* (a combination of a compound with a mixt or another compound). As with the older alchemical tradition, the principles or elements could never be obtained in a pure or isolated state. Their presence had to be inferred from the properties of the mixts in which they were found.

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[15] Fichman, "French Stahlism."

[16] J.B. Gough, "Lavoisier and the Fulfillment of the Stahlian Revolution," *Osiris* 4 (1988): 13-33.

[17] Rapport, "Phlogistic Revolution in France."

The mechanical philosophy now provided a new justification for the philosophical inability to isolate the elements. Bodies combined with one another because of some kind of attractive force, and the strongest such attraction would be between the two principles which combined to form a mixt. The force between two mixts would be much smaller because much of that attractive force had been used up, so to speak, in forming the mixts themselves. Thus there came to be a rule that the more compounded a body was, the easier it would be to decompound it. Running that rule in the other direction, the simpler a body was, the harder it would be to decompound it further. The only way to decompound a mixt containing only two principles, was to offer another mixt with which the principles in the first could exchange partners. There was nothing that could take one principle from another and leave it in isolated state. Whatever the origin of this idea, it readily served as a mechanistic rationalization for what had been the traditional view from Aristotelian times, that the elements cannot be isolated in material reality.

Let us now examine how Rouelle's new element/instrument system gave rational coherence to both the metaphysical tradition of the four elements, as well as incorporating their recently developed materialities of composition. Rouelle has not left us with an account, so the following conjecture is circumstantial, though plausible.

As we have already seen, there was throughout this period a steady increase in the materialization of the chemical elements, whether one believed in three, four, or five. In the case of FIRE the phlogiston concept is certainly in that pattern. But the chief ancestor lies in the even older tradition of the sulphur principle. The sensation of heat is seen as distinct from the particles of FIRE, which for many chemists, Boyle among them, were responsible for the increase in weight when metals were calcined. There is no problem in finding a source for Rouelle's idea of FIRE as occurring both fixed and free.

That AIR can also be a part of chemical combination had been pretty much established by the work of Stephen Hales, whose results had been published in his *Vegetable Staticks* in 1727. As we have seen, this work had been translated into French by Rouelle's own sponsor in the Jardin du Roi, Georges Louis Leclerc le conte de Buffon (1707–1788), in 1735. The idea of air thus occurring in both the fixed and free states was readily available to Rouelle.

Rouelle himself had studied the presence of water in chemical compounds, especially in the neutral salts where the water of crystallization is a readily demonstrated example of water in a fixed, combined, and solid form. In 1744, he coined the phrase "water of crystallization"[18] that distinguished its chemical role from its physical role as solvent. We can leave to Rouelle's creativity the explanation of how he must have soon recognized the parallel patterns among these elements, and organized his chemical thinking accordingly. How EARTH became a part of this pattern is readily seen in the history of the matrix concept recounted in Chapter Four. The instrumental role of the matrix became the crucible of the experimentalist, and the earthy part became the chemical EARTH of Rouelle's scheme:

	FIXED (chemical element)	FREE (physical instrument)
FIRE	*phlogiston*	*sensible heat; promotes chemical change*
AIR	*fixed air*	*assists in distillations, evaporations*
WATER	*water of crystallization*	*solvent or menstruum, divides bodies*
EARTH	*base of neutral salts*	*crucibles in which reactions took place*

Conceptually, the most important point here is the clear distinction Rouelle made between the chemical and physical aspects of behavior. Historically, the most important point was the preparation this view made for the return of air, or gases, to chemical attention. As we shall see in Chapter Nine, the focused attention on air made possible the extension of the phlogistic doctrine to pneumatic chemistry, to the increased benefit of both.

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[18] G.-F. Rouelle, "Sur les sels neutres," *Mémoires* (Paris) 1744: 353-364.

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FRENCH CHEMISTRY CIRCA 1760

A CASUAL READING of the traditional literature devoted to the chemical revolution would lead the reader to believe that phlogiston was the chief theoretical conception of that period. Certainly the disputes associated with the revolution in the 1770s and 1780s were almost entirely focused on phlogiston and the nature of combustion and had little to do directly with Rouelle's chemical philosophy generally. As previously indicated, Rouelle had achieved a loose synthesis of the chemical knowledge of the previous fifty years. Although phlogiston was a part of his teaching, that concept had not been extended significantly beyond the applications traditionally associated with the old sulphur principle, by whatever name. By the middle of the eighteenth century, phlogiston had become the chief term representing the inflammable principle because it carried none of the ambiguous meanings associated with the words sulphur, oil, oily principle, etc., but its conceptual use was little different from that of the older terms.

Chemical systems in those days were little more than assemblies of more or less independent rules and concepts, lacking the interdependent structure of a coherent system of concepts and practice we would today call a theory. The rejection of one part did not necessarily invalidate any of the others. This is certainly the case with the chemistry of Rouelle, whose teaching nonetheless colored the attitudes and writings of his pupils. The two major expressions of Rouelle's influence are found in the writings of Gabriel-François Venel (1723–1775), the principle contributor of the chemical articles in the *Encyclopédie* of Denis Diderot (1713–1784), and the textbook and Dictionary of Pierre-Joseph Macquer (1718–1784).

Encyclopédie

Toward the middle of the eighteenth century a remarkable cluster of critical writings appeared in France, written by a variety of authors, but the climax of this activity was the publication of the *Encyclopédie* under the editorship of Denis Diderot and Jean Le Rond d'Alembert. The initial intention of its publisher had been to prepare a French translation of the 1728 *Cyclopaedia* of Ephraim Chambers, which had been a very successful reference work in Britain. But after Diderot and d'Alembert became the editors of the project, its scope was greatly expanded to become the most ambitious and significant publishing venture of the century. Conceived in the spirit of the Enlightenment, the *Encyclopédie* was written by a group of men "who were convinced that through their combined efforts they could substantially contribute to the progress of humanity."[1] The French *philosophes* saw their century as the first to be freed from superstition and in possession of the power to comprehend rationally the entire universe and control the course of the future. Newton's monumental success in giving mathematical expression to the laws of the heavens provided the justifying example for such intellectual optimism that all nature could be similarly rationalized. The *Encyclopédie* was not the first systematic effort to consolidate the accumulated knowledge that would form the basis of universal education and the launching pad into the future, but it was the most ambitious and the most inspirational.

The first of twenty-eight volumes (eleven were devoted to engraved plates of industrial workings) appeared in 1751, but the work was not completed until 1772. The most important chemical article, "Chimie," written by Venel, appeared in the third volume (1753); this and the new textbook written by Macquer about the same time form a summary of French chemistry at mid-century.

Venel's chemistry is definitely derivative of Rouelle's, but his expressed loyalty is to Stahl. It is not clear just what he thought Stahl did for chemistry, for his praise is general rather than specific. With regard to phlogiston,

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[1] Richard N. Schwab, "Translator's Introduction" to d'Alembert's "Preliminary Discourse to the Encyclopaedia of Diderot," (Indianapolis: Bobbs-Merrill, 1963), xi.

Venel follows Rouelle's view that it is fixed FIRE. Peculiarly, however, although Jean-Claude Guédon's careful and extensive study of chemistry in the *Encyclopédie*[2] has identified twenty-one references to the article "Phlogistique," the article itself, in volume XII, consists in its entirety of only one sentence: "It is the same as elementary fire." It is obvious that a larger and more elaborate article was once planned but, for reasons now unknown, abandoned.

If one follows the implied suggestion and looks up fire, "Feu," there will be found the following remarks:

> Chemists—at least Stahlian chemists—consider *fire* from two quite different points of view.
>
> First, they see it as one of the materials or principles of composition of bodies for, according to Stahl's well summarized theory, the principle which chemists have called by names such as *sulphur, sulphurous principle, flammable principle, flammable and coloring earth* and by some other, less known names, which we will mention elsewhere, see "Phlogistique," their principle, I say, is nothing else than *fire* itself —a pure and elementary substance, the true matter, the proper being of *fire,* the *fire* of Democritus and of some modern physicists.[3]

This is clearly a Rouellean view of fire, but the evidence hardly supports the view that the chemistry of the *Encyclopédie* is characteristically phlogistic. For example, Venel follows this passage by noting that "phlogistique" is not a well-defined term, it "is but one of these undetermined names which must always be ascribed to substances on the essence of which several extremely conflicting opinions exist."[4] Guédon, from his extensive study of the chemistry in this major work, states quite flatly that "There is no theory of phlogiston as such in the chemistry of the *Encyclopédie* ... the chemistry of the *Encyclopédie* does not rest on a theory of phlogiston, but on affinities."[5]

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[2] Jean-Claude Guédon, *The Still Life of a Translation: Chemistry in the* Encyclopédie (Unpublished Ph.D. dissertation, University of Wisconsin, 1974).

[3] *Encyclopédie,* vol. VI, 609a; quoted and translated by Guédon, *Still Life of a Translation,* 269.

[4] *Encyclopédie,* 269.

[5] Guédon, *Still Life of a Translation,* 292.

How then is the chemistry of the *Encyclopédie* to be summarized? The work is, after all, an encyclopedia, a collection of topical information and not intended to present a system of chemistry or of anything else. Hence most of the articles are descriptive accounts of observational facts. Guédon makes the case for its Rouellean character.[6]

Macquer

Pierre-Joseph Macquer's *Elémens de chimie théorique,* (1749) and *Elémens de chimie practique* (1751) became the first significant French successor to Nicholas Lemery's *Cours de chymie,* first published in 1675. Unlike earlier works it was an attempt to offer chemistry for its own sake, independent of medicine. It was intended for the "absolute Novice in Chymistry; to lead him from the most simple truths ... to the most complex." Hence he begins with the elements, then moves on to saline substances (acids, alkalies, and their combinations); the volatile sulphureous spirit, sulphur, phosphorus, and the neutral salts, which have an earth or a fixed alkali for their bases. Then on to the metals, which "are scarcely more compounded than the saline...."

> The Object ... of Chymistry is to separate the different substances that enter into the composition of bodies.... But this Analysis, or Decomposition, of Bodies is finite.... In whatever way we attempt to go further, we are always stopped by substances in which we can produce no change, which are incapable of being resolved into others.... To these substances we may ... give the title of Principles or Elements.... Of this kind the principal are Earth, Water, Air, and Fire.[7]

Nowhere in this work is there a discussion of what seems to have figured so prominently in Rouelle's chemistry, the element-instrument theory. There is one significant residue of that scheme, however, for one of the elements does exist in two forms for Macquer: FIRE, which can appear free when it manifests itself as sensible heat, and fixed, when it is called phlo-

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[6] Guédon, *Still Life of a Translation,* 370f.

[7] P.-J. Macquer, *Elements of the Theory and Practice of Chemistry,* translated by A. Reid, 2 vols. (London, 1758), vol. 1, 1-2.

giston. Phlogiston becomes for Macquer the fifth principle or element of bodies.

Of AIR he says little, other than to state that it enters into the composition of many bodies, especially those of animal or vegetable origin. But he offers no explanation of how a body characterized by its elasticity can be fixed into a solid state.

Earths are difficult to obtain in a truly pure form, "for after our utmost endeavours to purify them, the Earth we obtain from different compounds are found to have different properties according to the different bodies from which they are procured; or else, if these earths be pure, we must allow them to be essentially different, seeing they have different properties."[8] He apparently sees each of these different earths as a modification of EARTH as a First Principle or element.

"The matter of the Sun, or of Light, the Phlogiston, Fire, the Sulphureous Principle, the Inflammable matter, are all of them names by which the Element of Fire is usually denoted." But he adds that we need to distinguish between its free and combined states. In the free state, FIRE is the essential fluid, it makes all other bodies fluid if present in sufficient quantity. "Air itself might become solid, if it could be entirely deprived of the Fire it contains...."[9] This view is also to be found in the lectures of his teacher, Rouelle.

Phlogiston or fixed FIRE differs from free FIRE in that "it communicates neither heat nor light" to the compounds in which it is combined. Nor does it produce a change in its state. "We can convey it from the body with which it is joined into another body, so that it shall enter into its composition thereof, and remain fixed in it." When this happens, both bodies show considerable change: this is what requires its distinction from free FIRE "and to consider it as the element of Fire combined with some other substance...."[10] It is ironic that Macquer's clear distinction of chemical from physical change is associated only with phlogiston.

> The inflammability of a body is an infallible sign that it contains a phlogiston, but from a body's not being inflammable, it cannot be in-

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[8] Macquer, *Elements,* 5-6.

[9] Macquer, *Elements,* 8.

[10] Macquer, *Elements,* 9-10.

> ferred that it contains none: for experiments have demonstrated that certain metals abound with it, which yet are by no means inflammable.[11]

Note that this statement can be seen as a means for determining composition, which after all is the main goal of chemistry. Thus if a body is inflammable, it is at least partly composed of phlogiston. Indeed, a similar statement can be made for any principle that is closely associated with an external property, a traditional view of composition for centuries.

There are only two ways of separating phlogiston from its combination:

> (1) By having the compound react with a body for which the phlogiston has a greater affinity than it has for the one with which it was originally combined. Thus the phlogiston will still be in combination, though with a different body.
>
> (2) By calcination or burning, when "it is entirely dissipated in the decomposition, so that no part of it can possibly be secured."[12]

Thus does Macquer "explain" why phlogiston can never be obtained pure. Note also, that the phlogiston is simply "dissipated" during the burning process, and we must ask if this statement is inconsistent with his earlier one that states that there are only two ways of separating the phlogiston from its combinations. He does not explain what he means by dissipation, nor does he indicate the role of air in combustion.

But the operating core of Macquer's chemistry is not the particular elements, but the rules of combination, or affinity. There are seven given.

> (1) If one substance has any affinity or conformity [*rapport*] with another, the two will unite together and form one compound.
>
> (2) It may be laid down as a general rule, that all similar substances have an affinity with each other, and are consequently disposed to unite; as water with water, earth with earth, &c.
>
> (3) Substances that unite together lose some of their separate pro-

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[11] Macquer, *Elements,* 10.

[12] Macquer, *Elements,* 10.

> perties; and the compounds resulting from their union partake of the properties of the substances which serve as their principles.
>
> (4) The simpler a substance, the stronger its affinity, and the more difficult its decomposition.
>
> (5) If a substance A has no affinity for a substance B which is part of a compound BC, but has a stronger affinity for C than B has for C, then it will form a new compound AC.
>
> (6) Sometimes A does not displace either substance in a compound BC, but joins them to form a "compound of three principles." This happens when A has an equal or almost equal affinity for B and C, or an affinity with B equal or almost equal with B's affinity for C.
>
> (7) If a substance A has not sufficient affinity with B to decompose the compound BC by itself, it may be able to do so when combined with another substance D which has an affinity for C, and so bring about a double decomposition and a double union.[13]

Macquer calls these statements, "fundamental truths, from which we shall deduce an explanation of all the phenomena in Chymistry...." Numbers 1, 5, 6, and 7 come from Geoffroy and are statements of well-established laboratory experience. According to Alistair M. Duncan,[14] numbers 2, 3, and 4 came from Stahl, and represent conjectural or theoretical assertions, though 2 and 3 had long been traditional views. As we shall eventually see, the latter group becomes increasingly in conflict with the behavior of real chemical entities. But first let us see how Macquer utilizes these truths to explain "all the phenomena of chemistry."

Macquer discusses saline substances in accord with these rules, adopting the view from Becher and Stahl that all saline bodies are composed of elemental earth and elemental water.

> If a particle of water be intimately united with a particle of earth, the result will be a new compound which, according to our third proposition of Affinities, will partake of the properties of earth and of water;

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[13] Macquer, *Elements,* 12-14.

[14] "Some Theoretical Aspects of Eighteenth-Century Tables of Affinity – I," *Ann. Sci.* 18 (1962): 177-194 at 191. See also Alistair M. Duncan, *Laws and Order in Eighteenth-Century Chemistry* (Oxford: Clarendon Press, 1996), 192 ff.

> and this combination principally forms what is called a *Saline Substance.* Consequently every saline substance must have an affinity with earth and with water, and be capable of uniting with both or either of them, whether they be separate or mixed together: and accordingly this property characterized all Salts or Saline Substances in general.[15]

His third rule implies that the properties of a compound are a blend of those of its ingredients, a concept of long standing. In his next paragraph he gives examples of salts that are more volatile than EARTH, but less volatile than WATER, thus again implying the confirmation of the original position that all salts are composed of EARTH and WATER. Clearly he has in mind something other than ordinary earth and water when he uses the terms this way.

His illustrations offered to justify the tradition of Becher and Stahl that all salts are composed of EARTH and WATER are easily found.

> The first is, the conformity Salts have with earth and water, or the properties they possess in common with both.... The second is, that all Salts may be actually resolved into earth and water by sundry processes; particularly by repeated dissolutions in water, evaporation, dessication, and calcination.

He tacitly states the ideal confirmation of composition by the cycle of analysis/synthesis, but admits that chemists "have not yet been able to produce a Saline Substance, by combining earth and water together." He concludes the discussion at this point by saying that "it is sufficient to our purpose, that water and earth are demonstrably amongst the real principles of Saline Substances, and that no experiment hath ever shewn us any other."[16] He accounts for the enormous variety of saline substances in part by suggesting variations in either the quantity or quality of the EARTH they contain. Or they may contain yet another principle in a quantity too small to destroy completely its saline qualities. It seems that Macquer's whole rationale leads to, or derives from, the idea that chemical combination is

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[15] Macquer, *Elements,* vol. 1, 14.

[16] Macquer, *Elements,* 15.

a blending of properties, that chemical change is continuous not a discontinuous process, that is, Rule 3, above.

In his *Dictionary of Chemistry* published in 1766 Macquer states the rule again that "all compound bodies have properties partaking of the properties of the principles of which these bodies are composed." This applies, he further states, to volatility, gravity, opacity, transparency, ductility, hardness, fluidity, etc., "so that, supposing we knew perfectly the properties of the principles of a compound, we might, by examining the properties of this compound, discover its principles, even though its analysis were impossible." He soon tempers this confident assertion by stating in the next paragraph that the rule is subject to a "considerable number of restrictions and modifications," properties are sometimes cancelled or created by combination, and not always blended.[17]

Macquer's textbook and his Dictionary made him one of the most authoritative chemists of the century. Yet the translator of the Dictionary, James Keir, clearly expressed a view contrary to Macquer's with regard to the rule on the blending of properties. In a footnote, Keir wrote that the case might be just the reverse of that stated by Macquer:

> [A] change of properties, and a production of new properties, may be considered as criterions, by which compound bodies, chemically combined, may be distinguished from bodies formed merely by mixture or apposition of integrant parts; in which latter kind of bodies, the properties are intermediate betwixt the properties of several component parts, and no new properties are produced.

Keir then gives several examples, the most familiar being that acids and alkalies destroy each other's properties in forming neutral salts. In another place Keir is gently critical of Macquer's choice of elements, for philosophers have not proved the existence of even *one* particular element.

> Our incapacity to decompose does not necessarily imply an impossibility of decomposition. For if we should call every substance an *ele-*

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[17] P.-J. Macquer, *A Dictionary of Chemistry*, 2nd English edition, 3 vols. Unpaginated (London, 1777), vol. 1, article "Affinity."

> *ment* that we cannot analyse, (and thus we might speak precisely concerning *elements*) then certainly many other substances besides fire, air, water, and earth, might be enumerated as elements.

From this view, Keir adds, the number of elements so defined must eventually decrease as the progress in chemical knowledge discovers new ways of decomposition.[18]

It is unfortunate that Keir did not push on with this idea of an element as any body that we have not yet been able to decompose. As we shall see later, this is precisely the definition that comes to be utilized by many later chemists, and constitutes the operational basis for the new nomenclature and ultimately the expression of composition in terms of atomic weights. I know of no earlier advocacy of this idea so clearly stated as this by James Keir.

Another historiographic point is worth mentioning here. The traditional problem of the chemical revolution has been long identified as that of combustion. Certainly, as we shall see, the great debates between Lavoisier and the phlogistonists of the 1770s and 1780s centered on that phenomenon, and on the roles of phlogiston and/or oxygen in that process. The implication has been in this tradition that combustion was a great chemical problem in the seventeenth and eighteenth century, before the discovery of oxygen created the debates. We have already seen, however, that in the seventeenth and early eighteenth centuries combustion was not viewed as a problem; and my reading of Macquer indicates that it was not a problem with him, either, right before it became the battleground of the chemical revolution. Macquer's was a renowned and widely recommended text of the mid-century, and to the extent that his views are representative, combustion was *not* of great concern to chemists before the advent of serious studies of pneumatic chemistry, about 1770.

Macquer defined combustion as "nothing else than the disengagement of the inflammable principle contained in several kinds of bodies, which are therefore called combustibles." He had rather little else to say about it. His entries in the Dictionary under air and combustion indicate that the

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[18] Macquer, *Dictionary,* article "Affinity."

"access of air is indispensably necessary to maintain the combustion of bodies," but much of his discussion is concerned with obviously unsatisfactory ways of explaining that fact, though being unable to find an acceptable explanation doesn't seem to have bothered him much, either.[19]

What happens to the phlogiston whose disengagement constitutes the combustion process? Later in the century after the role of the atmosphere was better understood, Joseph Priestley had the departing phlogiston become a part of the atmosphere, combined with it so that the air was phlogisticated. Macquer, writing before pneumatic chemistry had become widely significant, described the burning of sulfur as a decomposition in which "The Phlogiston is destroyed by the flame, and the Acid exhales in vapour."[20] In another passage, the phlogiston is similarly said to be destroyed in quite a different kind of process, the precipitation of metals from acid solution by the addition of alkali. In this case the phlogiston is destroyed "by the solution and precipitation, and must be restored before they can recover their [true metallic] properties."[21]

I have found no evidence that Macquer considered the possibility that ordinary kinds of matter could be destroyed. Only phlogiston and possibly the matter of heat (which is closely related to phlogiston) seem to have been subject to this kind of destruction.

The science of chemistry in France in the 1750s was still largely without a clear organizing scheme. Nicholas Lemery's venerable textbook, originating in 1675, had finally been superceded by P.-J. Macquer's *Elémens* about 1750, though Théodore Baron had thought Lemery's still worth a new edition published in 1757. But Macquer's text contained nothing really new. The deliberate discussion of composition was still in terms of metaphysical elements, though the empirical descriptions had become increasingly material, especially that centered on the behavior of the neutral salts and the acids and bases from which they were synthesized and into which they were commonly analyzed. In spite of this apparent move toward experientially defined composition, chemists such as Macquer and other followers of Rouelle still discussed composition in metaphysical terms.

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[19] Macquer, *Dictionary*, article "Combustion."

[20] Macquer, *Elements*, 26.

[21] Macquer, *Elements*, 48.

Empirical affinity rules as summarized in Geoffroy's table from 1718 were widely used as explanation of common chemical behavior, but only Macquer had attempted to organize the rules into a chemical system. But here his use of Stahlian philosophical rules thwarted his chances of a successful organization.

Phlogiston, though soon to become elevated into a vigorously promoted system, had not yet become much more than another chemical agent different from other material bodies only in its elusiveness, a distinction occasionally noted but rarely questioned, at a time when metaphysical composition still dominated explicit thought. Even those who, like Macquer, gave it prominence did not organize general knowledge around it. Phlogiston theory did not yet exist in any meaningful way.

At least one man, G.-F. Venel, sensed the indeterminate state of the science and called for a revolution that would give chemistry its proper place in the pantheon of the sciences:

> It is clear that the revolution that would place chemistry in the rank that it merits, that would put it at least at the side of mathematical physics; that this revolution I say, can be carried out only by an able, enthusiastic and bold chemist who, finding himself in a favorable position, and profiting ably from several fortunate circumstances, would know how to attract the attention of learned men, first by a noisy ostentation, by a decided and affirmative manner, and then by reasons, if his first weapons would have subjugated prejudice.[22]

Venel did not offer any opinion on the nature of the improvements that chemistry needed, but we can take his statement as recognition that he thought it was time chemistry received something better than it yet had. The 1760s brought new knowledge of the chemical behavior of gases, which received immediate explanations in phlogistic terms, giving that concept its most significant application beyond the place of its origin. The phlogiston theory, so-called, was created by the opportunity to encompass the new

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[22] From Venel's article "Chymie" in the *Encyclopédie*, vol. 3, 409-410. Quoted and translated by Jerry Gough, "Some Early References to Revolutions in Chemistry," *Ambix* 29 (1982): 106-109 at 107.

chemistry of gases into its already existing pattern of thought. Hardly had this success been achieved when the very existence of phlogiston was challenged, and the debates of the chemical revolution quickly followed.

With regard to composition, chemists of pre-1760 France had hardly made any progress or significant change from their ancestors of the earlier years of the century. Macquer had attempted to put some of the traditional practices into explicit verbal form, specifically the relationship of properties to composition, but the lack of a measurable concept of a component body continued to inhibit the appearance of a functional compositional system.

However, we have arrived at the eve of the chemical revolution which produced a very profound change in the way chemists were forced to consider the composition of long-familiar bodies. And until that had been accomplished it was not possible to organize general chemical knowledge on the basis of composition.

9

THE MARRIAGE OF AIR AND PHLOGISTON

WE HAVE SEEN in Chapter Six that even though Stephen Hales had clearly demonstrated the necessity for chemists to include AIR among the material components of bodies, and that Rouelle had included AIR in his four Element/Instrument component/operator scheme, air—both as an element and as actual air—continued to be ignored by most mainstream chemists well into the 1760s. Hales, it will be recalled, made no distinction between the different kinds of air that he obtained, and presumably had no thought that there were different kinds. His loyal adherence to the mechanical principles of Newton perhaps precluded the likelihood that he would conceive of AIR in any way other than mechanically fixed in bodies.

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 showed AIR to be obtainable from a wide variety of substances. Two examples from Hales are offered without suggesting that the work is of chemical significance.

A few papers in the *Mémoires* of the Paris Academy and quite a few in the *Philosophical Transactions* of the Royal Society took careful notice of the air to be found in many mineral spring waters. In addition to these, there were a couple of papers on the cause of the asphyxiation of small animals in the infamous Grotto del Cane.[1] Beyond the bare awareness of some gaseous activity, these few papers show no recognition that air had anything more than a curious role to play in chemical behavior. All this changed, though not right away, following the splendid work of Joseph Black (1728–1799) in Edinburgh, published in 1756.

Joseph Black

Before pneumatic chemistry could be said to exist, some distinctions had to be made between different kinds of "airs." Shortly after the middle of the century, Joseph Black was the first to accomplish this. In his study on *magnesia alba,* a naturally occurring hydrated magnesium carbonate, Black first noted 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, showing that the AIR was indeed gone. 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 as "fixed air," distinct from common atmospheric air.

$$\begin{array}{ccccc} \text{Limestone} & = & \text{quicklime} & + & \text{fixed air} \\ [CaCO_3] & & [CaO] & & [CO_2] \end{array}$$

$$\begin{array}{ccccccc} \text{Slaked Quicklime} & + & \text{mild alkali} & = & \text{limestone} & + & \text{caustic alkali.} \\ [Ca(OH)_2] & & [K_2CO_3] & & [CaCO_3] & & [2KOH] \end{array}$$

From these he concluded that mild alkali = caustic alkali + fixed air.

