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THOMAS DUCHÉ MITCHELL AND THE CHEMISTRY OF PRINCIPLES

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That Lavoisier's work constitutes, in some fundamental sense, a true chemical revolution has never been doubted by chemists, whether his contemporaries or those later generations blessed with the gift of historical, albeit whiggish, hindsight. Historians of science, on the other hand, have been less certain and a small, but vocal, literature has evolved debating the exact revolutionary content of Lavoisier's work, whether it was indeed a true revolution, and even the question of whether scientific revolutions exist in the first place (1). At times, and with more than a little exaggeration, one is tempted to compare this state of perpetual historical uncertainty with David Donald's evaluation of the state of American Civil War history - namely



Thomas Duché Mitchell

that "there must be more historians of the American Civil War than there were generals fighting it and, of the two groups, the historians are the more belligerent" (2).

It has been said that the art of revolution is really the art of making explicit the implicit and, on my better days, I delude myself that this simple aphorism is able to account for both the elements of continuity and discontinuity present in all such conceptual upheavals. If this characterization is even approximately acceptable, then there is one very fundamental aspect of the older chemistry which Lavoisier's work failed to transform immediately and that is the question of how to theoretically rationalize the specific or intrinsic properties of matter. For though, as I will argue later, Lavoisier implicitly provided the techniques which would lead to the modern viewpoint, he did not himself explicitly confront this issue, let alone revolutionize it.

As even a superficial glance at 19th century chemistry textbooks (and some of the better 20th century textbooks) will show, this problem lies at the very core of chemistry's identity as an independent science (3). Whereas classical physics deals with the general properties common to all matter, such as mass, inertia, the laws of motion, etc., it is chemistry which deals with the individuality of different kinds of matter; with their specific properties; with why they possess the colors, textures, odors, and flavors they have; and with why they can be interconverted into certain kinds of materials with equally mysterious arrays of specific properties, but not into others.

The modern interpretation of this problem is based on the atomic-molecular theory and the hypothesis that these properties are in some manner the emergent result of the number, kind, and arrangement of a substance's component atoms or, in more reductionist terms, of its ultimate electronic composition and structure. But from the time of the Greeks until the end of

the 18th century, the accepted rationale was quite different and was based instead on the concept of property-bearing principles or elements - the idea that the most important or salient characteristics of a substance were in some fashion the additive reflection of the properties of its components (much as a reddish color in a paint mixture automatically implies the presence of a red pigment). Instead of being discontinuous and emergent, specific properties were thought to be continuous and variable like those of physical mixtures (to make the paint redder one simply adds more red pigment). Though the identification of both the most important properties and their material approximations would vary from the earth, air, water, and fire of the Greeks, through the sulfur, salt, and mercury of the iatrochemist, to the various hybrid four and five element theories of the 17th century, and finally to the phlogiston of the 18th century, the underlying assumptions remained the same. Indeed, this concept was analyzed in some detail by David Oldroyd in 1970, who found that it had an almost bewildering array of philosophical precedents, the most important of which was the Neoplatonic concept of ideal forms - the view that there existed ideal essences corresponding to each of the characteristic properties which, though nonisolable, were transferable from substance to substance and of which the isolable material analogs of earth, air, sulfur, etc. were but imperfect reflections (4).

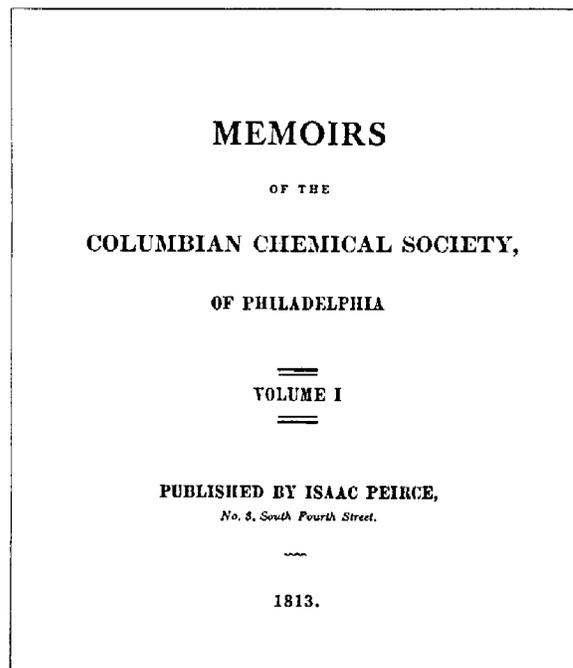
The point of this rather lengthy philosophical digression is, of course, that not only did Lavoisier fail to affect an explicit revolution in this time-honored mode of explanation, he actively carried it over into his new chemistry, albeit in a slightly modified form, and, in actual fact, it died a slow and very obscure death in the early decades of the 19th century.