Here, for the first time, it had been demonstrated that the presence or

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[1] Abbé de Nollet, "On the Grotto del Cane," translated from the French, *Phil. Trans.* 47 (1751-1752): 48-61.

absence of a particular air was explicitly related to the presence or absence of particular chemical behavior. Although Black did not weigh 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.[2]

Black's work eventually prompted both positive and negative responses, and studies of the chemistry of gases, pneumatic chemistry, became prominent from the middle of the 1760s. In 1764, David Macbride (1726–1778), an Irish chemist and physician who had studied at Glasgow and London, published *Experimental Essays* on various aspects of fixed air. He thought fixed air was a preservative of animal tissues, and that when these tissues putrefied, the fixed air was given off. This idea was inspired, I suspect, by Hales, whom he mentions having suggested that the cohesion of the solid parts of bodies depended on the presence of fixed air.[3] Macbride thought that scurvy was owing to a lack of vegetables in the diet that contained a lot of fixed air. Quicklime promotes the decomposition of animal bodies by extracting their fixed air. "Macbride's theories made a great impression in France and Germany."[4] J.F. Meyer (1705–1765) became the most vigorous opponent of Black's views on fixed air and its relationship to the mild and caustic alkalies, in 1764 inventing an oily acid, *acidum pingue,* as the fiery agent that supplied the causticity of quicklime formed by the calcination of limestone. Meyer's offering of *acidum pingue* is apparently the last and most elaborate effort to utilize the concept of FIRE particles in chemical explanation. The importance of Meyer's work in our story is that it prompted vigorous attacks by Nicholas Joseph von Jacquin (1727–1817), who demonstrated the error of Meyer's views by repeating Black's experi-

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[2] Joseph Black, "Experiments on Magnesia Alba," in Henry M. Leicester and Herbert S. Klickstein, *A Source Book of Chemistry 1400–1900* (New York: McGraw Hill, 1952). The complete paper is available as *Alembic Club Reprint*, No. 1 (Edinburgh, 1898). For a splendid account of Black's work see Henry Guerlac, "Joseph Black and Fixed Air: A Bicentenary Retrospective, with Some New or Little Known Material," *Isis* 48 (1951): 124-151.
[3] James R. Partington, *A History of Chemistry,* vol. 3, 143. See also Stephen Hales, *Vegetable Staticks* [1727] (London: Oldbourne Press, 1961), 178-179.
[4] Partington, *History,* 144.

ments on fixed air and causticity and confirming Black's findings. Jacquin's original paper was published in Latin in Vienna in 1769, and accounts of it appeared in France in 1774.[5] Thus it appears that the interests of French chemists were drawn to the study of airs first through the medical theories of Macbride and received a chemical direction because of Jacquin's refutation of Meyer.

Another very important point for the compositional story is Black's recognition that fixed air plays the part of an acid in saturating the caustic alkali, and thus pneumatic chemistry joins with the major body of empirical chemical knowledge, that of neutral salts:

> These considerations led me to conclude, that the relation between fixed air and alkaline substance, was somewhat similar to the relation between these and acids: that as the calcareous earths and alkalis attract acids strongly, and can be saturated with them, so they also attract fixed air, and are, in their ordinary state, saturated with it: and, when we mix an acid with an alkali, or with an absorbent earth, that the air is then set at liberty, and breaks out with violence; because the alkaline body attracts it more weakly than it does the acid, and because the acid and air cannot both be joined to the same body at the same time.[6]

Black's use of affinity in explaining the release of the fixed air strongly implies that the fixed air is considered to be an acid. But Black did not emphasize that connection, so again we have to recognize that so much of the order we can see retrospectively in eighteenth-century chemistry was not consciously perceived by the practitioners of the time. A few years later, however, Torbern Bergman strongly emphasized the acidic nature of fixed air, by giving it the name of "aerial acid."

Henry Cavendish

Pneumatic chemistry expanded beyond the fixed air of Black when the Englishman Henry Cavendish (1731–1810) published his "Three Papers,

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[5] Partington, *History,* 143-147 provides a summary of these writers.

[6] Black, "Magnesia Alba," *Source Book,* 86; *Alembic Club Reprint,* 22.

Containing Experiments on Factitious Air."[7] His presentation is a model of clarity and simplicity well illustrated by his opening sentence: "By factitious air, I mean in general any kind of air which is contained in other bodies in an unelastic state, and is produced from thence by art." In the three parts Cavendish describes his experiments relating to inflammable air, fixed air, and the air produced by fermentation and putrefaction.

Inflammable air from the solution of metals in acids had been observed and commented on for at least a hundred years, but only after the attention of chemists had been directed toward gases generally did a systematic study appear. Cavendish obtained the inflammable air by dissolving zinc, iron, and tin in dilute vitriolic acid or in spirit of salt. The same metals also dissolved readily in nitrous (nitric) acid, and in concentrated vitriolic (sulfuric) acid with heat, but the resulting airs were not at all inflammable. He interpreted these reactions as follows:

> It seems likely from hence, that, when either of the above-mentioned metallic substances are dissolved in spirit of salt, or the diluted vitriolic acid, their phlogiston flies off, without having its nature changed by the acid, and forms the inflammable air; but that, when they are dissolved in the nitrous acid, or united by heat to the vitriolic acid, their phlogiston unites to part of the acid used for their solution, and flies off with it in fumes, the phlogiston losing its inflammable property by the union. The volatile sulphureous fumes, produced by uniting these metallic substances by heat to the undiluted vitriolic acid, shew plainly, that in this case their phlogiston unites to the acid; for it is well known, that the vitriolic sulphureous acid consists of the plain vitriolic acid united to phlogiston. It is highly probable too, that the same thing happens in dissolving these metallic substances in the nitrous acid; as the fumes produced during the solution appear plainly to consist in great measure of the nitrous acid, and yet it appears, from their more penetrating smell and other reasons, that the acid must have undergone some change in its nature, which can hardly be attributed to any thing else than its union with the phlogiston.[8]

(At that time, sulfur was seen by the chymists to consist of the plain

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[7] *Phil. Trans.*, 1766: 141-184.

[8] *Phil. Trans.*, 145-146.

vitriolic acid united to phlogiston. The volatile sulphureous acid appears to consist of the same acid united to a lesser proportion of phlogiston than what is required to form sulfur.)

Though Cavendish's paper is impressive for the clarity and precision of his descriptions and the care taken in confirming his observations, there is a surprisingly casual use of the phlogiston concept in interpreting the production of the inflammable air. Note that in this, the very first systematic study of gases beyond that of Black's fixed air, Cavendish is easily able to give his results phlogistic interpretations, thus extending that concept into the new territory of pneumatic chemistry. First he virtually identifies the inflammable air (hydrogen) with the phlogiston escaping from the metals. The phlogistic view of volatile sulphureous acid (sulfur dioxide) as a partially phlogisticated acid is not new, but Cavendish's extension offered the parallel idea that the air from the nitrous acid is also a partially phlogisticated acid. Only in the passages just quoted does Cavendish speak of phlogiston at all, yet the language strongly suggests that what he is saying is almost common knowledge. Stahl himself had suggested that the volatile sulphureous gas was a compound of vitriolic acid and phlogiston, intermediate between the vitriolic acid and its total combination with phlogiston as sulfur. But nowhere in the intervening years is this relationship made a part of an expanded phlogistic system as Cavendish has expressed it here.

Cavendish does not suggest or imply that his views might be either new or contentious. Though I have found little evidence that the phlogistic doctrine had provided anything more than a convenient new term for the old sulphur principle of the seventeenth-century textbook tradition, Cavendish had immediately vaulted it into the newly opened realm of pneumatic chemistry. For a short time in the early years of pneumatic chemistry phlogiston provided useful and consistent rationales, even as the pneumatic chemistry gave an extended application for the phlogistic doctrine. But almost as soon as this marriage of convenience took place, vigorous doubters of its sanctity were attacking the intellectual integrity of the phlogistic partner. But before phlogiston disappeared entirely by end of the century, it enjoyed a period of new vigor in large part through the discoveries and interpretations of Joseph Priestley.

Joseph Priestley

Joseph Priestley (1734–1804) is surely one of the really enigmatic characters in the history of eighteenth century chemistry.[9] A man who made more discoveries in pneumatic chemistry than anyone else, he nevertheless insisted that he was not a chemist and that his discoveries were more or less accidental. He was a dissenting minister and found his greatest pride in his theology, which was very definitely not mainline doctrine. This and his political activism in open support of the French revolution generated public antagonism that led to the destruction of his Birmingham home and all his belongings by a mob in 1791. Three years later he found it expedient to follow his sons across the Atlantic to settle in the upper reaches of the Susquehanna River in Pennsylvania. He defended the phlogiston theory to the end of his life, as late as 1803 publishing a pamphlet entitled *The Doctrine of Phlogiston Established.* Ironically he was the discoverer of oxygen, the very gas which allowed Lavoisier to accomplish the overthrow of phlogiston in what has ever since been called the chemical revolution.

Priestley's first chemical paper, "Observations on Different Kinds of Air" appeared in the *Philosophical Transactions* of the Royal Society in 1772.[10] The results are described within a phlogistic terminology sufficiently well developed that it is easy to believe that phlogistic thinking guided the formulation of the very experiments he is reporting.

The paper opens with a discussion of the difficulties of finding "proper terms," by which to distinguish the different kinds of air. "Those in common use," he says, are "fixed air, mephitic, and inflammable." Priestley's concern with nomenclature led him in the course of his investigations to offer terms for new gases dictated by his commitment to the phlogistic way of thought. Of these, phlogisticated air (nitrogen) and dephlogisticated air (oxygen) are the most important examples.

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[9] Robert E. Schofield, *The Enlightenment of Joseph Priestley: A Study of his Life and Work* (University Park, Pennsylvania: Pennsylvania State University Press, 1997). There is also much of interest on Priestley in Jan Golinski, *Science as Public Culture. Chemistry and Enlightenment in Britain, 1760–1820* (Cambridge and New York: Cambridge University Press, 1992), esp. chapters 3 and 4.

[10] *Phil. Trans.*, 1772: 147-267.

Though Priestley often expressed the idea that his discoveries were the result more of chance than design, his rationalization of that position led him to a very positive view of the nature of science. Here he further justifies it by connecting it with God's design.[11] Perhaps it all comes the other way, that is from his theological view that God is "infinite and inexhaustible":

> My first publication I acknowledge to be very imperfect and the present, I am as ready to acknowledge, is still more so. But, paradoxical as it may seem, this will ever be the case in the progress of natural science, so long as the works of God are, like himself, infinite and inexhaustible. In completing one discovery, we never fail to get an imperfect knowledge of others, of which we could have no idea before; so that we cannot solve one doubt without creating several more.[12]

In the preface of his *Experiments and Observations on Different Kinds of Air,* a collection which grew too large for publication in the Royal Society's *Transactions,* Priestley expressed his views on experimentation and theorizing in terms reminiscent of Boyle's comment of a century before. Priestley expressed his distrust of premature explanations in the following passage.

> When, for the sake of a little more reputation, men can keep brooding over a new fact, in the discovery of which they might, possibly, have very little real merit, till they think they can astonish the world with a system as *complete* as it is *new,* and give mankind a high idea of their judgment and penetration; they are justly punished for their ingratitude to the fountain of all knowledge, and for their want of a genuine love of science and of mankind, in finding their boasted discoveries anticipated, and the field of honest fame pre-occupied, by men, who, from a natural ardour of mind engage in philosophical pursuits, and

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[11] Priestley's empiricism has been discussed by Jan Golinski, "Utility and Audience in Eighteenth-Century Chemistry: Case Studies of William Cullen and Joseph Priestley," *Br. J. Hist. Sci.* 21 (1988): 1-31. See also Golinski, *Science as Public Culture.*

[12] Joseph Priestley, *Experiments and Observations on Different Kinds of Air* [Birmingham, 1790] (New York: Klaus Reprint, 1970), Preface, vii. The insight is remarkably similar to that in the quotation from Veblen on p. 18, above.

> with an ingenuous simplicity immediately communicate to others whatever occurs to them in their inquiries.[13]

In spite of his disdain for those who offered a complete system to support a single dubious fact, Priestley was himself quick to give his many newly discovered facts a phlogistic interpretation without considering alternatives.

Priestley's Discovery of Dephlogisticated Air

Joseph Priestley, for all his protestations of inexpert chemical training, was an ingenious experimenter. Very early he had devised a test for the "goodness of the air," that is, good for breathing. In Priestley's view, a body burning in a closed vessel went out because the phlogiston escaping from the combustible soon saturated the ambient air. This residual air he denominated "phlogisticated air." It had long been known that such air would no longer support either flame or the life of small animals. Priestley's chemical way of measuring the goodness of the air was much more convenient than that of using sparrows or mice, the usual test animals. It consisted of mixing the air to be tested with nitrous air (nitric oxide, NO) confined over water. With common air there was a net shrinkage from the total volume of the two original gases, and the resultant mixture was less able to support either life or combustion. Priestley saw this shrinkage as a measure of the phlogistication of the air. We can describe this process in modern symbols.

$$2NO + O_2 = 2NO_2$$

The nitrogen dioxide formed dissolves in the water with a consequent shrinkage in the volume of the gases. By repeated trials Priestley established that maximum shrinkage occurred when two volumes of common air were mixed with one volume of nitrous air. When this procedure was tried on air left after combustion had taken place in it, the shrinkage would be less than with common air (some of the oxygen would have been used up) and

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[13] Priestley, *Experiments,* xvii-xviii.

the air would be judged less good than common air. This became a much-used tool for Priestley, allowing him to test the goodness of air from whatever source.

In his broad range of explorations of airs, he produced an air from the heating of the red calx of mercury (mercuric oxide). As with all the other airs he had prepared, he tested its goodness with the candle flame and with mice or sparrows. He was mildly surprised to find that both the flame and the animals survived in this air somewhat longer than in common air. When he applied the nitrous air test to the air from the red calx, he obtained about the same shrinkage as with common air, thus confirming that this air was as good as common air. Somewhat later, rather by accident, he tested the air remaining after the original nitrous air test and was highly surprised to discover that the volume shrank just as much as with the original test. Following up these clues, he finally determined that the air from the red calx was actually four to five times as good as common air. Since this air had a greater capacity than common air for the absorption of phlogiston, it must have less phlogiston than common air. Priestley named it "de-phlogisticated air," and this became the standard denomination for many years.[14]

Priestley's discoveries of many new gases required him to apply names, which were based chiefly on phlogistic relationships. His language does not always allow us to know if he saw these gases as distinct chemical species, or as common air variously modified by phlogiston, though the latter view seems to dominate. In this attitude he is reflecting the age-old tradition that chemical change is continuous rather than discontinuous.

With Priestley's work in the 1770s, the phlogiston concept was finally elevated to a veritable chemical theory. It had long been known that phlogiston or the inflammable principle departed in the decomposition process known as combustion. The residue in the case of common sulfur was vitriolic acid, and in the case of metals, the calx of the particular metal. Both these processes could be easily reversed by applying a phlogiston-rich body, typically charcoal, to the products of the first reactions. The original bodies were then restored. With the advent of enlarged interest in the role of air

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[14] *Source Book in Chemistry,* 112-125.

in chemical change, phlogiston gained several applications not previously apparent. Whereas before, the phlogiston from a burning body simply disappeared or was destroyed by the flame, it now combined in some way with the ambient air in which the combustion took place, a role that gave phlogiston a larger sense of substance. When that air was saturated with phlogiston, the combustion ceased. Priestley codified this view by assigning the name "phlogisticated air" to this saturated residue, and "de-phlogisticated air" to what we now call oxygen. Priestley was able to assign various degrees of phlogistication to other airs he prepared. Our nitrous oxide, for example, was more phlogisticated than nitrous air (our nitric oxide) but less so than phlogisticated air (our nitrogen). In a general sense, then, phlogiston showed real capacity for organizing chemical knowledge into a coherent descriptive science.

Hardly had this junction of phlogiston and air taken place when the union was met by criticisms that challenged the very existence of phlogiston itself. These attacks forced its adherents into an ever more vigorous defense of the traditional views, and for a time new experiments and ever more creative interpretations appeared to refute the attacks. Phlogiston theory as it developed in the 1780s was in a sense created in response to its attackers. Chief among these critics was Antoine-Laurent Lavoisier, whose alternative explanations eventually led to the complete rejection of phlogiston and the reversal of all phlogistic explanations. Lavoisier's own work can be seen as an inversion of everything phlogistic, a pattern so evident even to the chemists of the time that his views became universally known as the anti-phlogistic chemistry, whose successful introduction produced a chemical revolution.

10

LAVOISIER AND THE ANTI-PHLOGISTIC DOCTRINE

BY 1770 THE CHEMISTRY OF AIR had become the focus of intense activity. The physical behavior of air had been well worked out in the previous century, but the ability of air to lose its characteristic identity as an elastic fluid and become fixed in the solid state was a difficult fact to comprehend. In France, two men, Jean-Baptiste Michel Bucquet (1746–1780) and Antoine-Laurent Lavoisier (1743–1794), independently undertook systematic investigations of these phenomena. After a brief collaboration, the unfortunate Bucquet died in 1780, leaving to Lavoisier the completion of a chemical revolution he had anticipated in 1773.[1]

As is well known, Lavoisier's attacks on the phlogistic doctrine finally accomplished its abandonment, offering in its place a new perspective so totally different that it was commonly called the anti-phlogistic chemistry. This accomplishment was so dramatic that his contemporaries, supporters and opponents alike, recognized it as revolutionary. Two hundred years later the "chemical revolution" became one of the most studied events in the history of science. Henry Guerlac has been one of the most stimulating authors of Lavoisier's work in the post-war years of this century. His book *Lavoisier – The Crucial Year*[2] generated much additional study of Lavoisier, especially by his own students at Cornell University.[3]

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[1] E. McDonald, "The Collaboration of Bucquet and Lavoisier," *Ambix* 13 (1966): 74-83.

[2] Henry Guerlac, *Lavoisier – The Crucial Year* (Ithaca, New York: Cornell University Press, 1961).

[3] Perhaps the most prolific of Guerlac's students was Carlton E. Perrin, who wrote almost exclusively about Lavoisier. A few of his papers will be cited below.

Many recent publications have focused on the chemical revolution of Lavoisier, providing a much broader context within which this work clearly fits. Perhaps the most important contemporary writer is Frederic Lawrence Holmes, who has published two books on Lavoisier, both based on detailed examination of Lavoisier's laboratory notebooks. These have provided the modern reader with a reliable analysis of Lavoisier's chemical thinking.[4] Accounts of Lavoisier's broader activities have also been given by Arthur Donovan and Jean-Pierre Poirier.[5]

Since this book is a history of chemical composition, I will treat the traditional chemical revolution only as far as necessary to make my own story complete. Lavoisier's role in this account is equally essential. Lavoisier accomplished his revolution by a consistent application of the principle of the conservation of weight as a way of determining and confirming the results of chemical experiments. As we have already seen, the idea of conservation was not new, and a number of chemical experiments had been conceived under the guidance of that principle. But Lavoisier was the first to make it a systematic instrument of experimental investigation and confirmation.[6] The principle seems always to have been with him, for it is central to the argument of one of the earliest of his published papers. In 1770 he wrote a paper on the examination of the long-standing claim that WATER could be converted into EARTH by extended heating. After a systematic critique of earlier accounts, Lavoisier offered his own experimental demonstration that the earthy material that appeared in water long boiled in sealed containers was matter dissolved from the glass itself; the weight of the

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[4] Frederic Lawrence Holmes, *Lavoisier and the Chemistry of Life: An Exploration of Scientific Creativity* (Madison: University of Wisconsin Press, 1985); *Antoine Lavoisier: The Next Crucial Year* (Princeton: Princeton University Press, 1998). See also Holmes, "Lavoisier's Conceptual Passage," in Arthur Donovan, ed., "The Chemical Revolution. Essays in Reinterpretation," *Osiris* 4 (1988): 82-92. This special issue of *Osiris* also contains C.E. Perrin, "Research Traditions, Lavoisier and the Chemical Revolution," 53-81.

[5] Arthur Donovan, *Antoine Lavoisier: Science, Administration and Revolution* (Cambridge and New York: Cambridge University Press, 1996); and Jean-Pierre Poirier, *Antoine Laurent de Lavoisier, 1743–1794* (Paris: Pygmalion, 1993), translated into English as *Lavoisier Chemist, Biologist, Economist* (Philadelphia: Chemical heritage Foundation, 1997).

[6] Robert Siegfried, "Lavoisier and the Conservation of Weight Principle," *Bull. Hist. Chem.* 5 (1989): 18-24, and especially Frederic L. Holmes, "Lavoisier the Experimentalist," *Bull. Hist. Chem.* 5 (1989): 24-31.

earthy residue was very nearly equal to the loss of weight of the empty flask. It was this kind of bookkeeping for the weights of the bodies in gaseous reactions that effected a revolution.

The battles of the chemical revolution were fought over the nature of combustion. The older tradition, as we have already seen, treated combustion as a decomposition process, the combustible yielding up its phlogiston (the principle of combustion, by whatever name) and leaving behind the ash or, in the case of metals, the calx. Applying the principle of conservation of weight to this process meant that the ash or calx should weigh less than the original combustible. This was often the case because the reactions were not typically conducted in such a way that all the components and products were collected. That combustion could not take place in the absence of air had long been known, but the function of the air had not been much pursued. It was only with the work of Stephen Hales early in the eighteenth century that it was recognized that air had a *chemical* part to play in combustion. By adapting some of Hales's techniques for manipulating and measuring gases, Lavoisier was able to show that simple combustion was not a decomposition, but was rather a combination of a part of the air with the combustible. He confirmed this by carrying out his experiments in closed vessels and showing that the weights of all the products of the reaction were just equal to the weights of all the reactants. His reliance on weight as the measure of the quantity of matter essentially completed the long drift chemistry had made toward expressing composition in material terms. This inversion of the nature of combustion, from decomposition to combination, produced a similar reversal in the relative simplicity of composition of the bodies involved, the long-range consequences of which made possible the present organization of all chemistry on composition now expressed in terms of atomic formulas.

Lavoisier began his scientific career just about the time that pneumatic chemistry became widely recognized as important, so it is not surprising that he saw in this a great opportunity. Lavoisier had attended the chemistry lectures of Rouelle, and there witnessed the phenomena of aerial fixation and liberation, especially in effervescence. Before he was thirty years old, he initiated a systematic investigation of the manner in which gases were fixed into and liberated from solid bodies, the importance of which appeared to Lavoisier "to occasion a revolution in physics and chemistry."[7]

Recall that Rouelle had taught that the four elements could each occur either in a fixed, solid, combined state, or in the free state. This pattern had some organizing utility, but contained no causal relationships among the different elements. Lavoisier early began to develop a model of the gaseous state as being the combination of fixed FIRE (heat) with the ponderable, material part of the gas or air, an idea that guided much of his early work. The earliest evidence we have concerning this view dates to 1766, when he wrote brief memos to himself after reading some papers by the German writer Theodor Eller on the nature of the elements. Eller had only two elements, FIRE, the active one, and WATER, the passive. The solvent action of water (H_2O) was owing entirely to the presence of the fiery element in that liquid. Eller also suggested that air was nothing more than water combined with the matter of FIRE, which turned it into a vapor. Although in Eller's view, all the elements occur in a grand solution in the fire of the sun found in the earth's atmosphere, Lavoisier noted a special rapport between the element of FIRE and that of the air. "Is not air itself a fluid in expansion?" he asked. Not necessarily water (H_2O), as Eller saw it, but possibly some other fluid.[8] This idea led to a distinctly different view of the gaseous state than the traditional one that air was a permanently aerial element. As he later developed that model, air when it became fixed liberated the fire that had kept it in the gaseous state; when air was liberated as in effervescence, it had to absorb fire or heat from the surroundings in order to stay in the gaseous state. Instead of the parallel pattern of the fixed and free states for all the elements promoted by Rouelle in his lectures, Lavoisier proposed a reciprocal pattern for air and fire. When air is liberated, fire must be fixed in it. When air is fixed, the fire must be liberated. The model of the gaseous state remained the directional guide for his re-

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[7] Henry Guerlac, "The Chemical Revolution: A Word from Monsieur Fourcroy," *Ambix* 23 (1976): 1-4.

[8] Robert Siegfried, "Lavoisier's View of the Gaseous State and its Early Application to Pneumatic Chemistry," *Isis* 63 (1972): 59-78 at p. 62. See also Jerry Gough, "The Origins of Lavoisier's Theory of the Gaseous State," in *The Analytic Spririt: Essays in the History of Science in Honor of Henry Guerlac,* ed. Harry Woolf (Ithaca, New York: Cornell University Press, 1981).

search for the rest of his life. Perhaps influenced by Rouelle, Lavoisier's name for fixed fire in his early writings was phlogiston.

Up to 1772, Lavoisier's view of analysis by fire appears to have been conventional, that heating decomposed bodies. He noted, for example, that metals when heated in the focus of a large burning lens smoked and fumed, and he suggested that those fumes might be collected and their nature investigated. But in that year he also learned from the work of Guyton de Morveau that *all* metals gained weight when calcined. In accepting the validity of this, Lavoisier immediately recognized that the followers of Stahl, who claimed the loss of phlogiston in the process of metallic calcination, had "fallen into a labyrinth of difficulties." How could one explain that the "weight of a body is increased when a part of its substance is removed from it"? Of course Lavoisier's view encountered the same difficulty, and he was forced to reverse his thinking on the calcination of metals. Instead of fumes or air leaving metals when heated, some kind of air is combined with them.[9]

In the autumn of 1772 he conducted experiments on sulfur and phosphorus designed to show that the products of their combustion also increased in weight over that of the original material, and that there was a corresponding decrease in the volume of the air in which the combustion took place. By the spring of 1773 his thinking had progressed to the point that he was able to present publicly how his model of the gaseous state could be applied not only to combustion but also to the reduction of metallic calxes to their respective metals. In the phlogistic view a metal consisted of a combination of the calx with phlogiston, the principle of inflammability. The restoration of the metallic state was accomplished by reacting the simple calx with a body rich in phlogiston, usually supplied by powdered charcoal:

$$\text{calx} + \text{phlogiston} = \text{metal}$$

Lavoiser's interpretation now was that a calx was the combination of the metal with the ponderable part of some kind of air. When the calx was

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[9] Siegfried, "Gaseous State," 70. For the very best general account of the beginning of Lavoisier's career, see Guerlac, *Crucial Year.*

heated with the charcoal, the fixed fire (phlogiston) of the charcoal combined not with the metal, but with the ponderable part of the air in the calx and returned it to the aeriform state. To liberate the air fixed in a metallic calx, Lavoisier wrote, one must

> place it in contact with the phlogiston of a glowing coal, immediately the fixed part of the air which had combined with the metal and reduced it to the state of calx, takes back some phlogiston, is combined with it and forms an elastic air. Such, in a few words is the whole theory of the reduction of metals. It is not, properly speaking, the reduced metal to which the phlogiston is returned, as Stahl had thought, it is the air itself which is revived, which regains its state of expansion by combining with the phlogiston.[10]

Let us examine briefly the logic of Lavoisier's model of the gaseous state. His earlier view, when he planned to collect and study the fumes emitted from heated metals, appears to have been that the fumes were no more than a simple physical vaporization, the combination of the solid body with the free fire of the direct heat. In his new view, however, the fire that liberates the air from the calx comes from the chemically fixed fire, phlogiston, in the charcoal.

Note that in Lavoisier's account of these relationships, the metal is simple and the calx is compound, just the reverse of the phlogistic view, which had the calx simple, and the metal compound. This interpretation derives from his model of the gaseous state as a combination of "some solid or fluid body with the inflammable principle." Lavoisier clearly summarized his

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[10] René Fric, "Contribution a l'étude de l'évolution des idées de Lavoisier sur la nature de l'air et sur le calcination des métaux," *Arch. Int. d'Hist. Sci.* 12 (1959): 137-168. This paper printed three previously unpublished manuscripts by Lavoisier. The first is titled "Essay sur la nature de l'air," and is dated only by the note of Fouchy, the permanent secretary of the Royal Academy, on 19 August 1772; the second has the same title and is dated in Lavoisier's own hand as 15 April 1773; the third, "Sur une nouvelle theorie de la calcination et de la reduction des substances metalliques sur la cause de l'augmentation de poids quelles aquirent au feu et sur differens phenomenes qui appartiennent a l'air fixe" carries no date, but Fric assigns as probable 21 April 1773. Quotation from the second Fric Mémoire, 150.

views on the calcination and reduction of metals in another paper read to the Academy of Sciences in April of 1773:

> 1. That a metallic calx results from the combination of any metal whatever with fixed air;
>
> 2. that metallic reductions consist essentially in the disengagement of this same air with which the metal was in some fashion saturated;
>
> 3. finally that it is to the fixed air abundantly contained in the atmosphere that the metals owe the augmentation of weight which they acquire during calcination.[11]

It was at this point in the Spring of 1773 that Lavoisier embarked on a systematic study of the fixation and liberation of airs, a topic much pursued in other countries but "The French Chemists alone seem not to take any part in these important inquiries...." The results of this intensely pursued task were published in January of 1774 as *Opuscules physiques et chymiques* (Physical and Chemical Essays). In the first half of this book, Lavoisier thoroughly reviewed the work previously published on the topic; in the second part he described his own experiments, consisting chiefly of repetitions of earlier work, though often with different observations and interpretations. Here for the first time he put into print his view of calcination and reduction of metals.[12]

> If it were permitted me to indulge in conjectures, I should say, that some experiments, which are not sufficiently complete to submit to public inspection, induce me to believe that every elastic fluid results from the combination of some solid or fluid body with the inflammable principle, or perhaps even with the matter of pure fire, and that on this combination the state of elasticity depends. I should add that the substance fixed in metallic calces, and which augments their weight, would not be, properly speaking, on this hypothesis, an elastic fluid, but the fixed part of an elastic fluid, which has been deprived of its inflammable principle. The principal action of charcoal, and all other

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[11] Third Fric Mémoire, 158.

[12] *Essays Physical and Chemical*, translated from the French by Thomas Henry [London, 1776] (London: Cass Reprint, 1970), 2.

> substances of that nature employed in reductions, would then be, to restore the phlogiston or matter of fire, to the fixed elastic fluid, and with it the elasticity which depends on it.[13]

At this time Lavoisier did not know whether the air of the atmosphere or some part of it was the material fixed in the calcination process. Perhaps because he was entirely ignorant on this matter, he identified it as "fixed air" (carbon dioxide) of Joseph Black, the only specific example then known of a specific air that could be fixed. It was of course already well known that fixed air was produced from the reduction of metallic calx.

Lavoisier did not long identify the air fixed in these experiments as Black's "fixed air," but moved on to the possibility that it was the air itself or some other unidentified part of the air. In the summer of 1774, he began a series of studies extending the preliminary work reported in the *Opuscules.* The first results were published in December of that year with the title "Memoir on the calcination of metals in closed vessels and the cause of the increase in their weight during that operation."[14] Some preliminary results reported in the *Opuscules* had confirmed Lavoisier's view that the increase in weight experienced by tin and lead when heated in the presence of air was owing to the fixing of some of the air with the metal to form the calx. Because his interpretation was in contradiction to that of Robert Boyle from similar experiments carried out a century earlier, Lavoisier felt obliged to repeat Boyle's experiments carefully. After placing an ounce of metallic lead in a flask which was then sealed and heated, Boyle had reported: "After the metal had been for two hours or better kept in the flame, the sealed neck of the retort being broken off, the external air rushed in with a noise (which showed the vessel to have been very tight)...." Boyle found that the lead had been partially turned to a greyish calx, whose

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[13] Lavoisier, *Essays Physical and Chemical,* 224-325.

[14] "Mémoire sur la calcination des métaux dans les vaisseaux fermés, & la cause de l'augmentation de poids qu'ils acquièrent pendant cette opération," *Observations Physiques,* 4 (1774): 446-449. Because so many of Lavoisier's papers have been published in many different places, I will cite only those sources directly used. In order to facilitate the location of other publications of the same work, I will also give the appropriate reference number assigned by Denis I. Duveen and Herbert S. Klickstein, *Bibliography of the Works of Antoine Laurent Lavoisier* (London: William Dawson, 1964). In this instance, DK-26.

weight compared to that of the original metal, showed a gain of nearly six grains. Boyle had interpreted the gain in weight as confirmation of his hypothesis that fire particles were of so fine a caliber that they passed easily through the enclosing glass and accounted for the gain in the total weight.[15]

Though conducting essentially the same experiment, Lavoisier was testing a different hypothesis, namely that it was the air that combined with the metal to increase its weight. He therefore weighed the sealed flask both before and after the heating, establishing that there was no change in the total weight until the seal was broken. It is worth noting how their separate expectations guided their attention and interpretations.

In support of his hypothesis, Lavoisier noted (1) the amount of calx was larger in larger retorts; (2) if weighed before breaking the seal, the flasks weighed the same both before and after the calcination; (3) when the seal was broken a whistling sound was heard, attributed to the reentry of air from the outside; (4) when weighed again after the reentry of the air, the gains in weight were in rough proportion to the size of the flasks.

> From these experiments it follows that the increase in weight of the calcined metals inside closed vessels comes neither from the matter of fire, or from any other substance from outside. It is only from the air contained in the flask that the metal borrows the substance that increases its weight, and converts it into a calx. What led Boyle astray was that he neglected to weigh the vessels before opening them, and he attributed to the matter of fire the increase in weight that really came from the outside air having reentered the vessel.[16]

An expanded version of this work was later published in the *Mémoirs* of the Paris Academy for the year 1774, which however appeared only in 1778. This delay in the publication of the Academy's *Mémoirs* was typical at that time, and generates frequent problems in establishing the true chronology in the development of Lavoisier's chemistry.

In April of 1775, Lavoisier read the first version of a paper that focused

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[15] Quotation from Marie Boas Hall, *Robert Boyle on Natural Philosophy* (Bloomington, Indiana: Indiana University Press, 1965), 269-270.

[16] Lavoisier, "Mémoire sur la calcination," DK-26, 451.

"On the Nature of the principle which is combined with metals during their calcination, and occasions an increase in their weight."[17] This paper, in its later, improved form, has become something of a classic example of Lavoisier's clear reasoning. The passage below was at the beginning of both the 1775 and the 1778 versions, illustrating some of the changes resulting from Lavoisier's having learned of and begun experiments on Priestley's "dephlogisticated air," that Lavoisier was later to rename "oxygen."

> 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 before the Academy. But since the time devoted to our public meetings does not allow me to treat any one of these question 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 ...
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> [April 1775] ... 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. [DK-29]
>
> [August 1778] ... 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. [DK-30]
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> 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

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[17] English quotation from James B. Conant, ed., *The Overthrow of the Phlogiston Theory* (Cambridge, Massachusetts: Harvard University Press, 1960), 22-23. DK-29.

> 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.[18]

In this paper Lavoisier describes a further experiment with mercuric oxide, first reducing it with charcoal and collecting the gas evolved which proved to be fixed air. By this procedure, since they behave in this way, he had established that *mercurius calcinatus* was a true metallic calx. Doubts that it was a true metallic calx arose from two facts, that mercury itself was a liquid, unlike any other metal, and that almost alone among metals, its calx could be reduced to mercury metal by heat alone, without charcoal.

Next Lavoisier reduced the mercury calx by heat alone, again collecting the gas evolved. From the volume collected and the difference in weight between the original calx and the residual metal, he calculated the weight of a cubic inch of the air "which does not differ much from the weight of ordinary air." This gas proved to have none of the properties of fixed air, but indeed "it could be used again for the calcination of metals."[19] In 1775 he identifies this air with common air, or sometimes "common air ... more respirable, more combustible."[20] In 1778, after having learned of and experimented extensively with Priestley's "dephlogisticated air," he concluded that this was the air combined with a metal in its calx; but he called it "the eminently respirable portion of the air."

This sequence of changes is summarized in the outline below.

April 1773 [DK-732]

CALX	+	CHARCOAL	=	METAL + FIXED AIR
(metal + matter of air)		(phlogiston)		(phlgstn + matter of air)

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[18] Conant, *Overthrow of Phlogiston,* 23.

[19] Conant, *Overthrow of Phlogiston,* 26.

[20] Conant, *Overthrow of Phlogiston,* 27.

April 1775 [DK-29]

CALX	+	CHARCOAL	=	METAL	+	FIXED AIR
(metal + matter of air)		(chrcl)		(metal)		(chrcl + entire air)

August 1778 [DK-30]

CALX	+	CHARCOAL	=	METAL	+	FIXED AIR
(metal + pure air)		(chrcl)		(metal)		(chrcl + pure air)

To complete the confirmation of his new views, it seemed necessary for Lavoisier to show their application to animal respiration which had from the beginning been closely associated with combustion and calcination. In the paper "Experiments on the respiration of animals, and on the changes that occur to the air in passing through their lungs," Lavoisier described an experiment that established the composition of the atmosphere as being composed of two distinct airs, one "eminently respirable," and the other unfit for respiration, or mephitic:

> In a convenient apparatus, which it would be too difficult to describe without the aid of engravings, fifty cubic inches of common air were inclosed, to which I introduced four ounces of very pure mercury, which I proceeded to calcine by keeping it, during twelve days, in a degree of heat almost equal to that which is necessary to make it boil.... On the second day I could observe some small red particles swimming on the surface of the mercury, which, in a few days, increased both in number and bulk. On the twelfth, having extinguished the fire and suffered the vessels to cool, I observed that the air, which they contained, was diminished in the amount from eight to nine inches, viz. about 1/6 of its volume; at the same time a considerable portion of mercurius precipitate per se, or calcined mercury, was formed, which I computed to be about forty-five grains.[21]

Lavoisier established that the residual air lacked the characteristic pro-

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[21] A.-L. Lavoisier, "Expériences sur la respiration des animaux, et sur les changemens qui arrivent à l'air en passant par leur poumon," *Mémoires* (Paris, 1777 [1780]): 185-191. DK-38. The English version is taken from *Essays on Atmospheric Air, by M. Lavoisier,* translated by Thomas Henry (London, 1783), 1-16, at 3-4.

perties of common air and of fixed air; it would neither support combustion, nor precipitate lime water. As Lavoisier stated it, the air "was absolutely reduced to a mephitic state."

Lavoisier then heated the mercury calx formed, collecting the gas produced. It proved to be the eminently respirable air, that is, Priestley's dephlogisticated air. When this air was recombined with the vitiated or mephitic air,

> [it] restored the [vitiated air], pretty exactly, to the same state in which it had been, previous to the calcination being performed in it, viz., that of common air; for now candles were not extinguished in it; animals no longer perished in it; and it was nearly as much diminished as atmospheric air, by the addition of nitrous air.
>
> We have here the most complete proof, that chemistry can afford, of the decomposition and recomposition of air, from whence it evidently results, 1st. that 5/6 of the air which we breathe, are mephitic, or incapable of supporting the respiration of animals, or the inflammation and combustion of bodies: 2dly. that the surplus, or 1/6 only of the volume of atmospheric air, is respirable: 3dly. that, in the calcination of mercury, this metallic substance absorbs the salubrious part, leaving only the mephitic portion of the air: 4thly. that by reuniting these two portions which had been separated, we can recompound air, similar to that of the atmosphere.[22]

In this most prolific of his years, Lavoisier was far from having finished the development of his new chemistry, and several more papers were printed in the *Mémoires* of the Academy for 1777. Two of these, along with a third published in the volume for 1778, are of particular interest for they each present a full account of one of the three fundamental ideas that dominated his chemical thinking. These basic points of view were:

(1) the model of the gaseous state, a chemical combination of the matter of fire with some solid or liquid body [DK-43]
(2) vital air as the sole supporter of combustion [DK-45]
(3) the same air as the principle of acidity; now called oxygen [DK-49]

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[22] Lavoisier, *Essays on Atmospheric Air,* 6.

We have already discussed his model of the gaseous state at sufficient length, but a systematic publication of it appeared only in 1780: "De la Combinaison de la Matière du Feu avec les fluides évaporables, Et de la formation des Fluides élastiques aëriformes."[23]

The *Mémoires* of the Academy were about three years behind in their scheduling, making the date of the actual composition of a paper very uncertain, for it was possible for the author to make corrections for nearly three years after the time of the original presentation to the Academy. In the case of the most famous of these three papers, "Mémoire sur la Combustion en Général," Lavoisier had presented his earliest version to the Academy in 1775; it was printed in the *Mémoires* for the year 1777, which appeared only in 1780.

In this paper Lavoisier offered "a new theory of combustion" designed to explain the "four recurring phenomena" characteristic of that process. These were:

(1) "In all combustions the matter of fire or light is evolved."
(2) Materials will burn only in that kind of air "which Mr. Priestley has named *dephlogisticated air* and which I name here pure air."
(3) "In all combustion, pure air in which the combustion takes place is destroyed or decomposed and the burning body increases in weight exactly in proportion to the quantity of air destroyed or decomposed."
(4) "In all combustion the body of which is burned changes into an acid by the addition of the substance which increases its weight."[24]

The first three of these phenomena will be sufficiently familiar, but the last involved a more hazardous hypothesis that Lavoisier made explicit only a little later. Hints of the idea that vital air, or as he renamed it, oxygen, was the principle of acidity appear early in his writings. He made a public commitment to that view in the paper published in the Academy *Mémoires* for 1778 that appeared in 1781: "General considerations on the nature of

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[23] *Mémoires* (Paris, 1777): 420-432. DK-43. English translation in Lavoisier, *Essays on Atmospheric Air,* 119-145.

[24] A.-L. Lavoisier, "*Mémoire sur la combustion en général,*" DK-45. English translation in *Source Book in Chemistry,* 168-180.

acids, and of the principles of which they are composed."[25] It was here that Lavoisier introduced the word *oxygen,* a neo-Greek compound meaning "acid-former."

> In the foregoing essays I have endeavoured to prove as clearly as is possible by physics and chemistry, that the very pure air which Dr. Priestley has denominated *dephlogisticated air,* enters, as a constituent part, into the composition of several acids, and especially into that of the phosphoric, vitriolic, and nitrous acids.
>
> Many additional experiments enable me to generalise this doctrine, and to declare that this pure and highly respirable air, is the constitutive principle of acidity, that this principle is common to all the acids....[26]

This bold extrapolation allowed Lavoisier to connect his work on combustion to the larger body of chemical knowledge centered on the neutral salts. He opened this paper with the following observations.

> When the ancient chemists had arrived at the power of reducing a body into oil, salt, earth, and water, they believed that they had attained the utmost bounds of chemical analysis, and they accordingly bestowed, on salt and oil, the appellation of chemical principles.
>
> But as the art was continually improving in its progress, succeeding chemists perceived that the substances which they had been taught to consider as principles, were still capable of decomposition; and they soon discovered that all the neutral salts, for example, were formed by the union of two substances, viz., of some acid, and a saline basis of either an earthy or metallic nature.
>
> Hence the whole theory of neutral salts, which engaged the attention of chemistry for more than a century, is at present brought to such a degree of perfection, that it may be regarded as the most certain and complete part of chemistry.
>
> In this state, in which the science of chemistry has been delivered

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[25] A.-L. Lavoisier, "Considérations générales sur le nature des acides, et sur les principes dont ils sont composés," *Mémoires* (Paris, 1778): 535-547, DK-49. English translation in Lavoisier, *Essays on Atmospheric Air,* 96-118.

[26] Lavoisier, *Essays on Atmospheric Air,* 97-98.

> to us by our predecessors, it remains for us to perform, on the constituent parts of neutral salts, what preceding chemists have effected on those salts themselves; to examine the acids and the bases of which they are composed, and to advance this kind of chemical analysis somewhat beyond the present limits.[27]

Lavoisier had established that the familiar mineral acids were compound bodies and further conjectured that oxygen was present in *all* acids and was the cause of their acidity. But he was not ready to give a complete presentation of his new chemistry; two inadequacies vis-à-vis its competition with the phlogistic view still were unexplained. Neither phlogisticated air (nitrogen) nor inflammable air (hydrogen) had any functional place in his chemistry, though both played important roles in the phlogistic view. According to the older view, when a substance burned it gave up its phlogiston to the ambient atmosphere. When this air became saturated with the phlogiston, it was said to be phlogisticated. No such role for this air was available in Lavoisier's scheme; the residual air from combustion was just residual air, and though it constituted five-sixths of the atmosphere Lavoisier could assign it no chemical properties or function.

Similarly, Lavoisier had no explanation for the origin of the inflammable air obtained when metals were dissolved in acids. In the phlogistic view metals contained phlogiston combined with the metallic calx. When the metal was dissolved in acid, the calx combined with the acid to form the neutral salt and the phlogiston was liberated as inflammable air. For Lavoisier, the metal and the water were considered elemental and the acid consisted only of oxygen combined with a simple acidifiable basis. There was no possible source for the inflammable air produced. As a further puzzle, inflammable air when burned ought to produce an acid, but earlier experiments had failed to confirm that hypothesis. As the gas had always been burned in the presence of water, the actual production of more water was overlooked.

News of Henry Cavendish's experiments showing that water was the only product of the combustion of inflammable air reached Lavoisier in

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[27] Lavoisier, *Essays on Atmospheric Air,* 96-97.

June of 1783. He immediately repeated the experiments with special attention to the quantitative production of the water. After a systematic investigation he concluded that the solution of metals in acids was just as much an oxidation process as their calcination in air, that the metals had to combine with oxygen to form the calx before they could dissolve in acids. The oxygen required was provided either by the acid, in which case the reduced acid gas was liberated (SO_2 or NO); or by the water, in which case the gaseous product was inflammable air (hydrogen). The resulting metallic calx then combined with additional acid to form the neutral salt.

Lavoisier could now identify inflammable air as a simple body, a component found widely in nature, and like oxygen, found in the gaseous state when uncombined with anything other than the matter of heat or fire. In 1785 Cavendish was unintentionally able to solve Lavoisier's other major problem regarding the role of phlogisticated air (nitrogen) by showing it to be the basis of nitrous acid. Lavoisier could now identify phlogisticated air as an acidifiable basis of the same sort as sulfur, phosphorus, and carbon.

The composition of water proved to be a turning point that allowed Lavoisier to make his chemistry completely competitive with phlogiston. Everything that the phlogistic chemistry explained could now be described by the anti-phlogistic doctrine. The new chemistry involved no hypothetical chemical ingredients, and all ponderable participants were accounted for by keeping track of their weights.

From December of 1783 through the next two years Lavoisier undertook detailed investigations designed to consolidate his chemistry in preparation of a direct attack on phlogiston. In a paper devoted to the solution of metals in acids, his aim was to demonstrate that the metals, in dissolving in acids, underwent a kind of calcination that was totally equivalent to ordinary calcination in the dry way. This could be shown to be true by defining calcination as the combination of a metal with oxygen, in the wet way the metal obtained the oxygen either from the water or from the acid.

After this brief introduction, he pointed out that in his previous memoirs he had never mentioned phlogiston:

> Those who recall what I advanced in this regard in my Memoir on Combustion, printed in the *Mémoires* for 1777, page 592 [DK-45] will easily devine the reason; it is that the existence of this principle appears

> absolutely hypothetical to me. This body, introduced into chemistry by Stahl, far from having brought light, appears to me to have made the science obscure and unintelligible for those who have not made a very close study of it; it is the *Deus ex machina* of the metaphysicians: a body which explains everything and explains nothing, to which are assigned opposite qualities by turns.[28]

He goes on to say that he will endeavor to show that the existence of that body has not been proved, and that all the phenomena of physics and chemistry can be explained without that body. But he admits that his views on this matter have not yet reached the point of maturity.

Lavoisier's next memoir is in a sense little more than a reinterpretation of a paper by Torbern Bergman, who measured the relative amounts of phlogiston in each of several metals. Bergman and his pupil, Andreas N. Tunberg, had conducted a lengthy series of experiments in which they measured the weights of silver precipitated from a solution in nitric acid by a fixed weight of other metals. Bergman assumed that the factor limiting the quantity of silver precipitated was the amount of phlogiston contained in the precipitating metal. When that quantity of phlogiston had been exhausted, no more of the silver could be precipitated. For example, Bergman found that 31 pounds [*libra*] of copper precipitated 100 pounds of silver, thus the quantity of phlogiston in the 31 pounds of copper is the same as in 100 pounds of silver. In order to calculate relative amounts of phlogiston in metals, Bergman assigned the arbitrary value of 100 units of phlogiston per 100 pounds of silver. Thus 31 pounds of copper contained 100 units of phlogiston, or 100 pounds of it would contain 323 units of phlogiston. The values for all the other metals were similarly calculated.[29]

It was a fairly simple task for Lavoisier to recalculate Bergman's data

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[28] Lavoisier, "Considérations générale sur la dissolution des métaux dans les acides," *Oeuvres de Lavoisier* (Paris: Imprimerie Impériale, 1864), vol. 2, 509-527 at 510. DK-70.

[29] The English pound was clearly not the actual weight unit used in the experimentation. The Latin word used by Bergman was *libra* (from which comes the English abbreviation *lb*). The English translator of Bergman's document uses the word pound as equivalent to Bergman's *libra* simply to indicate the relative weight relations of the metals in these reactions. See J.A. Schufle, "Torbern Bergman and Andreas N. Tunberg: The Different Quantities of Phlogiston in Metals," *J. Chem. Educ.* 49 (1972): 810-812.

to give the quantity of oxygen that combined with each of the metals, on the principle that oxygen and negative phlogiston were equivalent. Bergman was following the long familiar phlogistic view that metals had to give up their phlogiston before they could dissolve in acids, while Lavoisier was operating on the principle that metals had to combine with oxygen before they could dissolve. This formal equivalence between oxygen and negative phlogiston does not yield an equivalent scientific value. On the contrary, the difference between them is precisely what made Lavoisier's triumph possible. Where Bergman was calculating *relative* values of the impalpable phlogiston, Lavoisier was calculating *real* values of ponderable oxygen. Lavoisier saw this difference clearly when he wrote

> All this calculation [of Bergman] is founded on the supposition that the calcination of metals is the result of the loss of phlogiston. But what I have been saying (that has become rather well known by now) is that this loss of phlogiston, even its presence in metals [in the first place] is, according to me, nothing but pure supposition. What is *more real,* what can be known, by the balance and direct measurements, is that in all metallic calcinations, whether made in the dry or humid way, whether it is done with the aid of air or of water, or by means of acids, there is an augmentation of the weight of the metal, and that augmentation is due to the addition of vital air, or specifically the oxygen principle.[30]

The five memoirs that followed were also quantitative in their compositional results. We can almost say that these memoirs represent the beginning of the systematic quantitative chemical analysis. These experiences having thoroughly confirmed Lavoisier in his anti-phlogistic position, he finally produced an outright attack on the phlogistic doctrine. This memoir, "Reflections on Phlogiston," opens with the following two paragraphs:

> In the series of memoirs that I have communicated to the Academy I have reviewed the principal phenomena of chemistry; I have emphasized

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[30] Lavoisier, "Sur la précipitation des substances métalliques les unes par les autres," *Oeuvres de Lavoisier,* vol. 2, 528-545 at 529-530. DK-71. For more details on this point, see Robert Siegfried, "Lavoisier and the Phlogistic Connection," *Ambix* 36 (1989): 31-40.

> those that accompany combustion, the calcination of metals, and, in general, all the operations where there is absorption and fixation of air. I deduced all the explanations from a simple principle, that pure air, vital air, is composed of a particular principle that forms its base that I have named the *oxygen principle,* combined with the matter of fire and of heat. Once this principle is admitted, the principal difficulties of chemistry appear to evaporate and dissipate, and all phenomena are explained with an astonishing simplicity.
>
> But if everything in chemistry can be explained in a satisfactory manner without the help of phlogiston, it is by that fact alone infinitely probable that the principle does not exist; that it is a hypothetical body, a gratuitous assumption, and indeed, it is within the principles of good logic not to multiply bodies without necessity.[31]

Lavoisier's chemistry was now essentially complete, and we can turn to a brief account of the development of a systematic chemical nomenclature through which Lavoisier's pneumatic chemistry became joined with the mainstream of empirical knowledge of the neutral salts.

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[31] Lavoisier, "Reflexions sur la phlogistique," *Mémoires* (Paris, 1783): 505-538; *Oeuvres de Lavoisier,* vol. 2, 623-655 at 623. DK-76.

11

A COMPOSITIONAL NOMENCLATURE

IN THE SEVENTEENTH and early eighteenth centuries, before the sense of chemical identity or individual chemical species was clearly recognized, there was, nonetheless, a fair number of bodies whose properties made them more or less readily distinguishable wherever they occurred. Some of these, typically those found in nature, I have previously called the privileged bodies. But an ever-growing number of bodies prepared in the laboratories deserved individual names. In the absence of a coherent theory of chemistry, they were named without system. An outstanding physical property such as color was often used, perhaps combined with a second property: red lead, blue or green vitriol, and so forth. The names, though descriptive, were nonetheless arbitrary for they revealed little of a substance's chemical behavior. "Liver of sulphur" and "oil of vitriol" indicated something of the consistency of the body as well as a suggestion of its chemical relations, but these too were arbitrary, and the analogies were misleading. As long as the number of important bodies was small, chemists could get by; but the rapidly expanding chemical knowledge of the eighteenth century created a conscious need for a systematic way of identifying distinct chemical bodies.

It was not only chemistry whose body of experiential knowledge was growing so large that a need for better linguistic patterns of rational organization was recognized, and such patterns were actively sought. Perhaps the most familiar to readers today was that of the biological sciences and the introduction of Linnaeus' bipartite nomenclature of genus and species, which offered both analogy and direct influence on chemical nomenclature. Maurice Crosland has provided an excellent account of the influence of Linnaeus on the Swedish chemist Torbern Bergman and the latter's connection with Louis-Bernard Guyton de Morveau.[1] Guyton de Morveau's nomenclature of neutral salts in 1782 became the crucial beginning of the successful reform of chemical nomenclature in 1787, an essential part of the chemical revolution. The well-established definition and concept of neutral salts provided Guyton de Morveau with the practical knowledge for a nomenclature based on composition. He expressed the fundamental principle by saying that "the denomination of a chemical compound is clear and precise only to the extent that it recalls its component parts by names conforming to their nature."[2]

The component parts of the neutral salts were the acids and the bases from which they could be made and into which they could be analyzed. Guyton said that each of these "simple bodies" or "considered as simple" ought to have its own particular name.[3] For the most part they already had familiar names; the metals, the alkalies, and the earths had long been distinctly identified and named. The acids, he suggested, would serve to denominate the genus of the salt, and the base the species for each neutral salt.