The simplest evidence for this contention is Lavoisier's well-known use of oxygen as a principle of acidity. However, an even more pervasive argument was made by Carleton Perrin in 1973 as a result of analyzing the table of simple substances which appeared in Lavoisier's 1789 *Traité* (5). As Perrin noted, the first five entries in the table: light, caloric, oxygen, nitrogen (azote) and hydrogen are singled out and, in contrast to the other entries, which are always referred to as "simple substances", are alone in being given the name of "elements" - or to be more specific, are labelled as "simple substances belonging to all the kingdoms of nature, which may be considered the elements of bodies"(6). Since caloric is further described as being the principle of heat and Lavoisier considered oxygen to be the principle of acidity, nitrogen as a possible principle of alkalinity, and hydrogen as the principle of water, Perrin contended that the use of the word element in this context was intended in its older property-bearing sense and was a residual reflection of the older theory of property-bearing principles.

There are, however, some problems with this interpretation. In contrast to the older principles, which were both non-material and nonisolable, oxygen, nitrogen and hydrogen are

both material and isolable, though it might be argued that this materialization was the end result of the increasing tendency of later variants of the phlogiston theory to identify phlogiston with hydrogen. Likewise, unlike the older principles, which were literally the personification of the properties which they conferred on material substances, hydrogen, oxygen and nitrogen possess none of the properties of water, acidity or alkalinity which they supposedly imparted to their compounds. In passing, it should be noted that Robert Siegfried has also recently challenged Perrin's interpretation, arguing instead that this class of five elements is really a collection of odds and ends which Lavoisier was unable to group using his theory of salt formation, which forms the basis for classifying the other elements in the table - in short, that it is a kind of taxonomic miscellany (7).

Whatever the final consensus on this larger issue, there is no doubt that Lavoisier did use oxygen as a generic property-bearing principle and, if he failed explicitly to challenge the basic assumptions of the theory of principles, who did and at what point did chemists switch to the modern view? Alas, with the single exception which I will discuss in a moment, 19th century chemists - at least as far as I can tell - never did explicitly challenge this concept and, for that matter, never explicitly recognized that there was a fundamental difference between their premises and those of Lavoisier and his predecessors. Rather the change to the modern view seems to have occurred so slowly, or perhaps I should say, so obscurely, as to



Title page of the only published volume of the *Memoirs of the Columbian Chemical Society* in which Mitchell's initial essays appeared.

have been almost undetectable. Indeed, if we are to believe Oldroyd, historians of science have not done much better than the chemists with this subject, as he claimed in his 1970 article that they did not gain an explicit recognition and appreciation of the historical importance of the chemistry of principles until the 1960's.

The sole exception to this litany of ignorance is an obscure 19th century American chemist by the name of Thomas Duché Mitchell and, given the importance of this issue, as just outlined, in defining both the nature of Lavoisier's revolution and the course of its post-revolutionary consolidation, the relevance of briefly discussing Mitchell's critique of this concept, as well as its suitability as a concluding footnote to this symposium, are both self-evident.

Mitchell was born in Philadelphia in 1791 and studied medicine at the University of Pennsylvania, receiving his M.D. degree in 1812 (8). While still a student, he was drawn into the activities of the Philadelphia chemical-medical community, having spent a year in the drug store and chemical laboratory of Dr. Adam Seybert, a prominent member of the community who specialized in the chemical analysis of minerals, and his apprenticeship under Dr. Joseph Parrish, who had been active as a chemical lecturer in the Philadelphia area. Mitchell began to publish articles on chemistry and medicine while still a student, his first known chemical contribution, "On Nitric and Nitrous Acids", appearing in the *Medical Museum* in 1809. This was followed two years later by his organization of a student chemical society in collaboration with a fellow medical student named George Lehman. Known as the Columbian Chemical Society, it was the third such society organized in the Philadelphia area (9). The first, which had been organized in 1789 by John Pennington, had lasted only a year, whereas the second - The Chemical Society of Philadelphia, organized by John Redman Coxe in 1792 - had lasted for about 15 years (10). Though the Columbian Chemical Society would last for only three years (1811 - 1814), it was unique in that it succeeded, unlike its two predecessors, in actually publishing a volume of memoirs in 1813.