At the end of the paper, Guyton added a table giving extensive illustrations of how his system could be used. He first listed the eighteen known acids, followed by the corresponding list of the generic names of salts formed from these acids (e.g., "Vitriols, Nitres, Muriates, Arseniates, Phosphates," etc.). The next column listed the names of the alkalies, earths, and metals making up the three classes of bases; these, when combined with the names of the acids, gave the names of the neutral salts: "vitriol de plomb, arseniate de potasse, muriate de calcaire," and so forth. At the conclusion of this paper, Guyton could boast that the names of 474 substances could be provided according to a single system; that it was necessary only to know the names of the eighteen acids and twenty-four bases to be able

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[1] Maurice P. Crosland, *Historical Studies in the Language of Chemistry* (Cambridge, Massachusetts: Harvard University Press, 1962), Part 3, 133-224.

[2] L.-B. Guyton de Morveau, "Sur les dénominations chymiques," *Observations Physique,* 19 (1782): 37-382 at 374.

[3] Guyton de Morveau, "Dénominations chymiques," 374.

to create the names of the salts formed by their union. Reversing the process, it was easy, once given the name, to recall to mind the nature, that is, the composition, of the substance itself.[4]

The key to this system lies in the recognition that components by which compound bodies are named must be "simple bodies" or "considered as simple" rather than elements in the ultimate meaning of that term. This was not the first time Guyton had made the distinction between the philosophical and operational components. Only a few years earlier in his *Elémens de chemie,* he had carefully identified the ultimate, metaphysical components, the earth, water, air, and fire, as the "natural elements," and the more operational ones as "chemical elements."[5] The latter, though presumably composed of the natural elements, were still "simple according to art for it has not yet been possible to separate their principles...."[6] Nor was Guyton the first to make this kind of distinction. In the late seventeenth century Nicholas Lemery had written

> The word *Principle* in *Chymistry* must not be understood in too nice a sense: for the substances which are so called, are only *Principles* in respect of us, and as we can advance no farther in the division of bodies; but we well know that they may be still divided into abundance of other parts, which may more justly claim ... the name of *Principles:* wherefore such substances are to be understood by *Chymical Principles,* as are separated and divided, so far as we are capable of doing it by our weak imperfect powers. And because *Chymistry* is an Art that *demonstrates* what it does, it receives for fundamental only such things as are palpable and demonstrable.[7]

Similar statements can be found throughout the hundred years following Lemery, but it was not until Guyton de Morveau that a useful development of the operational simple body appeared. Of those who spoke of

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[4] Guyton de Morveau, "Dénominations chymiques," 382.

[5] Guyton de Morveau, *Elémens de Chemie,* 3 vols. (Dijon, 1777-1778), vol. 1, 12.

[6] See Robert Siegfried and Betty Jo Dobbs, "Composition: A Neglected Aspect of the Chemical Revolution," *Ann. Sci.* 24 (1968): 275-293 at 278.

[7] Nicholas Lemery, "Remarks upon Principles," in *Course of Chemistry,* 2nd English edition (London, 1686), 5-6. This passage is not in the first English edition.

this distinction before Guyton, one of the more thoughtful was René de Réaumur (1683–1757), who in 1730 wrote:

> We know only too well, that in physics the first principles are what we know the least about. It is not possible yet to give ourselves any clear ideas of these simple bodies which it is wished to make the elements of other bodies; the earth principle, the sulphur principle, the salt principle, etc. It is not even certain that we can succeed in knowing them, at least by the method of experience, the only one yet in Physics on which one can rely.[8]

Often, he adds, our analyses have to stop at the *élément prochain* (proximate element). Réaumur offers a specific example before he falls back into a more traditional use of the philosophical terms:

> There are a certain number of materials, all very compounded, which are combined rather ordinarily in most bodies, water, earth, fire or inflammable matter, salts, etc. Some of us take them all to be elements, others, according to their predelections, have taken only two or three, or only one as first principle. But having given them this quality, they have been more purified in imagination, than they are when they come under our senses. Earth is one of those which has been accorded this range.[9]

We have already seen in Chapter Nine how James Keir, the translator of Macquer's chemical works, conceived the operational idea of chemical simple body. But no one offered a more explicit definition before the new nomenclature than the Irish chemist Richard Kirwan in 1784:

> The principal reason why any simple substances are reckoned specifically different from each other, is their manifesting properties permanently different in the same circumstances, and every substance must be deemed simple, until it can be resolved into different principles, or

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[8] René de Réaumur, "De la nature de la terre en générale, et du caractère des différentes espèces de terres," *Mémoires* (Paris, 1730): 243-283 at 243.

[9] Réaumur, "Nature de la terre," 245.

> out of them. Every other indication is at best a surmise grounded on mere possibility, but destitute of probability, and therefore inadmissible in any exact scientifical system....[10]

Not all writers were so clear in making this distinction. Witness P.-J. Macquer's definition of chemistry in his mid-century textbook:

> The object ... of Chymistry is to separate different substances that enter into the composition of bodies.... But this Analysis, or Decomposition, of Bodies is finite.... In whatever way we attempt to go further, we are always stopped by substances in which we can produce no change, which are incapable of being resolved into others.... To these substances we may ... give the title of Principles or Elements.... Of this kind the principal are Earth, Water, Air and Fire.[11]

In spite of the seeming modernity of the opening statements, it is clear that Macquer's commitment to tradition has led him to identify the observed products of analysis with the philosophical elements of old. What Macquer and many other chemists still lacked was a clear sense of a chemical substance. Certainly Macquer could not have had in mind the concept of substance or body like that defined by Torbern Bergman a few years later when he wrote, "In general, any body which differs in properties from every other, and can be always had *similar to itself,* I consider as a separate and distinct body...."[12]

When Macquer refers to the earth resulting from analysis, he can hardly be intending more than that there is a solid residue that has the general properties of earth; that is, it is solid, insoluble, and so on. Not every one of the earths obtained from different analyses would (in Bergman's words) have properties always similar to itself, and different from those of any other. Macquer lacked a clear concept of chemical substance.

Yet Guyton de Morveau had the concept of simple body as distinct

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[10] Richard Kirwan, *Elements of Mineralogy* (London, 1784), 362.

[11] P.-J. Macquer, *Elements of the Theory and Practice of Chemistry*, translated by A. Reid, 2 vols. (London, 1758), vol. 1, 1-2.

[12] T.O. Bergman, *Physical and Chemical Essays*, translated by Edmund Cullen, 2 vols. (London, 1788), vol. 1, xxix.

from philosophical element when he offered his system of chemical nomenclature in 1782. Here again we are struck by the phenomenon of an idea or concept which has been kicking around for many years at a more or less conscious level suddenly becoming a very conscious and much-utilized intellectual tool. In the case of the simple body, it became, through the junction of Guyton's nomenclature and Lavoisier's theory of acidity, the basis for a whole new structure of chemical knowledge. It was brought to fruition through the new nomenclature published by Guyton de Morveau, Lavoisier, Fourcroy, and Berthollet in 1787, and publicized and extended by Lavoisier in his *Traité élémentaire de chimie* in 1789. We turn now to a brief account of the merger of Guyton's nomenclatural system with Lavoisier's pneumatic doctrine.

Early in 1787 Guyton came to Paris from Dijon to acquaint himself more fully with the latest developments in pneumatic chemistry, so that he might adapt his system of nomenclature to include this new branch of chemistry. Guyton was at this time a phlogistonist, though his system for naming the neutral salts was independent of that view, being entirely empirical. Yet chemistry of the gases could not be brought under a systematic nomenclature without resolving the disputed nature of combustion and calcination. For Lavoisier, the acids were compounds of oxygen and an acidifiable basis, while in the phlogistic view the acids were relatively simple.

During his stay in Paris, Guyton became converted to the oxygen chemistry of Lavoisier; and these two men, joined by Claude-Louis Berthollet (1748–1822) and A.-F. de Fourcroy (1755–1809), both previously converted, published jointly their *Méthode de nomenclature chimique* in August of 1787. The most important papers in this collection were those by Lavoisier and Guyton. Both strongly emphasized the importance of founding compositional nomenclature on the empirically based "simple bodies." Lavoisier urged the philosophical point that language is the essential analytical tool of thought itself, so that the perfection of the language was necessary to the perfection of the science. Within this context, he wrote, "We will be content here to regard as simple all those substances we are not able to decompose, everything we obtain as the final result of chemical analysis. No doubt some day these substances, which are simple for us, will be decomposed in their turn...."[13]

Guyton de Morveau's paper, "Mémoire sur le dévelopment des principes de la Nomenclature méthodique," made emphatic the intimate relationship between the nomenclature and the concept of simple body:

> In the order which we have proposed to ourselves, the simple substances, that is to say, such as chemists to the present time have not been able to decompose, ought chiefly to fix our attention, because the denominations of bodies which by exact analysis can be reduced to their elements, are properly expressed by the re-union of the names of those same principles.[14]

Of the five classes into which they divided the simple bodies, the metals, earths, and alkalies are the same as in Guyton's first system of 1782. The acceptance of Lavoisier's oxygen theory of acidity required Guyton de Morveau's former class of acids to be divided into two new ones. These were the "acidifiable bases" such as sulfur, phosphorus, and carbon; and a new class to include oxygen. In the *Méthode,* oxygen was joined in this new class of simple bodies by heat (as caloric), light, azote (nitrogen), and hydrogen. This made a pretty motley group, whose members, as Guyton admitted, did not present "any remarkable analogy with each other."[15] Nonetheless the new nomenclature established the identification of chemical bodies by their composition, the simple bodies were recognized as conditionally simple, subject to the results of later empirical evidence. Fourcroy later credited the nomenclature with the "consolidation" of Lavoisier's pneumatic doctrine, and I think this is about right in the sense

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[13] A.-L. Lavoisier, "Mémoire sur la nécessité de réformer et du perfectionner la nomenclature de la chemie," published in *Méthode de nomenclature chimique, proposé par MM. de Morveau, Lavoisier, Berthollet, et de Fourcroy* (Paris, 1787). Quotation from *Oeuvres de Lavoisier,* vol. 5, 354-364 at 361.

[14] English quotation taken from Henry M. Leicester and Herbert S. Klickstein, *A Source Book of Chemistry 1400–1900* (New York: McGraw-Hill, 1952), 184.

[15] Leicester & Klickstein, *Source Book,* 184.

that it integrated Lavoisier's pneumatic discoveries with the empirical main stream of the neutral salts. The compositional organization of chemistry was now constantly reinforced by its language, fulfilling Lavoisier's position that the perfection of the language will lead to the perfection of the science. The language itself constantly reinforces the compositional order of the chemical knowledge.

It is generally agreed that the new chemistry, now consolidated and made coherent by the nomenclature, achieved its wide acceptance chiefly through Lavoisier's *Traité élémentaire de chimie* published in 1789. This work was translated right away into several European languages.[16] Historians have seen this work chiefly as the completion of the chemical revolution, the overthrow of the phlogiston doctrine, but little attention has been given to more fundamental consequences deriving from the operational concept of simple body.[17] A brief analysis of Lavoisier's *Traité* will prepare us for an examination of subsequent developments.

Part I of the *Traité* is a lucid summary of Lavoisier's own pneumatic discoveries of the previous fifteen years. The three theoretical principles that guided his original research and organize Part I of the *Traité* itself are all implicit in the title, "Of the Formation and Decomposition of Aeriform Fluids, of the Combustion of Simple Bodies, and the Formation of Acids."[18] The caloric model of the gaseous state, his earliest theoretical construct, is in immediate and persistent evidence throughout this part. All gases are combinations of material bodies with weightless matter of heat, which he now called caloric. This is particularly important in explaining the role of oxygen in supporting combustion. When a body burns, it combines with the ponderable matter of oxygen, decomposing the gas and liberating the caloric as free fire, thus accounting for the heat of combus-

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[16] For a full account of the new nomenclature in different nations, see *Lavoisier in European Context: Negotiating a New language for Chemistry*, ed. Bernadette Bensaude-Vincent and Ferdinandro Abbri (Canton, Massachusetts: Science History, 1995).

[17] R. Siegfried, "The Chemical Revolution in the History of Chemistry," *Osiris* 4 (1988): 34-50.

[18] Lavoisier's *Traité de chimie* was translated into English by Robert Kerr with the title *Elements of Chemistry* (Edinburgh, 1790). Quotation from Dover edition (New York, 1965), 1.

tion. The third principle of his anti-phlogistic doctrine has oxygen serving as the principle of acidity, that all acids contain oxygen. These three principles, along with the definition of a simple body as any substance not yet decomposed, constitute the theoretical girders of the book. The principle of the conservation of weight is the operating basis of all the experimental evidence offered by way of illustration and justification.

> We may lay it down as an incontestible 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; the quality and quantity of the elements remain precisely the same; and nothing takes place beyond changes and modifications in the combinations of these elements. Upon this principle the whole art of performing chemical experiments depends: We must always suppose an exact equality between the elements of the body examined and those of the products of its analysis.[19]

He later makes explicit that it is the weights that must be measured: "[T]he usefulness and accuracy of chemistry depends entirely upon the determination of the weights of the ingredients and products both before and after experiments."[20] The title of Part II, "Of the Combination of Acids with Salifiable Bases, and of the Formation of Neutral Salts," is equally descriptive of the content, which is "composed chiefly of tables of the nomenclature of the neutral salts." But, as the author also points out, it "contains nothing which I can call my own."[21] By joining his pneumatic discoveries recounted in Part I with the empirical mainstream of the neutral salts under the guise of the new nomenclature in Part II, Lavoisier had created in the *Traité* a powerful device for propagating a new chemistry. Contemporary supporters and opponents alike recognized that Lavoisier had accomplished a revolution in chemistry, and the events of this time have been identified ever since as the "Chemical Revolution."

Most studies of the revolution have been directed to the elucidation of the details of Lavoisier's overthrow of phlogiston, and little thought is given to the larger context within which that dramatic success took place. As has

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[19] Lavoisier, *Elements,* 130-131.

[20] Lavoisier, *Elements,* 297.

[21] Lavoisier, *Elements,* Preface, xii-xiv.

been shown here, the elimination of phlogiston was merely the means to more significant accomplishments, most of which Lavoisier did not fully perceive himself.[22] Among the lasting contributions, we must rank first his introduction of the systematic application of the principle of the conservation of weight. Though this principle had been utilized in many chemical investigations before Lavoisier, he is the first to raise it to the conscious level of a required principle of universal application. This was the procedure that enabled him to establish the proper order of composition and simplicity, crucial for creating a reliable definition of "simple body" to be put into practice. As will be seen, though, this concept first caused much anguish within the chemical community, before the list of simple bodies was assigned atomic weights two decades later. The particular facts that he established by means of the conservation principle is too long to give here; it is enough to say that this principle made possible a science of quantitative chemistry.

Ironically, the three principles that had guided Lavoisier's creative researches and organized Part I of the *Traité* failed to become a permanent part of chemistry. The caloric model of gases, oxygen as sole supporter of combustion, and oxygen as the principle of acidity, were all quickly abandoned by nineteenth century chemists, chiefly through the discoveries of Humphry Davy.

The concept of "simple body" as the operational unit of composition became widely accepted. An examination of Lavoisier's "Table of Simple Substances" yields some significant insights into his way of thinking. Throughout the *Traité* he emphasized that *simple body* was a conditional assignment, that such are simple only in the sense that they have not yet been decompounded. But he was not consistent in his treatment of those bodies whose simple nature was still uncertain. In the case of the fixed alkalies, soda, and potash, which had not yet been shown to be compound, he omitted them altogether, "because they are evidently compound substances, though we are ignorant as yet what are the elements they are composed of."[23] He offered no specific evidence to support the compound

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[22] See Siegfried, "The Chemical Revolution," 34-50.

[23] Lavoisier, *Elements,* 178.

nature of the fixed alkalies, but apparently the recently discovered composition of the volatile alkali, ammonia, provided his justification by analogy.[24]

He also strongly suspected that "The salifiable simple earthy substances" lime, magnesia, and baryta would prove to be metallic oxides, but because they were still undecompounded, we must "consider them as simple bodies." Later he added, "these things we at present suppose simple may soon be found quite otherwise.... We may even presume that the earths must soon cease to be considered as simple bodies; they are the only bodies of this entire class which have no tendency to unite with oxygen; and I am much inclined to believe that this proceeds from their being already saturated with that element." But he adds that since this is only conjecture, the earths are properly listed among the simple bodies.[25]

No such admission of conjecture is to be found in his treatment of the undecompounded acids, which Lavoisier assumed to contain oxygen in conformity with his well-advertised theory of acids. His commitment to oxygen as the principle of acidity was strong enough that he created three imaginary radicals representing the unknown components for the muriatic, the fluoric, and the boracic acids. In the table of Simple Substances, these radicals are placed in the group of acidifiable bases along with sulfur, phosphorus, and carbon. Because these acids had not been shown to be decompounded, they could have been identified as simple bodies rather than as composed of oxygen. This classification question becomes overt in his discussion of muriatic acid (HCl) which, he admits, "does not appear to have been hitherto decomposed in any chemical experiment, so that we have no idea whatever of the nature of its radical, and only conclude, from analogy with the other acids, that it contains oxygen as its acidifying principle."[26]

It is interesting to see that Lavoisier resolved this problem by analogy with well-established composition of other acids, a more demonstrable analogy than that of the fixed alkalies' compound nature by analogy with ammonia.

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[24] For a detailed analysis of this whole sequence of Lavoisier's struggle with simple bodies, see Robert Siegfried, "Lavoisier's Table of Simple Substances, its Origin and Interpretation," *Ambix* 29 (1982): 29-48.

[25] Lavoisier, *Elements,* 177.

[26] Lavoisier, *Elements,* 233.

12

A COMPARATIVE VIEW OF THE PHLOGISTIC AND ANTI-PHLOGISTIC PHILOSOPHIES

> In the *old* Phlogiston Theory, phlogiston is equivalent to *minus* oxygen; in the later theory it was sometimes assumed to be hydrogen (Cavendish, Kirwan, Priestley), or the matter of light (Macquer). Practically every chemist adopted the theory during the eighteenth century.
>
> James R. Partington, *A Short History of Chemistry*[1]

I HAVE ALREADY challenged the validity of Partington's statement regarding the universality of the phlogiston theory in the eighteenth century. But it was in fact the *old* phlogiston that Lavoisier attacked and thereby created the "anti-phlogistic doctrine." We may never know how consciously Lavoisier recognized that his new doctrine was so intimately connected to the old as implied in Partington's statement. But an exploration of that connection is very informative of the conceptual thinking of both sides of the revolution.

Of all the well-known revolutions in the history of science, the chemical is perhaps the most dramatic.[2] The rapidity with which Lavoisier's views superceded those of the phlogistic tradition of the previous century is in contrast with the century and a half between Copernicus and Newton that defines the scientific revolution. Only twenty years separate Lavoisier's first explorations of the chemistry of gases and the public capitulation of

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[1] 2nd ed. (London: Macmillan, 1948), 146.

[2] For an extensive survey of scientific revolutions, see I. Bernard Cohen, *Revolution in Science* (Cambridge, Massachusetts: Harvard University Press, 1985). The Chemical Revolution is presented in chapter 14, 229-236.

Richard Kirwan, the last significant European defender of the phlogistic views. The dramatic quality of these events is intensified by their having been accomplished with deliberate intent by a single man, Antoine Laurent Lavoisier. Both he and his contemporaries acknowledged that he had indeed brought about a revolution. Finally, the totality of the conceptual transformation was acknowledged when Kirwan in 1787, observing that "Mr. Lavoisier [had] reversed the ancient hypothesis," introduced the term "Antiphlogistic" as an appropriate name for the new doctrine. The term became the common designation and was accepted by Lavoisier himself.[3] That the term became common is illustrated by two contemporary books: William Higgins, *A Comparative View of the Phlogistic and Antiphlogistic Theories,* London, 1791, and Christoph Girtanner, *Anfangsgründe der Antiphlogistiche Chemie,* Berlin, 1792.

Antoine-François de Fourcroy, the chief contemporary publicist for the chemical revolution, in 1797 described the reception of Lavoisier's work thus:

> From 1777 to 1785, in spite of great efforts and numerous memoirs of Lavoisier, he was truly alone in his opinion.... [There was] a sort of neutrality that resisted not so much his discoveries, but *the total reversal of the ancient order of ideas.*[4]

We find this same sentiment expressed more passionately by the men who reviewed the new nomenclature for the Academy of Sciences in 1789:

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[3] Richard Kirwan, *Essay on Phlogiston and the Constitution of Acids* (London, 1789), 4 and 7. The book was first published in 1787. The phrase was used by Lavoisier and his colleagues in their refutations of this work when translated into French by Madame Lavoisier in 1788. In 1789 William Nicholson translated the complete French version back into English. Note also the correspondence between Guyton de Morveau and Kirwan, which provides evidence that both men seem to have shared the same antiphlogistic perception of Lavoisier's work. Guyton's letter to Kirwan dated 14 June 1785 refers to "la secte anti-phlogistique." See *A Scientific Correspondence During the Chemical Revolution,* ed. Emmanuel Grison, Michelle Goupil & Patrice Bret (Berkeley, California: University of California, Office of History of Science & Technology, 1994), 111. Kirwan nevertheless appears to have been the first to use "anti-phlogistic" in print.

[4] Quoted by James R. Partington, *A History of Chemistry,* 4 vols. (London: Macmillan, 1961-1970), vol. 3, 488. The quotation is from *Encyclopédie méthodique, Chimie,* vol. 3, 541, emphasis added.

> If it is not easy to renounce all the principles of one's education, it is still more difficult, it seems to us, abruptly to admit that a large group of substances which all analogy with the order of natural philosophy seems to indicate as being more or less compound, must be regarded henceforth as simple substances, without counting the number of them which one will be forced to simplify every day—as though one yet dealt with the problem at the beginning of things and at the first moment of creation.[5]

There is in this passage an almost wistful air of longing for something now irretrievably lost from a world turned upside down. The universality of this feeling with regard to the new chemistry (some called it the French chemistry; Lavoisier called it "mine") is attested by the fact that the most common name for it was the antiphlogistic chemistry, a name commemorating the world now lost, not the system gained. Superficially, it seems odd that a revolutionary new system failed to gain a verbal identity of its own.

The name "antiphlogistic" identifies the conceptual inversion of the new chemistry, while at the same time it implies some sort of connection with the view it replaced. Let us examine the parallels of the two systems. Can it be that the new chemistry was in some essential way just the old chemistry turned upside-down or inside-out? The answer is, yes, and many scholars have noted that the chemistry described in phlogistic terms can be easily converted into antiphlogistic ones by replacing every reference to phlogiston with negative oxygen.

Phlogiston was not a ponderable substance in the modern sense, but a principle whose presence in a body was inferred from the properties it was apparently responsible for. Whatever other properties phlogiston might confer, all phlogistonists agreed that phlogiston was the principle of combustibility. When a body burned, the flame emitted was the visible manifestation of the departing phlogiston. The calcination of metals was also, by Lavoisier's time, recognized as being a species of slow combustion, so metals also contained phlogiston. Lavoisier's work reversed this pattern and established that instead of phlogiston leaving a combustible, oxygen from

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[5] "Rapport sur la nouvelle nomenclature; extrait de registres de l'Académie Royale des Sciences," signed by Baumé, Cadet, d'Arcet, and Sage. The report, dated 13 June 1787, was printed in *Méthode de nomenclature chimique* (Paris, 1787), 238-252. Quotation from 248.

the atmosphere was combining with it. He successfully argued his position by showing that the weight gained by the combustible was equal to the weight lost by the enclosing atmosphere. Lacking the materiality of weight, phlogiston became unnecessary, an imaginary fiction. Both views were rationalizing the same phenomena, hence the formal connection between the old and the new is a clear reversal. If in the old view phlogiston was emitted, then the new view had oxygen being added, and vice versa. In a simple calculus for converting the old terminology into the new, one simply substitutes negative oxygen wherever phlogiston is found.

Typical phlogistic accounts can be represented as below, where the calx is today called the metal oxide:

(heated)
METAL = CALX + PHLOGISTON (which escapes);
(heated)
SULPHUR = ACID + PHLOGISTON (which escapes).

These can be transformed into the antiphlogistic form by substituting negative oxygen for the phlogiston:

METAL = CALX + (−OXYGEN)

then becomes, quasi-algebraically rewritten:

METAL + OXYGEN = CALX
(metallic oxide)

A similar transformation can be written for the combustion of sulfur:

SULFUR = ACID + (−OXYGEN)

then becomes:

SULFUR + OXYGEN = ACID

There are other less familiar chemical behaviors that the phlogistic view readily described. Near the middle of the century Macquer discovered that if white arsenic (As_2O_3) was treated with nitric acid a new acid was formed which contained arsenic as its basis. Later phlogistonists explained this by extending the traditional relationship between a metal and its calx. In this case, the metallic arsenic by losing some of its phlogiston would form the calx (the white arsenic). Since nitric acid was known to have a very powerful affinity for phlogiston, when it was added to the calx of arsenic it extracted still more phlogiston to leave the acid of arsenic as the final residue. Torbern Bergman, after identifying other metallic acids, of molybdena and of tungsten, generalized this relationship by suggesting that "it is highly probable that all the metals are only different acids coagulated by a large quantity of phlogiston."[6] In this view it is the acids that are simple bodies, and the metals are the products of their saturation with phlogiston.

Lavoisier's views of these matters are characteristically the anti-phlogistic reversal of Bergman's view, and show up only after he had read Bergman's paper. For Lavoisier the metals are simple, and their oxides are only the first degree of oxidation, not themselves acidic, but on the way to becoming acids if they can be made to combine with enough oxygen, which was for him the principle of acidity. As it was with Bergman, arsenic was the best-known example of that relationship, but in the *Traité* this relationship is extended to all the metals.

Another example of what appears to be Lavoisier's views derivative from Bergman's phlogistic generalities relates to the solution of metals in acids. Whereas Bergman said that "no metal can be dissolved by acids unless sufficient phlogiston has previously been removed," Lavoisier said, "when we put a metal in an acid for solution, it is necessary, in the first place, that it become oxygenated."

Elsewhere the question has been raised of whether Lavoisier might have owed much of his program of research to an early recognition of this kind of relationship, that is, all he had to do to bring about the revolution in chemistry was to replace every departure of phlogiston with the addition of air (later of oxygen) and every addition of phlogiston with the departure of oxygen.[7] Now, however, our focus is broader: What is the nature of the transformation in thought that accompanies the move from phlogistic to antiphlogistic perspectives? Henry Cavendish acknowledged this inversion

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[6] Torbern Bergman, "On Arsenic," *Physical and Chemical Essays,* translated from Swedish by Edmund Cullen, 2 vols. (London, 1784), vol. 2, 288-289.