This 221-page volume contained 26 papers by members of the Society, nine of which were written by Mitchell, who had, incidentally, also served as the Society's first president in 1811. It is in these papers that Mitchell's initial critique of the chemistry of principles first appeared, largely in connection with his defense of Lavoisier's system against Davy's work on the elemental nature of chlorine and against a revival of the phlogiston theory proposed by John Redman Coxe, who was at the time Professor of Chemistry at the University of Pennsylvania.

Attacking Coxe's identification of hydrogen as a principle of inflammability on general philosophical grounds, Mitchell readily admitted that his objections applied with equal force to Lavoisier's use of oxygen as a principle of acidity. Mitchell wrote (11):

And in the first place, I would observe, that while the doctrine of an inflammable principle appears to me incorrect, it seems likewise unphilosophical. And while I say this, I am as willing to admit the error so often made in the use of the term, principle of acidity. Both alike are improper. It would be just as philosophical, when speaking of a neutral salt, to assert that the acid constituted the principle of neutrality as that it resided, exclusively, in the alkali. How absurd does this appear! Shall we then be excused, when we say that such a body is combustible, if we assert that the principle of inflammability belongs to one agent or, speaking of an acid, shall we be allowed to call one of its constituents the acidifying principle? ... it is an abuse of terms, a misapplication of words, to say that this or that is the principle of inflammability or of acidity. Inflammation and acidity are effects resulting from the action of relative causes and are not attributable to a single agent or principle.

In other words, Mitchell is contending that chemical and physical properties are not the inherent qualities of isolated substances, as implied by the chemistry of principles, but rather the relative, system-dependent result of the interaction of several substances, one of which could correspond to the organs of sensation in the human being. Thus, in another essay, Mitchell wrote (12):

Where was philosophy and reason when inflammability, or the power of burning, was consigned to one solitary agent? I challenge the whole host of opponents to the antiphlogistic system to adduce one single instance in all nature in which any body separately possesses an absolute principle or quality. When we speak of the properties of bodies, as taste, smell, etc., we do not mean that any of them possesses a positive quality. They are merely sensations or effects resulting from the actions of those bodies on our organs of taste, smell, etc. Inflammation, like odors, is the result of relative circumstances and not the product of a single agent.

Though other chemists would criticize Lavoisier's theory of acidity on purely chemical grounds, that is, in terms of whether or not all acids really did contain oxygen, it is important to realize that Mitchell is attacking on general philosophical grounds the premises behind the use of principles in general, be they of acidity or inflammability. And he is doing so on the basis of a critique of how we perceive and detect the properties of matter in general - namely, that all properties are due to purely relative effects in which all of the interacting agents play an equal role, for (13):

... what is a neutral salt, but the result of the mutual interaction of an acid and alkali, and what is combustion, but the effect of the mutual operation of oxygen gas, in some shape or other, and a combustible?

It is interesting to note that Mitchell's critique is virtually identical to that given a century later by the German philosopher, Ernst Cassirer, who, in discussing the physics of Anaxogoro-

ras and Aristotle, referred to their "hypostatization of sensuous qualities" or the "procedure of converting the relative properties of sensations into the absolute properties of things" (31).

In 1831 Mitchell, after practicing medicine for nine years in Frankford, Pennsylvania, just outside of Philadelphia, moved to Cincinnati to accept the position of Professor of Chemistry and Pharmacy at the Medical College of Ohio. The next year he published a 553-page textbook based on his lectures at the College, entitled *Elements of Chemical Philosophy*, in which he again reiterated his relativist position on the origins and nature of specific properties in chemistry (14):

On the subject of an acidifying principle, I have given my views at length, some years ago. It may not be amiss, however, to state, in this place, that the advances which chemical science is constantly making, have confirmed my early opinions on this point. I repeat, that the term acidifying principle is utterly unphilosophical, not only as applied to oxygen, but to hydrogen, and to every agent which may be supposed to exert an influence in developing acid properties. Every result in nature or produced by art, is a relative effect, and every item concerned, remotely or directly, in the accomplishment of the end, is essential to that end. Hence, I insist, that if an acid be discovered, which shall contain 50 component parts, all which are requisite in the formation of the compound, the only characteristic of which is acidity, I may affirm with equal propriety of any one, as of the other, of its constituents, that this or that is the acidifying principle. Abstract from the compound either of its parts, and you destroy the peculiar, distinctive character of the acid.