[7] Robert Siegfried, "Lavoisier and the Phlogistic Connection," *Ambix* 36 (1989): 31-40. This paper also provides a more detailed account of Lavoisier's reinterpretation of Bergman's work.

in 1784 when he wrote that "we must suppose, that water consists of inflammable air united to dephlogisticated air ... and indeed ... adding dephlogisticated air to a body comes to the same thing as depriving it of its phlogiston and adding water to it."[8]

Cavendish saw the two competing views as equivalent, stating that "the commonly received principle of phlogiston explains all phenomena, at least as well as Mr. Lavoisier's."[9] Cavendish was not altogether wrong on this point; all we have to do is neglect the arguments based on the conservation of weight, and the phlogistic view provided as much order and coherence to known chemical phenomena as did the antiphlogistic doctrine. The point of these illustrations is to confirm the idea that the explanatory rationale of the two systems is equivalent, virtually identical. Much of Lavoisier's thinking is clearly derivative of the chemical tradition of chemistry of principles, whether of combustion or of acidity. But his rigorous application of the criterion of weight conservation demanded the compositional reversal that turned a phlogistic perspective into an anti-phlogistic one.

With the rapid acceptance of the weight conservation for chemistry, phlogiston soon had no useful role to play. The phlogistonists who, like Cavendish, Kirwan and Priestley, identified phlogiston with hydrogen, were giving a material identity to what had been beyond direct experience. They may have been responding to the growing expectation that chemistry must deal with real, tangible bodies only, but in so doing they were putting their system at great risk by making them experimentally falsifiable. In the end the effort to make phlogiston materially real was self-defeating, as will be discussed again later.

There is an interesting parallel between the introduction of Newtonian mechanics and the introduction of Lavoisierian chemistry. As long as the planetary motions were only described, it was possible to evaluate all systems only on the basis of their accuracy of prediction. By this standard, the Ptolemaic and Copernican systems were not far apart and one might prefer

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[8] Henry Cavendish, "Experiments on air," *Phil. Trans.*, 1784, as quoted in Henry M. Leicester and Herbert S. Klickstein, *A Source Book in Chemistry 1400–1900* (New York: McGraw-Hill, 1952), 152-153.

[9] Cavendish, "Experiments on Air," 153.

either system on personal grounds. When Newton introduced mass into the system, that is, moved astronomy from kinematics to dynamics, such freedom of intellectual choice was no longer possible. Similarly, when Lavoisier introduced the conservation of weight into chemistry, the freedom to choose, with equal respectability, the phlogistic or the anti-phlogistic schemes was gone. In both cases mass provided a new measure of reality; the earth *must* move about the sun; the oxygen *must* be added to the combustible.

Chemistry by Principles

We have seen that phlogiston was the principle of inflammability, that as Macquer expressed it,

> The inflammability of a body is an infallible sign that it contains a phlogiston, but from a body's not being inflammable, it cannot be inferred that it contains none: for experiments have demonstrated that certain metals abound with it, which yet are by no means inflammable.[10]

But phlogiston and other property-endowing principles were not material substances, but metaphysical causes. Thus when a phlogistonist such as Macquer states that an inflammable body must contain phlogiston, he is not referring to a measurable quantity. The phlogiston can modify the behavior of body by its presence, but by the very definition of a principle it is non-isolable and immeasurable, though Bergman later did measure the *relative* quantities of phlogiston in the metals without isolating or weighing the phlogiston itself. Priestley's different airs were all common air variously modified with phlogiston, the phlogiston modifying the properties without itself being directly detectable, however much more phlogiston there was in phlogisticated air than in de-phlogisticated air. Chemistry by principles reduces the measurable distinctiveness of chemical species, erasing the boundaries between them.

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[10] P.-J. Macquer, *Elements of the Theory and Practice of Chemistry*, translated by A. Reid, 2 vols. (London, 1758), vol. 1, 10.

We have also seen that Lavoisier identified dephlogisticated air as the principle of acidity, and accordingly renamed its material substance oxygen. And in parallel to Macquer's phlogiston, Lavoisier's oxygen principle was known to be infallibly present in acids, but its presence did not necessarily confer acidity on all bodies that contained it. Let us briefly examine the use of principles that was so common in chemical descriptions of the seventeenth and eighteenth centuries, and compare it with Lavoisier's use of the principle of acidity.

The French writer Molière in 1673 produced his play *Le Malade Imaginaire,* in which he satirized the medical profession for the verbosity and ineffectiveness of contemporary medicine and the circularity of its pompous explanations.[11] Argan, the hypochondriac, has been persuaded to become a physician so that he can treat himself. In the play's final scene, a group of physicians gathers to test his knowledge.

> ARGAN: I have been asked by the doctors the cause and the reason why opium produces sleep. To which I reply, there is in it a dormitive virtue whose nature is to stupefy the senses.[12]

The chorus of the examining physicians was unequivocal; "Bene, bene, bene, bene respondere." Here we can laugh at Argan for a non-explanation where cause and effect become one and the same thing. And we might want to laugh also at the identical argument for the existence of phlogiston and its ancestral sulphur principle, for as Macquer stated, "The inflammability of a body is an infallible sign that it contains a phlogiston,"[13] that is, that it contains the principle of inflammability. The utilization of such *ad hoc* and circular explanations for chemical causes represents not so much the ignorance of good reasoning as it does the intrinsic difficulty of chemical understanding and the centuries-long failure to find an indigenous theoretical frame for chemical explanation and description. The chemical tradition had long ago selected composition as the identifying quality of the various substances they dealt with, but the identification of the right components

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[11] Molière was the pseudonym of Jean Baptiste Poquelin (1622–1673). See *Molière. The Misanthrop and Other Plays,* translated with an introduction by John Wood (New York: Penguin Books, 1959).

[12] Molière, *The Misanthrop and Other Plays,* 276.

[13] Macquer, *Elements,* vol. 1, 10.

had proved to be elusive. Oddly enough, when chemists in the eighteenth-century began describing chemical changes in terms of material components, phlogiston (as the inheritor of the fiery principle tradition of antiquity) continued to be included among the material constituents, treated and utilized in quite the same way as any acid, alkali, earth, or metal. This in spite of the fact that phlogiston had never been isolated, and sometimes protected from that possibility by assigning it to the ultimate class of principles that by definition could not be isolated.

But what looks here like empty circular reasoning may be the first resort of the philosophical mind: one effect–one cause. The cause and effect are one, essentially a tautology; experience and explanation are one. It certainly has a respectable history that goes back at least as far as Anaxagoras and the explanation of gross qualities by the assumption of identical qualities in the infinitely small particles, the *homœomeria,* that made up the larger body. Further questioning will push the explanation back whatever number of steps is sufficient to satisfy their creator. When pushed to the point that no new cause can be conceived, we have the first cause of Aristotle. This is an inherent requirement of deductive reason itself: there must be a beginning truth from which all details of experience derive. In geometry it is the set of axioms that serves this ultimate origin which requires no origin of its own. It has not been satisfying to the rational mind to accept a world that simply *is;* it must be explained in terms of pre-existing causes.

But how does all this relate to eighteenth-century chemistry of principles, the idea of the universal acid, the inflammable principle, and so on?

The escape from the tautology of one effect–one cause is possible if the hypothesized cause can be demonstrated to have an independent existence. After we have laughed at Molière's Argan, remember that opium does in plain fact contain "a dormitive virtue whose nature is to stupefy the senses." Its name is morphine, and it has been isolated and its composition determined. Argan's tautology has been broken by pushing the cause back another step to experiential reality.

Phlogiston, then, is the notorious example of Argan's method of explanation in eighteenth-century chemistry. Throughout the century chemists stated that the presence of phlogiston could be known only by its effects, thus denying that it could be isolated. Richard Watson's essay on phlogiston, written shortly before the demise of that concept, summed up the century-long attitude in the following words:

> All bodies are more or less susceptible of combustion, according to the quantity of this principle which enters into their composition, or what degree of force with which it adheres to them. In the act of burning, and it may very probably be during the fermentation, and putrefaction, and chemical solution of various bodies, it recovers its fluidity, is expanded and dispersed into the air, or combined anew with such substances as it has an attraction to. Notwithstanding all that perhaps can be said upon the subject, I am sensible the reader will be still ready to ask—*what is phlogiston?* You do not surely expect that chemistry should be able to present you with a handful of phlogiston, separated from an inflammable body; you may just as reasonably demand a handful of magnetism, gravity, or electricity to be extracted from a magnetic, weighty, or electric body. There are powers in nature which cannot otherwise become the object of sense, than by the effects they produce; and of this kind is phlogiston.[14]

Following Lavoisier's demonstration that oxygen from the atmosphere actually combined with metals when they were calcined, and with sulfur and phosphorus when they were burned to form their respective acids, the defenders of the phlogistic view were themselves forced to accept those demonstrations. They were, after all, based on the principle of the conservation of weight, which no phlogistonist was prepared to reject. Some phlogistonists did attempt to explain the gain in weight by metals when calcinated by assigning a negative weight to the phlogiston which was driven off.[15] This claim accepts the imperatives of the conservation of weight principle, in effect, but with an interesting and ironic twist. They also argued that the fact that oxygen combined with the combustibles did *not*

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[14] Richard Watson, "Of Fire, Sulphur, and Phlogiston," in his *Chemical Essays,* 5 vols. (London, 1781-1787), vol. 1, 166-167.

[15] See James R. Partington and Douglas McKie, "Historical Studies on the Phlogiston Theory," published in *Ann. Sci.* in 1937-1939. I. "The Levity of Phlogiston," 2 (1937): 361-404; II. "The Negative Weight of Phlogiston," 3 (1938): 1-58; III. "Light and Heat in Combustion," 3 (1938): 337-371; IV. "Last Phase of the Theory," 4 (1939): 113-149.

prove that phlogiston was not also involved. This is a valid point, logically, but its implications can be rigorously worked out only with a certain fixed disregard for Occam's Razor. Richard Kirwan, for example, argued that in the calcination of metals, the phlogiston left the metal to combine with the oxygen to form fixed air; the fixed air then combined with the metal to form the calx. Cavendish, equally reluctant to abandon phlogiston, held that during combustion, the phlogiston combined with the oxygen of the air to form water, which then combined with the combustible.

To us it is obvious that these men were reaching desperately for a way to hold onto a familiar idea, and it is equally obvious that their efforts were doomed once they had admitted the conservation of weight as an active and decisive criterion for testing chemical phenomena. These devices of Kirwan and Cavendish *permitted* phlogiston to retain a role, but the chemical behavior at stake could be easily described without reference to that elusive body; it was not needed. Kirwan finally admitted as much when he wrote to the editor of Crell's chemical journal in 1791:

> I know of no single clear decisive experiment by which one can establish that fixed air is composed of oxygen and phlogiston, and without this proof it seems to me impossible to prove the presence of phlogiston in metals, sulphur or nitrogen.[16]

By this analysis, phlogiston as an explanatory device failed because it could not be isolated, indeed its identification as a principle precluded the expectation of its ever being isolated. Kirwan's rejection of phlogiston for lack of its experienced existence reflects his emphasis on empirical evidence for reality. In spite of its lack of material existence, the theory of phlogiston had earlier given significant organizational function to much of eighteenth-century chemistry.[17]

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[16] Quoted by Partington, *History of Chemistry,* vol. 3, 664.

[17] Carleton E. Perrin, one of the most productive of Lavoisier scholars, provided a thorough account of the phlogiston chemistry that dominated French chemistry before Lavoisier: "Research Traditions, Lavoisier and the Chemical Revolution," *Osiris* 4 (1988): 53-81. In the same issue of *Osiris,* J.B. Gough offered a unique but dubious view of the importance of Stahl's phlogistic theory: "Lavoisier and the Fulfillment of the Stahlian Revolution," *Osiris* 4 (1988): 15-33.

Two questions are fundamental in defining the aims of the scientific thinking about nature: is it true; and/or is it useful?

It is easier for us as historians two centuries later to see the distinction between these evaluations than it was for the practitioners whose writings we study. For the most part the chemists of the eighteenth century did not systematically make that distinction. Anything that seemed to make sense of their data took on the aura of truth itself, and systems multiplied almost as rapidly as experiments, and favorite theories staggered under the load of too much data. Consider Priestley's remark of 1790, previously quoted in Chapter Nine:

> [M]en can keep brooding over a new fact, in the discovery of which they might, possibly, have a very little real merit, till they think they can astonish the world with a system as complete as it is *new,* and give mankind a high idea of their judgment and penetration....

But the acquisition of "new facts" had far outstripped the capacity of chemical theory to absorb them rationally into any existing system.

> At present all our *systems* are in a remarkable manner unhinged by the discovery of a multiplicity of *facts,* to which it appears difficult, or impossible, to adjust them.[18]

Though it should be easier for modern historians to maintain the distinction between utility and truth, it isn't always done. In particular, if we wish to understand the loyalty of the eighteenth-century chemists to the phlogiston doctrine, we must recognize that they accepted it as both useful and true, and indeed it was perhaps their recognition of its utility in providing organization for combustion and calcination that they confused with truth.

But recognizing today that the phlogistic view is *not* true, we tend to ignore its utility in its own time. We should recognize that Lavoisier's *anti-phlogistic* doctrine replaced its predecessor not only because it was "truer"

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[18] Joseph Priestley, *Experiments and Observations on Different Kinds of Air,* 3 vols. [Birmingham, 1790] (New York: Kraus Reprint, 1970), vol. 1, xvii-xviii; and xliii.

but also because it became equally useful after Lavoisier was able to incorporate the consequences of the composition of water into his system. It is my contention that at the time of Lavoisier's overthrow of the phlogiston doctrine, the utility of the new anti-phlogistic doctrine was hardly greater than that of the system being rejected. That Lavoisier himself was at least subliminally aware of this is suggested by his acceptance of "anti-phlogistic" as an appropriate denomination for his new chemistry. But that he saw the new chemistry as truer is evident by the nature of his arguments, always based on the weight relationships. Phlogiston was an imaginary body, "a *Deus ex machina* of the metaphysicians," whereas oxygen, his equivalent agent of organization, was materially real.[19]

Discontinuity and Identity

It was not only chemistry in the eighteenth century that illustrates the problem of discontinuity and distinct identity. Denis Diderot in the Prospectus for the great *Encyclopédie,* 1751, described the recalcitrant tendency of nature to resist categorization: "Nature presents us only with particular things, infinite in number and without firmly established divisions. Everything shades off into everything else by imperceptible nuances."[20]

There is a clear connection with the doctrines of plenitude and continuity associated with the Great Chain of Being. Arthur O. Lovejoy says that in natural history, there was a conscious search for the connecting links in the Great Chain, striving to reduce the gaps to "imperceptible nuances."[21] He quotes from the article "Cosmologie" of the *Encyclopédie* that, since "everything in nature is linked together" and since "beings are connected with one another by a chain of which we perceive some parts as continuous, though in the greater number of points the continuity escapes us,"

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[19] A.-L. Lavoisier, "Considérations générales sur la dissolution de métaux dans les acides," *Oeuvres de Lavoisier* (Paris: Imprimerie Impériale, 1864), vol. 2, 509-527 at 510. DK-70.

[20] Quoted by Robert Darnton in "Philosophers Trim the Tree of Knowledge: The Epistemological Strategy of the *Encyclopédie,*" in his *The Great Cat Massacre and other Episodes in French Cultural History* (New York: Random House, 1984), 195.

[21] Arthur O. Lovejoy, *The Great Chain of Being* [1936] (New York: Harper Torchbooks, 1960), 227f.

the "art of the philosopher consists in adding new links to the separated parts, in order to reduce the distance between them as much as possible."[22]

Another passage from the *Encyclopédie* echoes the same preference for continuity rather than distinction:

> Nature's products are too numerous and too varied; most differ from the others by such insensible nuances that we cannot hope ever to capture them in sentences.... To be convinced of this truth, it is enough to glance at the systematic nomenclatures which have been constructed in natural history: they are all faulty.[23]

But the chemists' struggle with chemical identity was mostly empirical, and toward philosophy chemists remained indifferent, or more precisely entirely unconscious of it. The chemists' pride had long been in their devotion to the laboratory, an emphasis that kept chemistry separate from and independent of the more philosophical traditions of the universities, partially isolating chemical thought from mainstream thought. At best it enabled chemistry to resist the attempted incursions of the mechanical philosophy, and to ignore the species debates of the naturalists as unreal or arbitrary.

Perhaps because of this focus on actual practice, chemists did not write much directly on the question of continuity and discontinuity. Among those who did, the most prominent in the eighteenth century was Pierre-Joseph Macquer, who attempted a system of chemistry based on a set of rules of affinity (see Chapter Eight). His third rule, which Duncan says he inherited from Stahl, reads: "Substances that unite together lose some of their separate properties; and the compounds resulting from their union partake of the properties of the substances which serve as their principles."[24]

Antoine Baumé in his textbook of 1773, tried to have it both ways: a compound was both different from and like its components:

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[22] Lovejoy, *Great Chain of Being*, 232.

[23] *Encyclopédie*, article "Histoire Naturelle," vol. 8, 225a (anonymous). Quotation from Jean-Claude Guédon, *The Still Life of a Transition: Chemistry in the Encyclopédie* (unpublished PhD thesis, University of Wisconsin, 1974), 314-315.

[24] For the details of Macquer's efforts, see Chapter Eight. For the larger context of these problems, see Alistair M. Duncan, *Laws and Order in Eighteenth-Century Chemistry* (Oxford and New York: Clarendon Press, 1996).

> Chemical combination or chemical composition is the union of several heterogeneous bodies from which results a new mixt body which has properties different from and intermediate between the substances which served to form it; it is what Becher and Stahl have denominated *mixtion,* and what we call *chemical combination* or *chemical composition.*[25]

Lavoisier, in his "Reflections on Phlogiston" published in 1786, points out that in Baumé's view of the phlogiston theory, the combination of free fire and the earthy element "can be combined in an infinity of proportions, and that there exists in consequence an infinity of intermediate states between the free fire and the phlogiston properly speaking."[26] Lavoisier clearly recognizes the error of this view of continuous chemical combination, but he does not elaborate or generalize on this point. In his *Traité* of 1789, he focuses chiefly on the empirically based distinction of the neutral salts, whose composition is expressed in terms of the operationally defined simple bodies. But in general he avoids the philosophical analysis.

Richard Watson, in his *Chemical Essays* of the 1780s, also reflects contemporary difficulties with finding ways to recognize distinct chemical identities. In an essay on saline bodies, he writes:

> It may be expected that this disquisition should be commenced by giving a rigid definition of the term salt, or saline substance. But the complex ideas of natural substances are not subject to very definite descriptions, nature in her several productions proceeds by imperceptible gradations, seldom having any decisive marks, by which we can invariably discriminate them into sorts.[27]

Though Watson recognized the need to identify some sort of classification, he finally decides that "we may proceed to one or other of the three following kinds, they are either *acid salts – alkaline salts –* or *neutral salts.*"[28] A reluctant acceptance of an operational identification.

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[25] A. Baumé, *Chymie expérimentales et raisonnée,* 3 vols. (Paris, 1773), vol. 1, 11.

[26] A.-L. Lavoisier, "Reflexions sur le phlogistique," *Mémoires* (Paris, 1783): 508; *Oeuvres de Lavoisier,* vol. 2, 626. DK-45.

[27] R. Watson, "Of Saline Substances," *Chemical Essays,* (London, 1781) vol. 1, 109-110.

[28] Watson, *Chemical Essays,* vol. 1, 112.

Before the appearance of Dalton's theory, the idea of chemical change as discontinuous was one of the most difficult to conceive. The concept of distinct chemical substances was there, but what was missing was the concept that their interactions do not consist of a blending of their properties, that things do *not* shade into one another following chemical change, but that new and distinct chemical bodies are produced. Even Bergman, who considered "any body which differs in properties from every other, and can be always had *similar to itself* ... as a separate and distinct body," apparently used this criterion more as an operational convenience than as a philosophical principle, for he also wrote that "Nature proceeds by insensible gradations; but it is not in our power to follow her closely, being only capable of distinguishing the more remarkable steps."[29]

Perhaps no one countered this chemical philosophy of continuity of properties in chemical change more explicitly than Antoine-François de Fourcroy, the most vigorous advocate of the new chemistry initiated by Lavoisier. In the fifth edition of his popular text, he presented his list of six rules of chemical affinity. His sixth rule was given as follows, a direct and conscious contradiction of Macquer's third rule:

> Two or more bodies, united by the attraction of composition, form a substance whose properties are very different from those of any one of the bodies before their combination.

He further comments,

> Stahl and his followers, whose abilities in other respects have been of much important service to chemistry, have affirmed, that compounds always partake of the properties of the bodies that enter into their composition; and that their properties are intermediate between those of their principles. They have even carried this notion so far, as to imagine that it was possible to conjecture, from the properties of a compound, the nature of the bodies that compose it.[30]

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[29] Bergman, "Of metallic precipitates," *Physical & Chemical Essays,* vol. 2, 374.

[30] A.-F. de Fourcroy, *Elements of Chemistry and Natural History,* 5th edition with notes by John Thomson, 3 vols. (Edinburgh, 1798), vol. 1, 113-114.

One of the most dramatic of his many illustrations of the validity of his rule 6 is given as follows.

> The attraction of composition, has a singular influence on the form. It often happens, that two matters, that are not susceptible of crystallization alone, assume a regular form when they are united, as is the case with the muriatic acid gas, and ammoniac or alkaline gas, which, in the instant of their union, constitute crystals of muriat of ammoniac.[31]

A few years later, in his major lifetime work, he summarized this view as follows. "Compounds formed by chemical attractions, possess new properties different from those of their component parts." By way of elaboration he added

> [C]hemists have long believed the contrary took place.... They thought, in fact, that the compounds possessed properties intermediate between those of their component parts, so that two bodies, very coloured, very sapid or insipid, soluble or insoluble, fusible or infusible, fixed or volatile, assumed, in chemical combination, a shade of colour, or taste, solubility or volatility intermediate between and in some sort composed of, the same properties which were considered in their principles. This is an illusion or error which modern chemistry is highly interested to overthrow.[32]

Like so many clear statements in the chemical literature of this century, this one appears as an explicit verbalization of previous implicit usage rather than as an initiator of something previously unsuspected. Bill Jensen neatly summarized this pattern when he defined a scientific revolution as "the art of making explicit the implicit."[33] The eighteenth century presents many

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[31] Fourcroy, *Elements of Chemistry*, 115.

[32] A.-F. Fourcroy, *A General System of Chemical Knowledge*, translated by William Nicholson, 11 volumes (London, 1804), vol. 1, 102-103. The quotation is taken from William B. Jensen, "Thomas Duché Mitchell and the chemistry of principles," *Bull. Hist. Chem.* 5 (1989), 46.

[33] Jensen, "Thomas Duché Mitchell," 42.

illustrations of this pattern of latent, unconscious usage suddenly becoming conscious in the form of verbal statements of axioms, definitions, or principles. Among these I would immediately list *phlogiston* as a connotation-free word that replaced sulphur, sulphur principle, oily principle, and so forth. Rouelle's definition of the neutral salt about 1750 confirms fifty years of an operationally known but generally unstated relationship. Lavoisier's statement of the principle of conservation of weight is yet another such example, for the literature has many examples of experiments conceived on the assumption of conservation.

In response to a paper by Joseph Gay-Lussac, Humphry Davy in 1816 gave what appears to be a final criticism of chemistry by principles. To the best of my knowledge, explanations by property-principles never show up again:

> I cannot admit M. Gay-Lussac's views on the classification of the undecompounded substances, nor can I adopt his ideas respecting their properties as chemical agents. He considers hydrogen as an *alkalizing* principle, and azote [nitrogen] as an *acidifying* principle. This is an attempt to introduce into chemistry a doctrine of occult qualities, and to refer to some mysterious and inexplicable energy that must depend upon a peculiar corpuscular arrangement. If hydrogen be an alkalizing principle, it is strange that it should form some of the strongest acids by uniting with bodies not in themselves acid; and if azote be an acidifying principle, it is equally strange that it should form nearly nine-tenths of the weight of the volatile alkali. It is impossible to infer what will be the qualities of a compound from the qualities of its constituents; and if M. Gay-Lussac's view were correct, the prussic basis of azote and carbon ought to have its acid properties diminished, and not increased, as he has proved them to be, by combination with hydrogen.[34]

It appears that by 1816, the chemistry of principles is a thing of the past, "a doctrine of occult qualities" no longer appropriate in chemical explana-

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[34] Humphry Davy, "On Some Analogies Between the Undecompounded Substances, and on the Constitution of Acids," *The Collected Works of Sir Humphry Davy*, ed. John Davy, 9 vols. (London: Smith Elder, 1826-1832),vol. 5, 513.

tions. The notion that the properties of an individual chemical species result from "a peculiar corpuscular arrangement" glancingly suggests the influence of Dalton's atomic theory, introduced a few years earlier. In the next chapter we examine the history of the simple body concept and its reception in the years before Dalton's atomic theory about 1810.

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ASSIMILATION AND ANTICIPATION

As described in earlier chapters, three fundamental developments of the eighteenth century reached a climax of visibility and utility in the work of Lavoisier. The recognition of the *materiality of gases* made possible the deliberate introduction of the *conservation of weight* as a fundamental principle in chemical studies. The consequent development of analytical chemistry required the introduction of the *simple body* as the operational concept for expressing chemical composition. Both the conservation of weight and the simple body concept had earlier histories that reached fruition only with the acceptance of gases as ponderable chemical components. All these things reached a happy coalescence in the chemical revolution of the 1780s.

"The revolution is complete," Lavoisier wrote in a letter to his disciple Chaptal in 1791.[1] But how was the chemical world different? Lavoisier, who claimed credit for having created the revolution, was not entirely clear about what he thought he had accomplished, though he spoke most often of the overthrow of phlogiston, and let his new views become known as the anti-phlogistic chemistry. The battles of the revolution had been fought over the utility and the reality of phlogiston as the inflammable principle, but the disappearance of phlogiston was not in itself a very significant event. It was rather Lavoisier's systematic application of the conservation of weight principle that not only made the phlogistic doctrine unnecessary,

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[1] See Henry Guerlac, "The Chemical Revolution: A Word from Monsieur Fourcroy," *Ambix,* 23 (1976): 2.

it also established the correct order of simplicity in the composition of familiar chemical compounds and reactions. Lavoisier did not live long enough to witness or participate in the assimilation of these changes, and he apparently remained unaware of their long-term significance.[2]

In the two decades between Lavoisier's *Traité* and Dalton's *New System of Chemical Philosophy,* we find a conscious effort to accommodate chemical knowledge to a systematic compositional framework. This assimilation was organized through the new nomenclature and the operational concept of simple body. At the same time, there was a great increase in the gathering of quantitative data and attempts to find rational patterns to incorporate them. The results anticipated empirically the laws of constant composition and multiple proportion that reached full rationality in Dalton's atomic theory early in the next century.

Assimilation

Lavoisier's systematic use of the conservation of weight principle inverted the relative simplicities of the metals and their calxes, the combustibles and their products, a compositional reversal of such clarity that the new doctrine was universally called the anti-phlogistic chemistry. Fourcroy, the chief contemporary publicist for the chemical revolution, described its reception thus:

> From 1777 to 1785, in spite of great efforts and numerous memoirs of Lavoisier, he was truly alone in his opinions.... [There was] a sort of neutrality that resisted not so much his discoveries, but the total reversal of the ancient order of ideas.[3]

The committee who reviewed the new nomenclature for the Paris Academy in 1787 had deeply regretted the reversal of traditional simplicity of composition (see Chapter Twelve), but Joseph Black's views are characteristic of those in the 1790s:

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[2] See Robert Siegfried, "The Chemical Revolution in the History of Chemistry," *Osiris* 4 (1988): 34-50.

[3] Quoted from James R. Partington, *A History of Chemistry,* 4 vols. (London: Macmillan, 1962-1970), vol. 3, 488.

> [T]he advantages of a regular and decent nomenclature were so sensible, that this method became very prevalent, and would, in all probability have soon obtained the acquiescence of all the philosophical chemists, had not the science itself experienced, at this very time, a great and almost total revolution.
>
> A number of most important discoveries were made, about this time, by the chemists of Britain, France, and Sweden, relating to the constituent parts of principles of natural substances. New objects have been discovered, which required new names: and some of the substances already known, which had formerly been considered as simple, and perhaps elementary, were now found to be compounded; while others, formerly held as compounds, were now found to be more simple than the substances of which they had been thought to be compounded.[4]

But as long as simple bodies were defined as anything not yet known to be compound, chemists felt it necessary to call their readers' attention to the limited meaning of such a conditional identity. Fourcroy's statement in 1800 is typical:

> When one uses in chemistry the designation "simple substance," it does not mean that the substance is indecomposable. It cannot be claimed that these substances are really simple in themselves, or that they are not formed from elements more simple than themselves....[5]

Thomas Thomson only a little later:

> Simple substances ... signify merely bodies which have not been decompounded, and which no phenomenon hitherto observed indicates to be compounds. Very possibly the bodies which we reckon simple, may be real compounds; but till this has actually been proved, we have no right to suppose it.[6]

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[4] Joseph Black, *Lectures on the Elements of Chemistry,* edited by John Robison, 2 vols. (Edinburgh, 1803), vol. 1, 342-343.

[5] A.-F. de Fourcroy, *Système de connaissances chymiques,* 10 vols., (Paris, 1802), vol. 1, 55.

[6] Thomas Thomson, *A System of Chemistry,* 2nd ed., 4 vols. (Edinburgh, 1804), vol. 1, 16.

The introduction of the simple body was in a sense the final step in the move toward the materialization of chemical composition that we have traced from the early seventeenth century. Though largely unconscious throughout most of the eighteenth century, this move became quite conscious and deliberate with the systematic introduction of the simple body concept in the new nomenclature of the chemical revolution. Metaphysical entities would no longer serve. Chemistry had lost its fumbling adolescence and become a deliberate, self-consciously pursued science.

Too Many Elements

The simple body concept provided an almost universally accepted way of expressing chemical composition, but the conditional assignment of any body as simple carried with it a philosophic discomfort frequently expressed. Nearly every chemical writer of this period who mentioned the idea of elements or simple bodies also took the trouble to emphasize the distinction between simple body and the philosophical element. The conditional nature of simple body that made it operationally useful also allowed the indefinite expansion of their number. Nearly twenty new metals were discovered and identified between 1789 and 1810, raising plaintive cries that there were too many elements, together with the hope that ultimately their numbers would be reduced. In 1796, Nicolas-Louis Vauquelin was almost apologetic in reporting a new simple body from his analysis of the "red lead of Siberia" [lead chromate]:

> In spite of the repugnance which I feel in admitting new simple bodies ... I am nevertheless forced by the large number of new characteristics which this substance enjoys ... to regard it as a metal naturally acidified which has no known analogue.[7]

Charles Hatchett reported in 1802 his discovery of columbium (niobium), and expressed a recurring view that the seemingly endless discovery of new elements would eventually cease.

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[7] N.-L. Vauquelin, "L'Analyse du plomb rouge de Siberie," *Jour. de Mines,* 6 (1797): 737-760, at 749.

> I am inclined to believe, that the time is perhaps not very distant, when some of the newly discovered metals, and other substances, which are now considered as simple, primitive, and distinct bodies, will be found to be compounds. Yet I only entertain and state this opinion as a probability, for, until an advanced state of chemical knowledge shall enable us to compose, or at least to decompose, these bodies, each must be classed and denominated as a substance *sui generis.*[8]

Thus it appears that there was a wide acceptance of the concept of simple body in the recognition of its utility in expressing composition. In spite of the philosophical unease exhibited from the growing number of them, consolation was available in the hope that ultimately there would be only a few.

Search for Order

If chemists perhaps longed for a return to a simpler world of fewer elements than their investigations were revealing, they were going to be disappointed. But if simplicity seemed increasingly unlikely as new elements continued to be discovered, the next best thing may be order, and that is what they finally received from the atomic theory of John Dalton. Meanwhile the ever busy chemical experimenters sought for order in the new numerical data generated by quantitative analyses.

From the time of Newton's lawful universe in the seventeenth century, the ideal order was implicitly held to be mathematical. When Venel in his article in the *Encyclopédie* called for a revolution in chemistry, he hoped that the revolution he called for would place the science at least in the same rank as "mathematical physics."[9] Lavoisier, thirty years later and approaching the completion of his revolution, could see more clearly than Venel the

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[8] Charles Hatchett, "An Analysis of a Mineral Substance from North America Containing a Metal Hitherto Unknown," *Phil. Trans.* 92 (1802): 49-66, at 65. For a more extended discussion of the problem of "too many elements," see Robert Siegfried and Betty Jo Dobbs, "Composition, a Neglected Aspect of the Chemical Revolution," *Ann. Sci.* 24 (1968): 275-293.

[9] "Chymie" in the *Encyclopédie,* vol. 3, 409-410. Quoted by Jerry Gough, "Some Early References to Revolutions in Chemistry," *Ambix,* 29 (1982): 106-109.

possibility of a mathematized chemistry. In one of the papers in a series of very important papers written after the discovery of the composition of water and before his *Traité,* he expressed the thought that:

> Perhaps some day the precision of data will lead to the point that a geometer can calculate in his study the phenomena of any chemical combination, in the same manner that he calculates the movement of the celestial bodies.[10]

Although it was Dalton's atomic hypothesis that first achieved the idealized goal of a true chemical calculus, the effort to acquire the requisite "precision of data" called for by Lavoisier had made substantial progress before 1808. Indeed without that accumulation of the empirical data, Dalton's hypothesis would have carried no persuasion at all in a climate still dominated by an inductivist epistemology.

Quantitative determinations of composition were not unknown before Lavoisier's introduction of the conservation of weight principle. But they were occasional, and accurate findings were confined chiefly to the analysis of minerals that had no gaseous components. During the 1770s and 1780s quantitative compositions began to be widely achieved for all natural bodies. This goal was largely made visible by the improved techniques in the handling of gases, whose gravitational participation in chemical reactions had been previously overlooked. Indeed Lavoisier's lonely battle against phlogiston had been fought chiefly on the basis of quantitative arguments, thus providing the gaseous complement to the quantitative analyses of solid mineral bodies in Sweden and Germany. Now that all participants of chemical change could be quantitatively accounted for, it was possible to think in terms of a true chemical calculus like that envisioned by Lavoisier. But the required "precision of data" for an empirical mathematical ordering of chemistry proved hard to come by.

Though chemical composition was now expressible in quantitative terms of materially real simple bodies, the values by which composition was ex-

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[10] A.-L. Lavoisier, "Mémoire sur l'affinité du principe oxygène avec les différentes substances auxquelles il est susceptible de s'unir," *Oeuvres de Lavoisier,* vol. 2, 546-556, at 550. [DK-72.]

pressed were determined entirely by the skill of the analyst. Every new and distinct chemical body was an unknown adventure to the chemist intrepid enough to undertake its analysis. There were no general laws of composition to guide his inquiries, and none to discipline his results. The quantitative values of analysis of one body bore no known relationship to those of any other body. When one chemist's results differed from those of another, who was to say which was more accurate?

Slowly, empirical patterns began to appear which would probably have eventually led to descriptive laws of chemical composition. But before the tedious empirical route to general order could be debated, argued, and reconfirmed to a level of community agreement, John Dalton's atomic hypothesis provided a surprising shortcut to the idealized goal of a true chemical calculus, "without passing through subordinate stages of painful inductive ascent."[11]

The intellectual tradition of this period was still very much what has come to be called "Baconian inductivist," that laws of nature must come from the accumulation of factual details. Hypothesis was still a dirty word essentially equivalent to idle speculation. This was particularly so in the chemical tradition, which had a long history of experimental practice. The dangers of speculation had recently been reinforced by the events of the chemical revolution, in the course of which phlogiston had been shown to have no real existence. Lavoisier, who had brought about the chemical revolution by the overthrow of imaginary phlogiston, had warned of the dangers of not disciplining our thoughts by facts:

> Imagination ... which is ever wandering beyond the bounds of truth, joined to self-love and that self-confidence we are so apt to indulge, prompt us to draw conclusions which are not immediately derived from facts; so that we become in some measure interested in deceiving ourselves.... We must trust to nothing but facts: These are presented to us by Nature, and cannot deceive.[12]

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[11] A comment by John Frederick William Herschel in *A Preliminary Discourse on the Study of Natural Philosophy* [1830] (New York & London: Johnson Reprint Corporation, 1966), 305.

[12] A.-L. Lavoisier, *Elements of Chemistry,* translated by Robert Kerr (Edinburgh, 1790); (New York: Dover paperback, 1965), Preface, xvii-xviii.

Later he made the danger of hypothesis explicit when he wrote

> The notion of four elements, which, by the variety of their proportions, compose all the known substances in nature, is a mere hypothesis, assumed long before the first principles of experimental philosophy or of chemistry had any existence. In those days, without possessing facts, they framed systems; while we, who have collected facts, seem determined to reject them, when they do not agree with our prejudices.[13]

From this critique, Lavoisier moved on to a rejection of any claim about the nature and number of the elements as being

> entirely of a metaphysical nature. The subject only furnishes us with indefinite problems, which may be solved in a thousand different ways, not one of which, in all probability, is consistent with nature. I shall therefore only add upon this subject, that if, by the term *elements,* we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable we know nothing at all about them.[14]

This passage led him directly to his introduction of the concept of simple body as any body not yet shown to be compound, thus establishing chemical composition on the experimentally defined component.

What stronger guidance could the chemical community receive than that from the actual architect of the chemical revolution? But Lavoisier was only reinforcing what was already strongly embedded implicitly in the empirical chemical tradition generally. Indeed, the eighteenth-century movement toward material composition outlined in earlier chapters had by the 1750s progressed to the point that phlogiston had become the sole nonmaterial component still left in the chemical literature. Lavoisier's elimination of phlogiston, that last remnant of the Paracelsian chemistry, helped elevate the habit of experiment into a more conscious Baconian philosophy.

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[13] Lavoisier, *Elements,* xxii.

[14] Lavoisier, *Elements,* xxiv.

The Empirical Tradition

Until near the end of the eighteenth century, analytical chemistry as a distinct activity did not exist. There were no general methods of analysis: analytical techniques and procedures were reported only insofar as they applied to the specific analysis being described, and every analyst was very much on his own, devising his approaches as intuition and experience would suggest. Every new body of unknown composition was a potential adventure into unknown territory.

There were, of course, numerous tests for the presence of particularly well-known bodies, the oak galls test for the presence of iron being perhaps the most familiar. Most of these, as well as most analyses, were only qualitative, the identification of the particular acid and the particular base being standard for the recognition of a neutral salt. By the late 1760s when Lavoisier began his career, this kind of analysis had become familiar. His analysis of gypsum ($CaSO_4 \cdot 2H_2O$) in 1765 is characteristic:

> All salts are composed of two parts, of an acid and of a base. To assure myself that the acid of gypsum was that of vitriol, as I naturally presumed it to be, I placed in a small crucible some calcined *pierre spéculaire* along with some powdered charcoal. As soon as the material became red, the cover of the crucible became surrounded by a small blue flame. When the lid was removed, the surface of the material was seen to be covered with the same flame, and a slight odor of the volatile sulfurous acid could be detected. When the mixture so calcined had cooled, I added some acid to it. Immediately there was disengaged the odor of rotten eggs so that it was easy to identify the presence of liver of sulphur. I remade the same mixture of plaster and of charcoal; in adding to it some fixed alkali, there resulted a true liver of sulphur.

To the chemical reader of that day this evidence was sufficient to confirm the presence of the vitriolic acid in the gypsum.

To determine the nature of the base, Lavoisier added to a solution of the gypsum some concentrated fixed alkali, drop by drop. "Immediately the vitriolic acid left its base to unite with the fixed alkali and form with it vitriolated tartar [potassium sulfate]. The solution became turbid and a white precipitate formed, which when washed proved to be a very pure calcareous earth similar to chalk. It was reduced to quicklime by calcination."[15] This was Lavoisier's first published paper, read to the Academy in February of 1765.

Note that Lavoisier's analysis is more a confirmation of what he already had good reason to believe than a true analysis. The test for the vitriolic acid involves a long-familiar procedure of heating a vitriol with charcoal to produce the sulfide, which formed the true liver of sulphur (potassium sulfide) when treated with alkali. The reduction of the sulfate by means of charcoal was the initial procedure in Geoffroy's synthesis of sulfur from the vitriolic acid in 1704 (see Chapter Four). The synthesis was completed when acid was added to the product of the original calcination, precipitating the sulfur as a "magistry." Lavoisier chose to add alkali rather than acid, and use the formation of the liver of sulphur as confirmation of vitriolic acid in the original salt.

His identification of the base, like that of the acid, depended upon the formation of a derivative product whose identity was made by the recognition of familiar properties. All this was familiar procedure by this time, illustrating the rather *ad hoc* selection of reactions to be carried out for the qualitative identification of the proximate components of a neutral salt.

Some quantitative experiments had been done and quantitative results attempted. For example, Homberg's effort to determine the amount of "solid acid" in his acid spirits was probably motivated by a recognized need for quantitative relationships (see Chapter Four). Black's recognition of the weight-quantity of fixed air in the *magnesia alba* is a more successful example. But until the importance of gases in chemical behavior was widely recognized, and the techniques for handling them were developed in the years after 1760, quantitative composition could hardly be attempted in a detailed systematic way. It is true, of course, that quantitative work was being done extensively in the larger social and economic areas, chiefly to be seen in the so-called industrial revolution.[16]

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[15] A.-L. Lavoisier, "Analyse du gypse," (DK-1), *Oeuvres de Lavoisier,* vol. 3, 111-127.

[16] Archibald Clow & Nan L. Clow have described areas of economic and technical development relating to gains in chemical comprehension of the seventeenth and eighteenth centuries in *The Chemical Revolution* (London: The Batchworth Press, 1952). Their title has an unconventional meaning.

Once gases were recognized as important in chemical reactions, they were immediately handled in quantitative ways, most conveniently through the measurement of their volumes and densities. Henry Cavendish was apparently the first to measure the densities of gases, as he did with inflammable air (hydrogen) and fixed air (carbon dioxide) in 1766.

Though quantitative assays of mineral ores had been common for centuries as an economic necessity of mining interests, these had not been directed to the analyses of anything but the desired metal, the other constituents of the ore being generally neglected. It is not surprising, however, that the first attempt to organize analytical procedures came from Sweden, a country rich in mineral resources and long involved in the metallurgical arts. Ferenc Szabadváry credits Torbern Bergman with the first efforts to create a systematic analytical science, as well as with calling attention to the distinction between the qualitative and quantitative branches of analysis. Through the 1770s and until his death in 1784, much of Bergman's researches were directed toward this end. Though he did not complete a textbook of analysis, his published researches collected as *Opuscules Physica et Chemica* from 1779, "give a methodical summary of the processes of analytical chemistry grouped according to the nature of the substance analysed." It was Bergman "who gave [chemical analysis] the status of a separate branch of science—Analytical Chemistry."[17]

It is interesting that one of Bergman's most successful quantitative analyses was to determine the relative quantity of phlogiston in the metals. But as it was based on the weight equivalents of metallic exchanges, all of Bergman's phlogistic-oriented data could be easily converted by Lavoisier into the weight units of oxygen required to calcine the different metals (see Chapter Ten).

Whether one takes Bergman's or Lavoisier's perspective, the modern reader can easily interpret these data as equivalent weights of the metals. But neither Bergman nor Lavoisier made any effort to give them the organizational advantages such a conscious conception provides. Significant progress was made in that direction through the experimental, empirical

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[17] Ferenc Szabadváry, *A History of Analytical Chemistry* (London & New York: Pergamon Press, 1966), 71.

work in the 1790s before the appearance of the atomic theory early in the next century.

Chemical Equivalents

Like so many other chemical concepts in the eighteenth century, the idea of chemical equivalents has a long implicit history before it became explicit in the work of Jeremias Benjamin Richter in the 1790s; and again the evidence lies chiefly in the empirical work on the neutral salts. Chemists of the seventeenth century were aware that acids and alkalies annihilated one another, and Boyle's introduction of vegetable indicators became one of the more popular ways of demonstrating when these opposite bodies had saturated one another. From the beginning of the eighteenth century, chemists had some concern for quantitative relationships, but in the absence of well-defined material components, no systematic work was possible. Homberg in 1699 had attempted to determine how much "solid acid" was in his acid solutions by neutralizing a measured quantity of alkali and determining the increase in weight (Chapter Four). The validity of the experiment depended upon not only the implicit assumption of the conservation of weight, but also on the presumption that every distinct chemical entity had a characteristic composition. Rouelle's work on neutral salts at mid-century likewise presumed that constancy of composition principle that allowed him to distinguish between neutral and acid salts and the recognition of neutrality.

From the early 1780s, many chemists were engaged in efforts to determine with greater accuracy the quantitative compositions of various chemical bodies, chiefly the neutral salts. These were especially appealing because of their easy synthesis from acids and bases and the recognition of a point of saturation. These investigations were largely motivated by the hope that they might lead to the discovery of general relationships that would give chemical composition more systematic generality.

Henry Cavendish, in an investigation of the water of Rathbone Place in 1767, speaks of using "as much fixed alcali, as was equivalent to 46 & 8/10 grains of calcarous earth, *i.e.* which would saturate as much acid."[18]

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[18] Quoted by Partington, *History of Chemistry,* vol. 3, 320.

Although the idea of chemical equivalent is quite explicit here and the word itself actually used, Cavendish did not elaborate or attempt to generate a lawful generality.

Richard Kirwan in 1781 and in 1782 undertook his analyses under the belief that the values could provide a measure of the affinity of an acid for different bases. He reported his analytical values in the form of a table. The following example is offered to illustrate the argument and the difficulty in the conception.[19]

Quantity of basis taken up
by 100 grains of the mineral acids

	Mineral alkali	Calcareous earth	Volatile alkali
Vitriolic acid	165	110	90
Nitrous acid	165	96	87
Marine acid	158	89	79

Kirwan interpreted these data to mean, for example, that vitriolic acid had a greater affinity for the mineral alkali than for either the calcareous earth or the volatile alkali, because it attracted a greater weight of it. That acid also had a greater affinity for each of these bases than did either of the other acids. In general, "the quantity of each basis, requisite to saturate a given quantity of each acid, is directly as the affinity of such acid to each basis." This identification of the strength of chemical affinity of acids with the weight of base combined was a common view well into the next century. This is surprising in the face of the fact that a simple reversal of the argument leads easily to obvious contradictions. For example, let us recalculate Kirwan's data to show the amount of each acid necessary to saturate 100 grains of the given bases.

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[19] Data taken from Partington, *History of Chemistry,* vol. 3, 665. My account of the "Foundations of Stoichiometry" owes much to this volume, chapter 14.

Quantity of acid taken up by 100 grains of each base
(Calculated from data in table on page 225)

	Vitriolic acid	Nitrous acid	Marine acid
Mineral alkali	61	61	63
Calcareous earth	91	104	112
Volatile alkali	111	112	126

Using the same reasoning as in the first representation, it could be said from this that the volatile alkali has the greatest affinity for the marine acid and the least for the vitriolic acid. But the interpretation from the earlier arrangement was that the vitriolic acid had a greater affinity for the volatile alkali than did the marine acid. This seems to mean that the greater the affinity of an acid for a base, the lesser the affinity of that same base for that acid. To confirm this strange conclusion, Kirwan earlier stated that "the quantity of real acid necessary to saturate a given weight of each basis, is *inversely* as the affinity of each basis to such acid." But this anomaly later became more significant in the reception of Berthollet's similarly-based study of affinity early in the next century.

The century-long focus of theoretical attention on affinity led much of the analytical chemistry at the end of the eighteenth century to interpret these quantitative data as measures of affinity, as we have illustrated with Richard Kirwan's work. But the lack of systematic analytical techniques and general rules of quantitative analysis left every analyst vulnerable to challenge by others with different results.

Among the workers attempting to find numerical order in the growing body of empirical analytical data without prior commitment to affinity measures, Jeremias Benjamin Richter (1762–1807) was the most successful. Partington characterizes his work as being "permeated with the idea ... that chemistry is a branch of applied mathematics."[20] Among other contributions we owe him the dubious honor of coining the word "stoichiometry,"

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[20] Partington, *History of Chemistry*, vol. 3, 675.

which has tied the tongue of nearly every freshman chemist. Most of his calculations depended upon what became known as the "law of neutrality." Richter observed that when solutions of calcium acetate and potassium tartrate are mixed, with the consequent precipitation of calcium tartrate, the residual solution of potassium acetate is still neutral. Since this is a familiar double exchange type of reaction in which the two bases trade their acid partners, the neutrality of the residual solution indicates that the acids and bases were present in equivalent quantities. Further experience gave Richter justification to state a general law that

> when two neutral solution are mixed, and decomposition follows, the new resulting products are almost without exception also neutral; the elements must, therefore, have among themselves a certain fixed ratio of mass.[21]

Though this concept is implicit in the works of Guyton de Morveau, Kirwan, Wenzel, Bergman, and Lavoisier, among others, Richter was the first to give it an explicit statement. But he was so determined to find mathematical order among these empirically obtained values that he more often arranged them to show some progressive numerical sequence than to illustrate chemical equivalence, sometimes adjusting the values to better fit his Pythagorean fantasies. Richter's data were given a direct representation of equivalent weights by another German chemist, Ernst Gottfried Fischer, along with "a clear summary of Richter's views, which he says were practically unknown even in Germany." (See Fig. 4, p. 228.)

> The meaning of this table is the following: if a substance is taken from one of the two columns, say potash from the first, to which corresponds the number 1605, the numbers in the other column indicate the quantity of each acid necessary to neutralise 1605 parts of potash.... If a substance is taken from the second column, the numbers in the first column show how much of each of the substances in this column will be necessary for its neutralisation.[22]

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[21] Partington, *History of Chemistry,* 676.

[22] Ernst Gottfried Fischer, taken from Partington, *History of Chemistry,* 678-679.

BASES		ACIDS	
		Fluoric	427
Alumina	525		
		Carbonic	577
Magnesia	615		
Ammonia	672		
		Sebacic	706
		Muriatic	712
		Oxalic	755
Lime	793		
Soda	859		
		Phosphoric	979
		Formic	988
		Sulphuric	1000
		Succinic	1209
Strontia	1329		
		Nitric	1405
		Acetic	1480
Potash	1605		
		Citric	1683
		Tartaric	1694
Baryta	2222		

Fig. 4. Fischer's Table of Equivalents.

Fischer's table, published in 1803 as an accompaniment to his translation of Berthollet's *Recherches sur les lois de l'affinité,* finally gave these data an appropriate conception. However, a comparison of the values in this table will show that they significantly deviate from those calculated from modern atomic weights, indicating the lack of analytic reliability. They also differ considerably from those of earlier workers. Analytical chemistry was still very much in its infancy.

Definite Proportions or Fixed Composition

The idea that every chemical body had a definite or fixed composition is another concept with a long history of implicit usage that becomes explicit only near the end of the eighteenth century. If composition is not a fixed value for each distinct chemical entity, there is hardly any point in attempting quantitative values for its ingredients. Georg Ernst Stahl spoke of a *pondus naturae* of bodies in combination, and G-.F. Rouelle in his mid-century studies of neutral salts clearly recognized that acids added to alkalies beyond the point of saturation merely acidified the solution without changing the composition of the neutral salts. Rouelle's pupil, Venel, writing in the *Encyclopédie,* claimed that it was "a dogma of eternal truth" that "compounds (*mixtes*) are composed of definite and invariable proportions of their constituents."[23] Of course Lavoisier's work that destroyed the phlogistic doctrine was firmly based on quantitative data that established the composition of the products of combustion, the phosphoric and carbonic acids, the composition of fixed air and of water. But again the idea of a fixed composition characteristic of each of these compounds is still implicit.

There does not seem to have been any challenge to this unspoken assumption, any more than there was any verbal affirmation. The point was hardly alive before the practice of quantitative analysis became widely practiced during the last couple of decades of the century. As we have earlier seen, chemical analysis in the 1790s was still not reliable enough to make a convincing case for any empirical law of quantitative relationship. In the face of nearly unreproducible results and the general inability to reach community-wide agreement on the composition of any particular body, chemists were allowed room to wonder if perhaps composition was *not* a fixed and definitive property. There was, after all, the really old tradition that chemical combination involved the blending of properties, as if chemical change was no different than the mixing of two liquids. We can illustrate how these evidences were viewed by looking no farther than to Lavoisier himself in his paper of 1783, "On the affinity of the oxygen principle with different substances to which it is capable of combining."[24]

While Lavoisier was perfecting a new chemistry in the 1780s, he felt obliged to offer an account of the affinities of various substances with oxygen whose properties and behavior dominated his antiphlogistic doctrine. Early in the paper he speaks of the shortcomings of the traditional tables of affin-

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[23] Venel, "Mixte et mixtion," in *Encyclopédie,* vol. 10 (1765), 585-588, cited by Henry Guerlac, "Quantification in chemistry," *Isis* 52 (1961): 202.

[24] Lavoisier, "Sur l'affinité du principe oxygène," *Oeuvres de Lavoisier,* vol. 2, 546-556.

ity, mentioning that affinities are different under different conditions, and pointing out that Bergman had divided the tables into two parts, presenting the different behavior of bodies in the wet and the dry ways. Nor did the tables take into account the effects of the attraction of water of solutions, and perhaps of its decomposition; water was regarded as passive, but it acts with a real and disturbing force, Lavoisier said, and this also ought to be accounted for.

> A third imperfection of the tables of affinity is that they cannot express the variation in the force of attraction of the molecules of bodies by reason of the different degrees of saturation. There are certain combinations for which there are two or three degrees of distinct saturation: others for which there are an even greater number; the formation of acids furnishes a large number of examples, and it will not be useless to pause here a moment.[25]

He then cites the sulfurous and sulfuric acids, as differing in the amount of oxygen they contain, with no combination lying between them; the muriatic acid and the oxymuriatic acid [chlorine] similarly exhibit different degrees of saturation with oxygen. But

> nitrous air is capable of holding with the oxygen principle, not only two degrees, but an infinity of degrees of saturation, resulting in an infinity of different nitrous acids, from that called dephlogisticated, and which is white and without color, to that which is the most red and smokey.[26]

He admits that the criticism that he has just presented would apply also to the tables he is offering in this memoir. But they are worth presenting anyway,

> at least until these experiences are extended, and the application of a calculus to chemistry places us in a state of extending our views. Perhaps some day the precision of data will lead to the point that a

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[25] "Sur l'affinité du principe oxygène," *Oeuvres de Lavoisier,* 548-549.

[26] "Sur l'affinité du principe oxygène," *Oeuvres de Lavoisier,* 550.

> geometer can calculate in his study the phenomena of any chemical combination, in the same manner that he calculates the movement of the celestial bodies.[27]

Lavoisier's ambiguity in offering on the one hand a hope for a calculus of chemical composition and, on the other, empirical evidence contradictory to such a calculus, accurately represents the fundamental problems of chemical organization at the end of the eighteenth century. The difficulties in the way of achieving chemical order were indeed great, but the hope of doing so is even greater.

The trend was definitely toward the principle of fixed composition, but the empirical evidence in its support was still unreliable and allowed room for the doubts of the honest sceptic. Credit is usually given to Joseph-Louis Proust for bringing the law of definite proportions into the continuing consciousness of the chemical community. Proust thought his data justified the assumption of fixed composition and took it as a firm operating principle, very much as Lavoisier had assumed the conservation principle as an axiom. For example, Proust claimed that the quantity of copper oxide prepared from copper carbonate was always the same whatever process used, and that every chemical entity was characterized by a fixed composition.

> If 100 parts of this carbonate, dissolved in nitric acid and separated by the alkaline carbonates, gives us 100 parts of artificial carbonate, and if the base of these two combinations is the black oxide, we must recognize that invisible hand which holds the balance for us in the formulation of compounds and fashions properties according to its will. We must conclude that nature operates not otherwise in the depths of the world than at its surface or in the hands of man. These ever-invariable proportions, these constant attributes, which characterize true compounds of art or of nature, in a word, this *pondus naturae* so well seen by Stahl; all this, I say, is no more at the power of the chemist than the law of election which presides at all combinations. From these considerations is it not right to believe that the native carbonate of copper

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[27] "Sur l'affinité du principe oxygène," *Oeuvre de Lavoisier,* 550.

> will never differ from that which art produces in its imitation? Is there actually any difference between native carbonate of soda and the natural? No. Why, therefore, should there be any difference between those of copper or of other metals when no other perturbing cause has disarranged the reciprocal forces of the factors of these combinations?[28]

Proust recognized the existence of two series of copper salts, each illustrating the pattern of constant composition. Yet his analytical skills were not good enough to reveal the two-to-one weight ratios between the corresponding salts in each series that would have revealed the law of multiple proportions. Although Proust offered a lot of evidence that supported his belief in the concept of fixed or definite proportions in chemical composition, he could not marshall the hard facts adequate for unchallenged belief. A law of fixed composition would establish order for the analytical science, but the variable experimental results continued to allow the possibility that composition was not necessarily constant.

This empirical tradition was challenged toward the end of the century by the theoretical work of Claude Louis Berthollet. Like many chemists of the eighteenth century, he saw affinity as properly investigated in the context of Newtonian forces between the chemical particles. Berthollet believed that chemical affinity was determined not only by the intrinsic chemical forces, but also by the "chemical masses" of the reacting bodies, a view that would also lead to variable composition of chemical compounds.[29]

Because Berthollet considered chemical affinity to be a form of universal gravitation, the shapes of the interaction particles would be significant at the short distances of chemical action, as they were not at astronomical distances. In addition, the idea of universal attraction meant that affinities would not be satisfied or saturated by a single combination, but would be variable according to the quantities of all the material there. He thus arrived at the concept of "chemical mass," which modified the conventional

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[28] J.L. Proust, "Researches on copper [1799], quoted in Henry M. Leicester and Herbert S. Klickstein, *A Source Book in Chemistry 1400–1900* (New York: McGraw-Hill, 1952), 203-204.

[29] See Arnold Thackray, *Atoms and Powers* (Cambridge, Massachusetts: Harvard University Press, 1970), especially Chapter Seven on "Quantified Chemistry," 199-203.

chemical affinity so that the composition of the product of chemical combination would be dependent upon the relative quantities of the reactants. Berthollet recognized that in some distinct cases, composition was fixed, but he saw these as limits determined by external causes such as insolubility or gaseous escape of one or another of the products. Between these limits reacting bodies might combine in all proportions. All this and more was extensively laid out in his *Essai de statique chimique* in 1803.

Berthollet insisted that his results supported the idea of variable composition, whose values depended upon the condition under which the reactions took place. Of special significance were the relative concentrations of the reactants. When he made these kinds of claims for the oxide of copper, Proust responded by claiming that Berthollet was expressing the composition of different *mixtures* of the two copper oxides whose fixed composition he had determined.

Berthollet's theory actually challenged Proust's basic rule of definite proportion, which was the cause of the debate, but the empirical evidence of both sides was inadequate to resolve the dispute. "The controversy was more important by what it suggested than by what it accomplished. Henceforth, it became imperative to seek a clear understanding of the causes underlying the apparent fact of constant proportions."[30]

Most chemists at that time would hardly have found Berthollet's view of variable composition a welcome idea, but even the acceptable (and empirically derived) chemical rules, such as definite proportions, needed a rational justification. Dalton's atomic theory in 1808, like that of Berthollet, came from outside the mainstream of the empirical chemical story that this account has been following, but it produced so functional a rationale for the explicit laws of chemical composition, that the whole dispute regarding definite or indefinite composition became moot.

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[30] Satish Kapoor, "Berthollet, Proust, and Proportions," *Chymia* 10 (1965): 53-110, at 108.

14

JOHN DALTON AND THE CHEMICAL ATOMIC THEORY

WHAT A BODY is made of, its qualitative composition, had been a central concern of chemistry from antiquity. After the chemical revolution, which established the rules of quantitative analysis, it became possible and desirable to determine not only what a body was made of, but how much there was of each of its components. Two principles newly introduced during the chemical revolution made this transformation possible: (1) the operational element, or simple body as it was then called; (2) the systematic application of the conservation of weight principle to all quantitative chemical work.

As seen in the previous chapter, these principles combined to create the science of analytical chemistry and the beginnings of the tedious search for quantitative chemical laws. It is now worth recalling Lavoisier's hope, expressed in 1783, quoted in the last chapter:

> Perhaps some day the precision of data will lead to the point that a geometer can calculate in his study the phenomena of any chemical combination, in the same manner that he calculates the movement of the celestial bodies.[1]

As analytical techniques continued to improve, empirical data might eventually have reached a level of precision and reliability sufficient to ful-

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[1] A.-L. Lavoisier, "Mémoire sur l'affinité du principe oxygène avec les différentes substances auxquelles il est susceptible de s'unir," [DK-72], *Oeuvres de Lavoisier* (Paris: Imprimerie Impériale, 1864), vol. 2, 546-556, at 550.

fill Lavoisier's expectations. Indeed some evidence suggests that this had begun to happen. As described in the last chapter, J.L. Proust before the end of the century had proclaimed fixed composition to be "an invariable law," but his experimental data did not firmly confirm that claim. Nor would his data have revealed the related law of multiple proportions. As will be seen, it was Dalton's atomic theory that intellectually created these quantitative relationships that were confirmed empirically only after his work was published. The achievement of these relationships by analytical improvements alone would have been tedious. But such a "painful inductive ascent," as John William Herschel later characterized it,[2] was made unnecessary by the appearance of Dalton's atomic theory, whose symbolic representations made obvious the patterns of compositional laws. The law of multiple proportions, so obvious from Dalton's atomic representations, was especially effective in gaining the attention of chemists for his theory.

Dalton's assumption that all ponderable matter is made of indestructible atoms carries with it the obvious consequence that whatever rearrangements these atoms may undergo, their total weight will not change, a theoretical equivalent to Lavoisier's axiomatic principle of the conservation of weight in chemical change. By assigning a characteristic weight to each kind of atom, and a different combination of atoms to each chemical compound, the principles of fixed composition and multiple proportions likewise became rational consequences of a simple theory. Expressed in atomic weight units and visualized by simple atomic symbols, these compositional relationships were so clearly seen that they became the standards to which empirical analyses were required to conform. Dalton expressed this clearly when he wrote that a knowledge of atomic weights would serve "to assist and to guide future investigations, and to correct their results."[3]

Ultimately, Dalton's theory completely transformed chemical composition, from a chaos of unorganized empirical knowledge into a highly rational science centered on the concept of atomic weight. The particular values

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[2] John Frederick William Herschel, *A Preliminary Discourse on the Study of Natural Philosophy* [1830], facsimile edition with introduction by Michael Partridge (New York & London: Johnson Reprint Corporation, 1966), 305.

[3] John Dalton, *A New System of Chemical Philosophy* [Manchester, 1808], facsimile edition (London: William Dawson, 1953), vol. 1, 213.

of those weights have been refined, but the basic compositional concepts of Dalton's early representation have been neither superceded nor seriously modified. Every symbol, every formula, and every equation we see today is a testament to the utility of Dalton's organization of chemical composition by atomic weights. Although the potential for this atomic organization of chemistry was immediately sensed, agreement on a uniform set of atomic weights took a half century to achieve; and the debate over the reality of the atom would not die away until the early twentieth century.[4]

Background to the Atomic Theory:
Incipient Atomism

As an intellectual enterprise, atomism is almost as old as philosophy. It lost out in antiquity to the more fully developed system of Aristotle, which dominated Western thought well into the eighteenth century. Atomism was revived in the seventeenth century and became a part of the new mechanical philosophy of Descartes, Boyle, and Newton. In spite of their serious efforts, Robert Boyle and the English Newtonians failed to make chemistry into a mechanical science, and experimental chemical practice continued on its empirical way unguided by atomic conceptions. The chief benefit chemistry derived from its coexistence with the mechanical philosophy was an increase in the sense of the materiality of chemical identity that the language of atomism and mechanics fostered. For everyone became, if not a mechanist or an atomist, nevertheless something of a particularist, at least in the manner of their speaking. From the time of the revival of atomism in the seventeenth century, chemical writers increasingly found it useful to speak of particles of matter as taking part in combinations or separations, but without either counting them or assigning them explicit properties. While matter was assumed to be made of particles, attention was invariably

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[4] W.H. Brock and D.M. Knight, "The Atomic Debates," *Isis* 56 (1965): 5-25; W.H. Brock, ed., *The Atomic Debates* (Leicester: University of Leicester Press, 1967). A more extended study can be found in Alan J. Rocke, *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro* (Columbus, Ohio: Ohio State University Press, 1984).

focused on the total assemblage, not on the particles themselves. There was no successfully developed theory.[5]

The closer followers of Newton took up serious efforts to deal with the forces between the unseen particles, and though their efforts continued with great loyalty to the Newtonian ideal, none produced much of utility for chemistry. Nor did these efforts form a progressive step on which John Dalton later built his successful chemical atomic theory. Dalton owed little to anyone other than Newton himself, and here probably less than he thought.

In spite of the apparent acceptance of the particulate nature of solid matter, the imponderable fluids of heat, magnetism, and electricity of Newtonian tradition were still indispensable instruments of discussion. In chemistry, phlogiston and the matter of heat, later called caloric, were typically treated as continuous fluids. John Dalton, who finally made the atomic idea functional for chemistry, continued to utilize heat or caloric as a fluid atmosphere that surrounded each atomic particle in the gaseous state. Though he did speak of the caloric as having particles, he always treated those particles collectively, never as discrete entities as he did the atomic particles of ponderable matter. Hence, early in the nineteenth century the vocabularies of both particulate and continuous views of matter remained in simultaneous usage.

Dalton was the first to give atomism a pictorial representation, and much of his success is due to this fact. Symbols had been used to designate *substances* for many centuries, but with Dalton the symbols represented individual atoms and a fixed unit of weight uniquely characteristic of that element. In a very real sense, this quantization of weight is the first such in modern science, and it led in a marvelously simple sequence to the concept of the quantized electric charge through the work of Faraday and the subsequent identification of the electron by J.J. Thomson late in the nineteenth century. It also led William Prout in 1815 to conceive the weight of the hydrogen atom as the single, idealized atomic weight quantum. These

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[5] Arnold Thackray, *Atoms and Powers: An Essay on Newtonian Matter-Theory and the Development of Chemistry* (Cambridge, Massachusetts: Harvard University Press, 1970).

ideas stimulated much research in the nineteenth century, and ultimately attained the status of reality early in the twentieth with the identification of the proton and neutron, and the isotopic conception of atomic weights.

Origin of Dalton's Theory

The origin of Dalton's chemical atomic theory has been much discussed since its very creation, but without leading to a final agreement among historians.[6] The general view has been that Dalton conceived his atomic theory without being much influenced by the writings of the many chemists of the late eighteenth century who were struggling to find ways of establishing quantitative chemical relationships, especially equivalents and affinities. In the last chapter we saw some of these from Richter, Berthollet, and Fischer. Much of this theoretical work was based on mental explorations of the nature of atomism derived largely from Newton.

In 1961 Henry Guerlac again raised the question. He summarized its history as follows.

> Scholars are virtually agreed that when John Dalton was developing his chemical atomic theory, between 1803 and 1805, he was probably ignorant of Richter's work on chemical equivalents. Yet it must have been by Richter's method, or a very similar method, that Dalton computed his first table of "atomic" weights using a set of combining weights determined, for the most part, by the analyses of other chemists. It may prove a useful exercise in historical method to examine the evidence both for and against this accepted view of Dalton's early ignorance of Richter.[7]

A number of publications have followed Guerlac's renewal of the ex-

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[6] In offering my version of the origin of Dalton's theory, I have generally followed the similarly titled account by Leonard Nash, "The Origin of Dalton's Chemical Atomic Theory," *Isis* 47 (1956): 101-116, and Arnold Thackray, "The Origin of Dalton's Chemical Atomic Theory: Daltonian Doubts Resolved," *Isis* 57 (1966): 35-55.

[7] Henry Guerlac, "Some Daltonian Doubts," *Isis* 52 (1961): 544-554. At 544.

ploration of the origin of Dalton's atomic theory.[8] In the following account, I generally accept the version given by Leonard Nash, reinforcing this from my own examination of Dalton's writings.

The idea of a quantum of weight, a concept of discontinuity, was entirely new in chemistry when Dalton wrote his first small table of atomic weights in 1803 along with crude symbols to represent each atomic weight unit. Though we know Dalton's atomic theory as intimately associated with chemistry, it originated in his wrestling with problems in meteorology, the evaporation and condensation of water, the behavior of mixed gases generally, and their thermal behavior. In his efforts to solve these problems, he created a mechanical model of the gaseous state based on that of Isaac Newton. In particular, Dalton took his model from Proposition XXIII of Part II of the *Principia Mathematica,* where Newton demonstrates by geometrical argument that if the particles of an air (or, in Dalton's terms, a gas) repel one another with a force inversely proportional to the distance of their separation, their resultant behavior is identical with Boyle's law. Such a demonstration assumed that the particles of the gas were all of the same size and in contiguous contact with one another, thereby filling all the space available. In Newton's time, air was the only gas known, and it was reasonable to assume that the similar particles were all of the same size. It was only in the 1770s that natural philosophers recognized that the atmosphere was a mixture, chiefly of nitrogen and oxygen, with a little fixed air and variable amounts of water vapor. Priestley and other pneumatic chemists had established that its composition, water vapor apart, was essentially constant; samples collected from balloon ascents, mountain tops, and

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[8] A representative, but not complete, sequence is: Robert Siegfried, "More Daltonian Doubts," *Isis* 54 (1963): 480-481; Thackray, "The Origin of Dalton's Theory," 35-55; Henry Guerlac, "The Background to Dalton's Atomic Theory," in *John Dalton & the Progress of Science,* ed. D.S.L. Cardwell (Manchester: Manchester University Press, 1968), 57-91; Seymour Mauskopf, "Haüy's Model of Chemical Equivalence: Daltonian Doubts Exhumed," *Ambix* 17 (1970): 182-191; Robin S. Fleming, "Newton, Gases and Daltonian Chemistry: The Foundations of Combination in Definite Proportions," *Ann. Sci.* 32 (1974): 561-574; Theron Cole, Jr., "Dalton, Mixed Gases, and the Origin of the Chemical Atomic Theory," *Ambix* 25 (1978): 117-130.

seashores provided evidence that the different gases were uniformly mixed in the atmosphere.

In its simplest presentation, Dalton's problem was to explain how it was that the different gases of the atmosphere, whose densities were not identical, were yet found uniformly mixed. In a lecture at the Royal Institution in London in 1810, Dalton pointed out that "Dr. Priestley, who discovered this compound nature of the atmosphere, ... 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."[9] This question hardly makes sense to us today unless we first remind ourselves that the eighteenth-century view of gases was a static one, where the particles were thought to be more or less adjacent to one another, and held apart by heat, which was generally credited as the cause of the expansion of all bodies. After about 1780, the heat was given a more specific identity as a subtle fluid called caloric, the matter of heat.

Toward the end of the eighteenth century, the uniform composition of the atmosphere was attributed to a weakly combined compound of the two main gases, which in turn dissolved the water vapor by a very weak affinity. This view was little more than an analogue of the familiar behavior of aqueous solutions that involved a weak force of attraction between the water and the soluble salt. There was a limit to the amount of water vapor that could dissolve in the atmosphere even as there was a saturation point for the salt in water. That the attraction of solution was weaker than ordinary chemical attraction was evidenced by the fact that the salt was easily obtained from the solution even as the water was easily obtained again from the atmosphere by cooling. But it was this weak attraction of solution that kept the different gases and the water uniformly mixed in the atmosphere. The solution analogy also implies the idea that up to the point of saturation, chemical combination is a continuous thing: any amount up to that limit can be incorporated. Thus the solution model of gaseous mixtures implies a continuous composition, a point of view that we have earlier seen

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[9] Dalton's lecture is printed in Henry E. Roscoe and Arthur Harden, *A New View of the Origin of Dalton's Atomic Theory* [London, 1896], facsimile reprint (New York: Johnson Reprint Corporation, 1960), 13-18, at 14.

was a most difficult one for chemists to abandon; the prevalence of the undeveloped solution theory of gaseous mixtures thus contributed to the maintenance of the traditional view of chemical change as continuous.

Writers before Dalton, though speaking of ultimate parts, generally treated a substance in a collective sense; gases were treated as continuous fluids as if their particles were dissolved in that ultimate fluid, caloric. Dalton, on the other hand, from the very beginnings of his atomic speculation described the atoms as individually distinct; each particle was viewed as surrounded by its own atmosphere of the caloric fluid. He emphasized their separateness with diagrams in his writings and in his many public lectures.

At the Royal Institution in 1810, Dalton described how he tested the prevailing chemical explanation of the uniform distribution of the atmospheric gases. Note the implicit assumption of simple combinations of only two or three particles in a new association:

> 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 [nitrogen], brought them together, and threw around them an atmosphere of heat, as per diagram; I repeated the operation, but soon found that the watery particles were exhausted (for they make but a small part of the atmosphere). 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.[10]

In combining the atoms on a one-to-one-to-one basis, Dalton assumed a numerical simplicity of combination. It is more important to note that the compound atom, as Dalton later called such combinations, was a distinct entity with its own atmosphere of caloric. Roscoe and Harden do not provide the diagram Dalton refers to, but from the context it was probably

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[10] Roscoe and Harden, *A New View*, 14-15. A useful anthology of Dalton's "unpublished" papers and letters is Arnold Thackray, *John Dalton: Critical Assessments of His Life and Science* (Cambridge, Massachusetts: Harvard University Press, 1972).

like that below (Fig. 5) from his *New System of Chemical Philosophy*, Part II, Appendix.

The effectiveness of Dalton's diagrams was later certified by Thomas Thomson, Dalton's first and perhaps most loyal publicist:

> It was this happy idea of representing the atoms and constitution of bodies by symbols that gave Mr. Dalton's opinions so much clearness. I was delighted with the new light which immediately struck my mind, and saw at a glance the immense importance of such a theory, when fully developed.[11]

In the elaborate mental experiment described above, Dalton arrived at the conclusion that these triple and double compounds also ought to tend to settle into layers with the heaviest on the bottom, even when each of the compound particles was surrounded with heat. "In 1801 I hit upon an

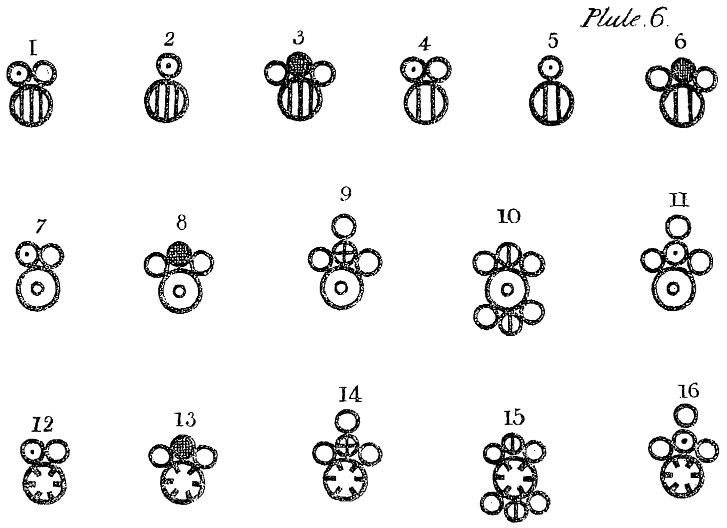

Fig. 5. Dalton Diagrams of Compound Molecules.

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[11] Thomas Thomson, *The History of Chemistry*, 2 vols. [London, 1830-1831] (New York: Arno Press Reprint, 1975), vol. 2, 291.

hypothesis which completely obviated these difficulties."[12] In this, his first model of mixed gases, he assumed that atoms repelled only those atoms like themselves, but had no interaction with atoms of a different kind. This view not only accounted for the uniform distribution of mixed gases, but it also implied the law of partial pressures, which Dalton published in the *Memoirs of the Manchester Literary & Philosophical Society* in 1802. At about this same time, William Henry enunciated his law of gaseous solubility, that the solubility of a gas in water was entirely a function of the pressure of that gas alone at the interface of liquid and gas. Here was another relationship in which a gas acted totally independently of other gases present, thus supporting Dalton's first model that gaseous particles repelled only those like themselves.

Inspired by Henry's work, Dalton spent much time in early 1803 measuring solubilities of various gases; the results of this work he published in the memoir "On the Absorption of Gases by Water and Other Liquids."[13] If his model of the gaseous state was correct, it would seem to follow that all gases at the same pressure would be equally soluble, but this was not what he had found, and Dalton was moved to ask, "Why does water not admit its bulk of every gas alike?" The pursuit of an answer led him to "an inquiry into the relative weights of the ultimate particles of bodies ... a subject, as far as I know, entirely new."[14] He had noted a rough correlation between solubility and the specific gravity of the gas: the least soluble of the gases appeared to be elements or very simple compounds—oxygen, hydrogen, azotic gas (nitrogen), and carbonic oxide (carbon monoxide). "I am nearly persuaded," he wrote, "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."[15] In order to test this purely mechanical hypothesis, Dalton needed information about the different weights of the ultimate particles that the physical properties

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[12] Roscoe and Harden, *A New View,* 15.

[13] John Dalton, "On the Absorption of Gases by Water and Other Liquids," *Memoirs of the Manchester Literary & Philosophical Society* 6 (1805): 271-287.

[14] Dalton, "Absorption of Gases," 286.

[15] Dalton, "Absorption of Gases," 286.

could not give him. He was thus forced to seek the information from chemical data.

In a notebook entry of 1803, Dalton recorded the first list of the relative weights of the ultimate particles of several well-known elements and compounds. These values were obviously calculated from known chemical analyses by applying a few rules of simplicity. Starting with Lavoisier's reported analysis of water as being 15 percent hydrogen and 85 percent oxygen, Dalton assumed that the "compound atom" of water consisted of one atom of each element. Because hydrogen was the lightest known of all gases, Dalton took its atomic weight to be unity, leading to a value of 5.66 for oxygen. Similar calculations from other chemical analyses led to the value of 4 for nitrogen (azote) and 4.5 for carbon. The weights of other compound atoms or molecules could be calculated from these initial four values.

Hydrogen	1
Oxygen	5.66
Azote	4
Carbon (Charcoal)	4.5
Water	6.66
Ammonia	5
Nitrous gas	9.66
Nitrous oxide	13.66
Nitric acid	15.32
Sulphur	17
Sulphureous acid	22.66
Sulphuric acid	28.32
Carbonic acid	15.8
Oxide of carbone	10.2

Fig. 6. Dalton's Table of Atomic Weights.[16]

Dalton's synthesis of the weights of the compound bodies from the weights of their atoms makes the pattern of multiple proportions quite

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[16] Roscoe and Harden, *A New View,* 28-29.

evident in these results. But that pattern is inescapably obvious when symbolized in a table that appeared on the following page of his notebook.

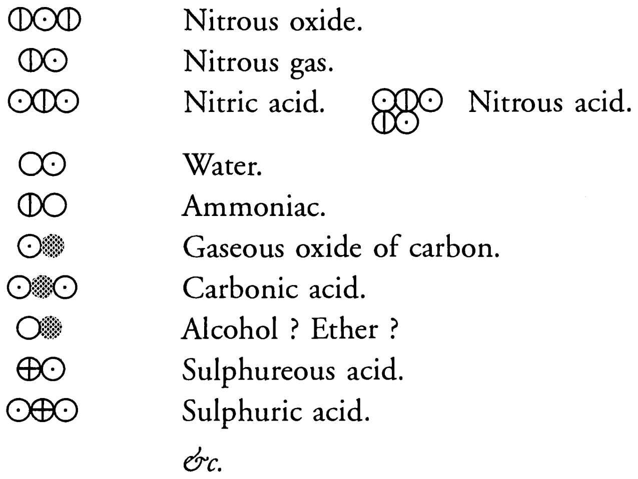

Fig. 7. From p. 249 of Dalton's Notebooks.

Looking only at the first two diagrams in the list, each containing one atom of oxygen, it is obvious that since there are twice as many atoms of nitrogen in nitrous oxide as there are in nitrous gas, there will be twice the weight of nitrogen for the same weight of oxygen. If empirical evidence could be found to confirm that pattern of multiple proportions, the theory would receive impressive support. Dalton found or perhaps created the evidence for two such examples, but did not publish them. As we shall see, public confirmation came shortly before the publication of the Part I of his *New System of Chemical Philosophy* in 1808.

Though Dalton had made these early estimates of relative atomic weights from chemical data, the foundation of his interests was still the physical nature of the gaseous state, and he soon became discontented with his first model of mixed gases according to which particles repelled only particles like themselves. "This hypothesis, however beautiful might be its application, had some improbable features," he recalled retrospectively in 1810. These included the necessity for as many different kinds of repulsive forces as there were different kinds of gaseous atoms. It also meant the abandonment of heat as the general cause of repulsion, a long tradition not easily given up. Moreover, such a model would produce a very rapid diffusion of one gas into another, a process that Dalton had himself demonstrated to be a very slow one.[17]

His account of 1810 gives the sequence and arguments that led to a second model of mixed gases:

> 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, 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 sizes pressing against each other.
>
> 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. Hence the suggestion 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.*[18]

Dalton's best explanation of how unequally sized particles would not reach a stable equilibrium occurs in Part II p. 548, of *A New System*, accompanying the diagram in our Fig. 8, facing page.

> Fig. 4 [in Dalton's plate] is the representation of four particles of azote with their elastic atmospheres, marked by rays emanating from the solid central atom; these rays being exactly alike in all the four particles, can meet each other, and maintain an equilibrium.

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[17] Roscoe and Harden, *A New View of the Origin of Dalton's Atomic Theory*, 16. Taken from a lecture Dalton gave at the Royal Institution in London in 1810.

[18] Roscoe and Harden, *A New View*, 16-17.

> Fig. 5 [in Dalton's plate] represents two atoms of hydrogen drawn in due proportions to those of azote, and coming in contact with them; it is obvious that the atoms of hydrogen can apply one to the other with facility, but can not apply to those of azote, by reason of the rays not meeting each other in like circumstances; hence, the cause of the intestine motion which takes place on the mixture of elastic fluids, till the exterior particles come to press on something solid.

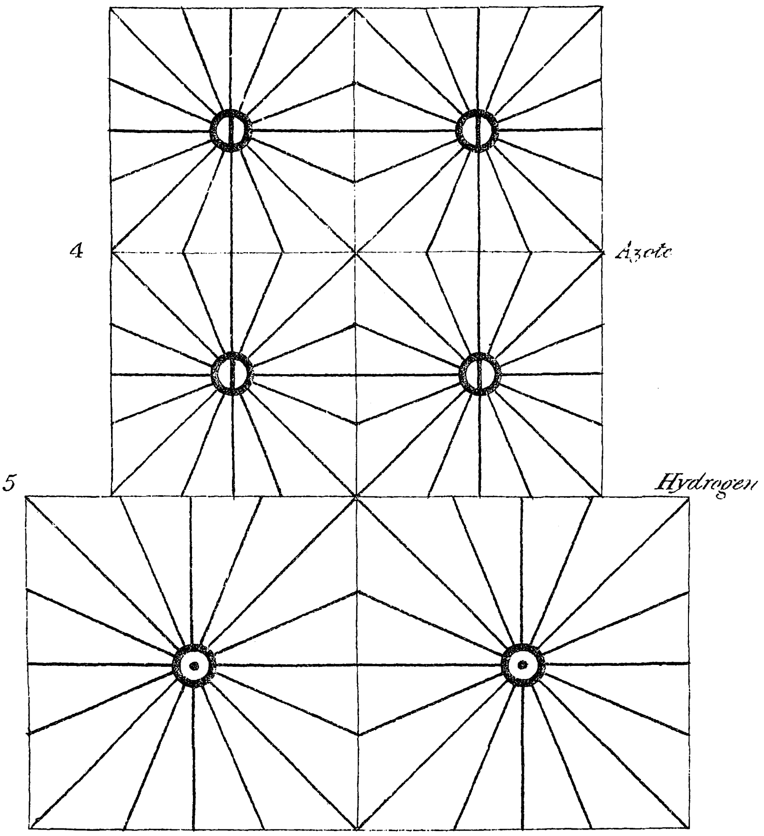

Fig. 8. Dalton's Models of Nitrogen and Hydrogen Atoms.

In the lower diagram, Dalton's use of both the square atoms and their rays appear to be entirely rhetorical devices, being a visual metaphor for his statement that "no equilibrium can be established by particles of unequal sizes pressing against each other." We have no evidence of what more persuasive conception lay behind this totally inadequate justification for the view that different atoms had different volumes. It was one of his most stubbornly held views, however, and one that forced him later into intractable opposition to Avogadro's hypothesis. But it led him into the fruitful investigation of the *weights* of the atoms, as the following quotation from his historical account of 1810 makes clear.

> 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 combination of gases, and to the *number* of atoms entering into such combinations.... 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.[19]

Thus we see that Dalton's original motivation for the calculation of atomic weights was to obtain sizes of the atoms as a test for his second theory for the explanation of the uniform mixing of gases. From 1805, however, he increasingly recognized the significance of atomic weights for chemistry, and by 1808 he published Part I of his *New System of Chemical Philosophy*, in which he was able to lay out the chemical virtues of his atomic theory. The most significant residue from his second theory of mixed gases was that gases could *not* have molecules of the same size. This position is in direct contradiction to Avogadro's principle, which states that equal volumes of different gases contain the same number of molecules. When that principle first appeared in 1811, Dalton immediately and forever denied its validity.

Chemistry of THE NEW SYSTEM OF CHEMICAL PHILOSOPHY

Part I of Dalton's *New System*, published in 1808, is almost entirely devoted

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[19] Roscoe and Harden, *A New View*, 17.

to a summary and elaboration of his own earlier work and thoughts on heat and the nature of gases. Chemistry as such is confined to a brief chapter (six pages) ending Part I. The book was continued in Part II, which appeared separately in 1810, with a systematic presentation of descriptive chemistry arranged in order of increasing complexity. A third part finally appeared in 1827, with the promise of yet another that never appeared.

The chapter at the end of Part I, brief as it is, contains the fundamental concepts and rules on which Dalton's deserved reputation is based. In these six pages, under the title "On Chemical Synthesis," Dalton expressed the benefits of determining atomic weights this way:

> 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 shew 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.*[20]

Dalton went on to explain how these weights can be obtained. It is clear that if one knew the number of atoms in the molecule of a compound, the relative weights of the different atoms could be calculated from the empirically measured composition. Dalton's procedure was to provide a set of rules of simplicity by which the formula could be reasonably assumed.

> 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

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[20] Dalton, *A New System of Chemical Philosophy,* 212-213.

must be presumed 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.

5th. A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients.

6th. A *ternary* compound should be specifically heavier than the mixture of a binary and a simple, which would, if combined, constitute it; &c.

7th. The above rules and observations equally apply, when two bodies, such as C and D, D and E &c. are combined.

From the application of these rules, to the chemical facts already well ascertained, we deduce the following conclusions: 1st. That water is a binary compound of hydrogen and oxygen, and the relative weights of the two elementary atoms are as 1:7, nearly; 2nd. That ammonia is a binary compound of hydrogen and azote [nitrogen], and the relative weights of the two atoms are as 1:5, nearly; 3d. That nitrous gas is a binary compound of azote and oxygen, the atoms of which weigh 5 and 7 respectively; that nitric acid is a binary or ternary compound according as it is derived, and consists of one atom of azote and two of oxygen, together weighing 19; that nitrous oxide is a compound similar to nitric acid, and consists of one atom of oxygen and two of azote, weighing 17; that nitrous acid is a binary compound of nitric acid and nitrous gas, weighing 31; that oxynitric acid is a binary compound of nitric acid and oxygen weighing 26; 4th. That carbonic oxide is a binary compound, consisting of one atom of charcoal, and one of oxygen, together weighing nearly 12; that carbonic acid is a ternary compound, (but sometimes binary) consisting of one atom of charcoal, and two of oxygen, weighing 19; &c. &c. In all these cases the weights are expressed in atoms of hydrogen, each of which is denoted by unity.[21]

And so on, through ever larger numbers of combinations. Knowing from Lavoisier that water was 15 percent hydrogen by weight and 85 percent oxygen, Dalton assumed water to be a one-to-one atomic combination, modern formula HO. Because hydrogen was the lightest gaseous element, he assigned its atoms a weight of one, with the result that oxygen would have a weight of 5.66 ($\frac{85}{15}$). By applying similar procedures to the known composition of other compounds, Dalton was able to prepare a complete list of atomic weights of the known simple bodies and the atomic composition of many of the better known compounds.

The first part of Dalton's book provided very few examples of compositions expressed in atomic formulas. Nor did he elaborate on his claim, quoted above, that from "the relative weights of the ultimate particles or atoms of the bodies ... their number and weight in various other compounds would appear, in order to assist and to guide future investigations, and to correct their results."[22] The evidence confirming the real usefulness of Dalton's conception of atomic weights was first provided by other more experienced chemists.

Reception of Dalton's Atomic Theory

Prior to the publication of the *New System of Chemical Philosophy* in 1808, Dalton's considerable reputation was based on his fundamental work on the behavior of gases. His atomic theory had received some publicity by Thomas Thomson in the third edition of his popular introductory text, *A System of Chemistry,* in 1807. Thomson gives what he calls "a short sketch" in a section devoted to the affinity of gases. Like Dalton, he presents the theory synthetically, using Dalton's symbols to construct and represent the compound atoms. Probably because the theory is introduced in the context of gases, Thomson always refers to the "density" of the atoms rather than

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[21] Dalton, *A New System of Chemical Philosophy,* 214-215.

[22] Dalton, *A New System of Chemical Philosophy,* 213.

their weight. Though his account is faithful to Dalton's own theory, he does not generalize beyond the illustrative data of his examples. The closest he comes to awareness of the law of multiple proportions lies at the end of the section on the combination of solids with one another. He presents a table of relative atomic "densities" of acids and bases, which, he points out, because they are "independent of the hypothesis of Dalton, they must be considered as approaching, as nearly as the present state of the science will admit, to the real weight of acids and bases which saturate each other respectively, and form neutral salts." In other words, it is a table of equivalent weights, which he calls "densities."

> The density of an atom of the neutral salt formed by the combination of these bodies, is obtained by adding together the numbers expressing the density of an atom of the acid and of the base.

In speaking of those salts known to contain an excess of either an acid or of a base, though exhibiting fixed composition, Thomson wrote

> The simplest way of considering those bodies is, to conceive the supersalts to be compounded of two atoms of acid with one of the base, and the subsalts of two atoms of base with one of acid. Thus supersulphate of potash is composed of one atom of potash united to two of sulphuric acid, or by weight of 33 parts of base and 54 of acid.[23]

Since the values in this table are taken from analytical experience, Thomson in effect is predicting the composition of the superacid by the rationale of the atomic theory, but he offers no evidence that the predicted compositions are confirmed by analysis. Early in the next year, however, Thomson delivered a paper on oxalic acid to the Royal Society. The oxalate of potash, he noted, "combines with an excess of acid, and forms a superoxalate.... The acid contained in this salt is very nearly double of what is contained in oxalate of potash. Suppose 100 part of potash; if the weight of acid necessary to convert this quantity into oxalate be x, then $2x$ will convert it into superoxalate." Later he notes "that there are two oxalates of

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[23] Thomas Thomson, *A System of Chemistry*, 3rd ed. (Edinburgh, 1807), 676.

strontian.... It is remarkable that the first contains just double the proportion of base contained in the second."[24]

Though Thomson cautiously refrained from generalizing the observed relationship, William Wollaston, who read a paper immediately following Thomson, was more forthright:

> 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, I thought it not unlikely that this law might obtain generally in such compounds and it was my design to have pursued this 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, 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.[25]

A few months after these papers were delivered by Thomson and Wollaston, Part I of Dalton's *New System of Chemical Philosophy* was published, in June of 1808. Dalton's own assessment of its importance was given in a prospectus published the month before: "The third chapter is

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[24] *Phil. Trans.* 98 (1808): 63; reprinted in *Foundations of the Atomic Theory* (Edinburgh: Alembic Club Reprints, 1899), 41. Note that doubt has been cast upon the experimental basis of Thomson's deduction. See Mel Usselman, "Multiple Combining Proportions: the Experimental Evidence," in *Instruments and Experimentation in the History of Chemistry,* eds. Frederic L. Holmes and Trevor H. Levere (Cambridge, Massachusetts: MIT Press, 2000), 243-262, at 254-258.

[25] William Hyde Wollaston, "On Super-Acid and Sub-Acid Salts," *Phil. Trans.* 98 (1808): 96-102. Quoted in Henry M. Leicester and Herbert S. Klickstein, *A Source Book in Chemistry 1400–1900* (New York: McGraw-Hill, 1952), 221-222.

on Chemical Synthesis; and tends to place the whole science of Chemistry upon a new, and more simple, basis than it has been upon heretofore."[26]

Although atoms are not mentioned in the brief prospectus, chemical atomism is the basis of Dalton's *New System,* in which the third chapter clearly "tends to place the whole science of Chemistry upon a new, and more simple basis." It is interesting that the "new" atomic chemistry does not occur in Dalton's book until the third chapter, which occupies less than ten percent of Part I. Chapter One is chiefly focused on heat and gases, and Chapter Two on the three states of matter. As we have already seen, the third chapter presents his method for determining the relative weights of the atoms, with the promise that from

> the relative weights of the ultimate particles or atoms ... their number and weight in various other compounds would appear, in order to assist and to guide future investigations, and to correct their results.[27]

Two years later, with the publication of Part II of *A New System,* his chemical atomism was essentially complete. Earlier that same year, 1810, when concluding his course of twenty lectures at the Royal Institution, Dalton had not lost confidence in the fundamental significance of his theory:

> I shall now return to comparative retirement, in order to prosecute the train of enquiry and investigation which I have briefly developed in the late lectures; the results, I am confident, will be found of importance; and will contribute to establish that beautiful and simple theory of chemical synthesis and analysis which I have adopted from a conviction of its application to the general phenomena of chemistry, and which will in due time, I am persuaded, be made the basis of all chemical reasoning respecting the absolute *quantities* and the *proportions* of all elementary principles, whether simple or compound.[28]

By expressing the composition of a body in terms of quantized weight

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[26] See photocopy of the Prospectus in Roy Neville, "Unrecorded Daltonia," *Ambix* 8 (1960): 42-45, at 42.

[27] Dalton, *A New System of Chemical Philosophy,* 212.

[28] Roscoe and Harden, *A New View,* 122-123. Dalton's emphasis.

units characteristic of each element (atomic weights), Dalton provided the basis for a simple mathematical organization for all chemistry. Once a set of atomic weights could be agreed upon, the whole body of chemical compositions could be established in a systematic and unifying way. The composition of every compound could be shown to have a definite numerical relationship with that of every other compound through their common association with a table of atomic weights. The advantage of this kind of organization was immediately sensed, and the chemical community began the task of establishing the list of atomic weights on which such an attractive potentiality depended.

Jöns Jakob Berzelius had recognized the wonderful opportunity offered by this kind of calculus even before he had read Dalton's own work. Reading in the researches of Richter he "was impressed by the light which I found there on the composition of salts and the precipitation of metals by each other.... It follows ... that by means of good analyses of several salts, one could calculate precisely the compositions of all the others."[29] After gaining a full knowledge of Dalton's work, Berzelius recognized that such calculations could be made for all chemistry.

No one saw more clearly than Berzelius did that achieving such a chemical calculus depended upon establishing with great precision the atomic weights of a few key elements as standards from which others could be calculated. And no one undertook the task more urgently and successfully.

> I came to think that Dalton's numbers lacked that accuracy which is necessary for the practical application of his theory. I realized that above all it is necessary to determine with maximum accuracy atomic weights of the majority of elements; otherwise it can hardly be expected that the dawn of chemical theory will develop into long-awaited day. At that time this was the most important task of chemical research and I devoted myself to this entirely.[30]

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[29] J.J. Berzelius, *Traité de chimie* (Paris, 1831), as quoted by C.A. Russell, "Berzelius and the Development of the Atomic Theory," in Cardwell, *Dalton & the Progress of Science,* 262.

[30] J.J. Berzelius, *Lehrbuch der Chemie* (Dresden and Leipzig, 1845), quoted by Yu.I. Solov'ev and L.P. Petrov, "Russian Scientists on Dalton's Atomic Theory," in Cardwell, *Dalton & the Progress of Science,* 300.

Almost single-handedly, Berzelius established standards of precision for chemical analysis from which atomic, or equivalent weights or proportions, could be reliably determined. Often new techniques had to be devised and new apparatus created. Since there were no supply houses for chemically pure materials, starting materials had to be prepared with particular attention to purity. In 1814, 1818, and 1827 he published tables of atomic weights of the elements and their compounds. In the table of 1818 Berzelius reported values for 45 of the 49 known elements, 39 of these having been determined by his own analyses and the other six by his pupils.[31] But whether these values represented a true atomic weight, or some integral multiple of it, was debated vigorously for the next half century before Stanislao Cannizzaro was able to establish a generally accepted solution to the difficulties. We will return briefly to this matter below.

Although Dalton's idea of expressing composition by discrete weight units unique to each element was quickly adopted by most members of the chemical community, philosophical opposition was quick and vigorous. As we saw in the previous chapter, France's leading chemist, Claude-Louis Berthollet, had opposed the doctrine of definite proportions as advocated by Joseph-Louis Proust in the late eighteenth and early nineteenth centuries, even before Dalton's theory had become publicly available. Berthollet's theoretical position, that the composition of compounds could vary between fixed limiting values, must have seemed the very antithesis of the mathematical order so long desired. Though treated with respect and admiration for their intellectual qualities, his views were very little adopted, and after Dalton's work revealed the pattern of multiple proportion, Berthollet's doctrine of indefinite composition quietly disappeared in the rush to establish a reliable set of atomic weights.

It is a pleasant irony of history that Berthollet was influential in making Dalton's views known in France, through arranging for the translation of the third edition of Thomson's *System of Chemistry* in 1809, and the sixth edition of William Henry's *Elements of Experimental Chemistry* in 1812.

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[31] Russell, "Berzelius and the Development of Atomic Theory," Cardwell, *Dalton & the Progress of Science,* 259-273.

Both these works contained extensive descriptions of Dalton's theory, and it was not long before French texts were recording composition in atomic weight units, whether they were called atomic weights, equivalents, or proportions.[32]

We have seen how Dalton's idea of quantized units of weight was quickly accepted and its virtues recognized. But serious reservations about Dalton's philosophical foundation were expressed by nearly everyone. Few had doubts that matter was made of atoms, but it was widely believed with Lavoisier that we know nothing at all about the atoms themselves. All this was neatly summed up by Berthollet when he wrote: "We know bodies only by the effects which they produce by their action, but nothing in this action can inform us of the distinct properties of their ultimate atoms."[33] Henry's *Elements of Experimental Chemistry* also warned the reader that Dalton's theory "cannot at present be regarded in any other light than that of an hypothesis" (i.e., a guess). And Dalton's rule of simplicity was "a gratuitous assumption."[34] As unfashionable as it had become to get involved in conjectures, it was even worse to take them for truth, as Dalton was frequently accused of doing. Berzelius wrote to the translator of Henry's text that Dalton "seeks everywhere to model nature according to his own hypothesis."[35] Henri-François Gaultier de Claubry's response was shock, "that a man of Dalton's ability should have been so carried away by his own theory that he had tried to make experience fit his theory, rather than modify his theory in the light of experimental evidence."[36]

No chemist was more consistent than Humphry Davy in maintaining the distinction between the useful parts of Dalton's theory and the conjectural. Davy's opinion echoed that of Berzelius when he wrote

> Dalton is too much of an *Atomic Philosopher;* and in making atoms arrange themselves according to his own hypothesis, he has often

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[32] M.P. Crosland, "The First Reception of Dalton's Atomic Theory in France," in Cardwell, *Dalton & the Progress of Science,* 274-289.

[33] Crosland in Cardwell, *Dalton & the Progress of Science,* 280.

[34] Crosland in Cardwell, *Dalton & the Progress of Science,* 281 and 282.

[35] Crosland in Cardwell, *Dalton & the Progess of Science,* 287, note 37.

[36] Crosland in Cardwell, *Dalton & the Progress of Science,* 282, paraphrasing Gaultier de Chaubry in a letter to Berzelius.

> indulged in vain speculation; and the essential and truly useful part of his doctrine, the expression of the quantities in which bodies combine, is perfectly independent of any views respecting the ultimate nature either of matter or its elements.[37]

This view was characteristic of the time. Davy and most of his colleagues fervently believed that the only hypotheses (in our sense of that word) justified in science were those induced directly from the factual evidence, and there was no evidence from which the nature of the invisible atoms could be directly inferred. But almost all chemists began expressing compositions by simple numbers of quantized elemental weights, and they recognized the validity of the laws of definite and multiple proportions. But they either rejected the reality of the atoms outright, or expressed great doubts that the weights being used bore any knowable relationship to the atoms themselves. Many chemists sustained their doubts by avoiding the word atom in their chemical discourses; Davy used the word proportions, Wollaston equivalents, and Berzelius for some time used volumes, to designate the fixed quantities of the elements that made up the composition of compounds.

It is interesting to note that Dalton's atomic theory had no means of confirming the existence of the atoms it assumed. How ironic that the theory of phlogiston was rejected largely because there was no observable evidence that phlogiston existed! How was it, then, that Dalton's theory became accepted when there was no direct evidence that atoms existed? The answer must surely be simply that it worked so extremely well in providing a rational, and quantitative, organization of chemical constitution.

Dalton's atomic concept not only created and illuminated the numerical relations of composition; it also created the possibility of molecular structure. Dalton himself defended his use of circular symbols for his atoms against the literal symbols of Berzelius because the circles allowed spatial representation. Berzelius' symbols, he wrote,

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[37] Humphry Davy, from an unfinished dialogue written in 1820 while in Italy. Parts of this were included by John Davy, editor of his brother's *Collected Works,* 9 vols. (London, 1839-1840), in a footnote to Humphry's Bakerian lecture of 1810. *Works,* vol. 5, 330.

> appear like a chaos of atoms. Why not put them together in some sort of order? Is not the *allocation* a subject of investigation as well as the weight? If one order is found more consistent than another, why not adopt it till a better is found.[38]

But the potentiality of molecular structure could not be successfully pursued until the atomic weights were reliably established and the number of atoms in the molecules could be reliably known. This was not accomplished until fifty years later, by Stanislao Cannizzaro, through a rigorous application of Avogadro's hypothesis first published in 1811. Since this long complex story does not involve any change in the compositional concepts introduced by Dalton, it is appropriate to offer only a brief account.[39]

Avogadro's principle derived directly from the law of combining volumes first stated in 1808. Joseph Louis Gay-Lussac having observed, as others had before him, that two volumes of hydrogen required just one volume of oxygen for its complete combustion, undertook a systematic study of many reactions that involved only or chiefly gases. In summary of his experiments he wrote that the volumes of "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."[40] He failed, however, to draw the conclusion about the molecular constituency of the gases that the Italian physicist/chemist Amedeo Avogadro found almost inescapable:

> 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

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[38] Letter to Thomas Graham, as quoted by William Charles Henry, *Memoirs of the Life and Scientific Researches of John Dalton* (London: Cavendish Society, 1854), 124.

[39] Extended accounts can be found in John Hedley Brooke, "Avogadro's hypothesis and its fate: a case-study in the failure of case-studies," *Hist. Sci.* 19 (1981): 255-273; and by Nicolas Fisher, "Avogadro, the chemists, and historians of chemistry," *Hist. Sci.* 20 (1982): 77-102, 212-231.

[40] Joseph Louis Gay-Lussac, "Memoir on the combination of gaseous substances with each other," [1809]. Quoted in Leicester and Klickstein, *Source Book in Chemistry,* 298. See M.P. Crosland, "The origins of Gay-Lussac's law of combining volumes," *Ann. Sci.* 17 (1961): 1-26.

> its components. But the quantitative proportions of substances in compounds seem only to depend on the relative number of molecules which combine, and on the number of composite molecules which result. It must be admitted then 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 gases is always the same for equal volumes, or always proportional to the volumes.

Avogadro recognized the significance of this principle for the determination of atomic weights as his paper's title makes clear: "Essay on a Manner of Determining the Relative Masses of the Elementary Molecules, and the Proportions in which They Enter into these Compounds."[41]

> Setting out from this hypothesis, it is apparent that we have the means of determining very easily the relative 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.[42]

In this paper and in several later publications, Avogadro calculated the formulas of many compounds by this method. In 1814, André-Marie Ampère stated the same principle, though without acknowledging Avogadro's earlier statement. Subsequent writers attributed this principle more often to Ampère than to Avogadro. In spite of its ready availability and the recognition by some that it offered a solution to the atomic weight/formula problem, the principle was generally ignored or rejected by chemists for fifty years. Once a set of atomic weights was established, after 1860, it became possible to invent realistic structural formulas, and modern organic chemical synthesis began its explosive career.

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[41] Leicester and Klickstein, *Source Book in Chemistry*, 232.

[42] Leicester and Klickstein, *Source Book in Chemistry*, 233.

Historians have been much exercised to explain this half-century delay in the recognition of the application of Avogadro's principle for the solution of the atomic weight problem. It is not a part of this story to attempt a deeper explanation here, but it is appropriate to ask in a general way if anyone could have done earlier what Cannizzaro did about 1860. For our purposes it is sufficient to offer two very broad general circumstances within which the many detailed factors may be subsumed.

First, it is important to recognize that the problem was intrinsically difficult. Chemistry is, after all, the science of the particular, and by the early nineteenth century, when the atomic theory appeared, chemistry already had a lot of particulars to deal with. The atomic theory gave hope for the organization of those details into rational arithmetic patterns. But every effort to solve the atomic weight problem produced particular exceptions, the anomalous gas densities of mercury, sulfur, and phosphorus being most disturbing to the application of Avogadro's principle. Newly discovered relationships, such as Mitcherlich's law of isomorphism and the Dulong and Petit law of specific heats, created small areas of coherence but also brought new problems of accommodation with what had already been determined or accepted. Too close an adherence to particular views also generated what Cannizzaro was later to call "prejudices" that narrowed the vision of many of the best chemists of the century. The broader needs of Cannizzaro's student audience, to whom his efforts were originally addressed, may have given him the perspective needed.

The other fundamental factor that delayed the successful application of Avogadro's principle to the solution of the problem was the stern reluctance of the chemical community to abandon the post-revolutionary view of chemistry as a strictly empirical science, with a corresponding suspicion of the hypothetical. When Avogadro's principle was first proposed, it was no more than an unsupported conjecture designed to explain a single very arguable phenomenon, Gay-Lussac's law of volumes. It had no other justification, for Dalton had much earlier found it inconsistent with his model of the gaseous state, and there was no better model to give it support against Dalton's objections. To take Avogadro's principle as an unexceptionable doctrine and rigorously explore its extended possibilities, as Cannizzaro did fifty years later, would have been quite beyond the philosophical courage of most chemists of that earlier time. Perhaps only John Dalton had that kind of courage, but he had from his very earliest endeavors rejected the idea that all gaseous particles occupied the same volume.

Summary

We have seen that Dalton's atomic theory provided chemistry with the possibility for mathematical order and simplicity that had long been hoped for. It created a coherent connection with empirical composition, the key concept being that composition can be expressed in terms of quantized weight units (atomic weights), characteristic of each different element. We have seen that this potentiality was immediately recognized, though half a century elapsed before a consistent set of atomic weights was established. This conceptual expression of empirical composition has remained functional in spite of the vast growth in our detailed understanding of such things as ionization, which forced the modification of the notion of the "molecule," and the structure of the atoms themselves. But the chemical formulas today still represent in their basic meaning the quantitative composition of the substance each represents. In the two centuries since the appearance of Dalton's theory, there have been no real changes in the way chemical composition is conceived and represented. Every chemical formula used today in its primary symbolism represents the atomic composition of its chemical compound just as the circle-symbols did for Dalton.

Only after the atomic weight units of composition were established, was it possible for chemists to arrange those units successfully in meaningful molecular arrays and conceive the ideas of valence and directional bonding. Molecular structure remains today the central theoretical focus of attention, whether in the realm of molecular biology, biochemistry, chemical pharmaceutics, or polymer plastics. Dalton's atomic theory must be seen as the climax of the history of chemical composition and terminates this story.[43]

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[43] For the later nineteenth-century developments, see Alan J. Rocke, *Chemical Atomism,* and the same author's *The Quiet Revolution: Hermann Kolbe and the Science of Organic Chemistry* (Berkeley, California: University of California Press, 1993).

Philosophers of antiquity had offered composition and structure as alternative explanations for chemical behavior. These were thought to be exclusive views, but they became one when joined by Dalton's inspired conception of a quantized atomic weight. By permanently solving the problem of composition, Dalton's theory also made possible the open-ended exploitation of molecular structure, the central theme of organic chemistry.

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