By way of biographical completeness, Mitchell left Cincinnati in 1837 to become Professor of Chemistry at the Medical School of Transylvania University in Lexington, Kentucky. In 1839 he gave up teaching chemistry, concentrating instead on therapeutics and materia medica. After serving as Dean of the Transylvania Medical School for several years, Mitchell returned to Philadelphia, where he died in 1865 at the age of 74.

Was Mitchell justified in his critique of the concept of property-bearing principles or was he merely an isolated American amateur flogging an already long-dead horse? In terms of his immediate environment, at least, the answer is that the attitudes of many of Mitchell's fellow chemists did indeed justify such a critique in 1813. As already mentioned, most of Mitchell's original comments appeared in his analysis of John Redman Coxe's recently published theory of combustion, which made controversial use of Humphry Davy's apparent discovery of hydrogen in such combustibles as sulfur, phosphorus and carbon, to support what was, in essence, a revival of a form of the phlogiston theory similar to the late 18th century variants proposed by the French chemists, Macquer and Guyton de Mourveau, and by the American chemist-physician, Samuel L. Mitchill (15). Essentially, the theory suggested that combustion involved not only the combination of the inflammable substance with oxygen, but the simultane-

ELEMENTS
OF
CHEMICAL PHILOSOPHY,
ON THE BASIS OF REID,
COMPRISING
THE RUDIMENTS OF THAT SCIENCE
AND
THE REQUISITE EXPERIMENTAL ILLUSTRATIONS,
WITH PLATES AND DIAGRAMS.

BY THOMAS D. MITCHELL, M. D.
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Medical and Columbian Chemical Societies, &c.

"Plusieurs sciences, arts et métiers tiennent presque uniquement sur la chimie, qui, de
toutes les sciences, est celle dont on fait le plus d'applications aux besoins de la vie."
Berzelius.

CINCINNATI:
PUBLISHED BY COREY & FAIRBANK.
NEW YORK: JONATHAN LEAVITT.
1832.

Title page of Mitchell's textbook in which he reiterated his criticisms of the chemistry of principles.

ous release and combustion of phlogiston (now identified as hydrogen) from the inflammable, the hydrogen having imparted the property of inflammability to the combustible in the first place. In addition, Franklin Bache, a fellow member of the Columbian Chemical Society, actually published a paper in the Society's memoirs entitled, "An Enquiry into What Circumstances Will Warrant Us Justly to Reckon Any Substance a Principle of a Common Property of Any Set of Bodies", in which he attempted to outline criteria for the development of a consistent chemistry of principles, albeit all now thoroughly materialized (16).

All of these cases indicate that not only chemists of Lavoisier's generation, such as Samuel L. Mitchill, but those of the next generation as well, such as Coxe and Bache, though apparently accepting the results of Lavoisier's system, continued to regress into explanations and modes of thought based on the concept of property-bearing principles - in short, that Lavoisier's work did not explicitly revolutionize this concept and that it lingered on well into the first decades of the 19th

century (17).

Even as late as 1832, Mitchell still had some justification for his remarks in his textbook. In 1828, just three years before Mitchell came to Cincinnati, Elijah Slack, his predecessor as Professor of Chemistry at the Medical College of Ohio, had published a small pamphlet on chemical nomenclature for the students at the college (18-19). This was the last of a long line of short chemical nomenclatures published in the United States, the first being Samuel L. Mitchill's *Nomenclature of the New Chemistry*, which appeared in 1794 (20). In this pamphlet, Slack continued to adopt an organization similar to that used by Lavoisier in his *Traité*, the sole difference being that the class of acidifying principles or supporters of combustion had now been generalized, via the suggestions of Davy, Gay-Lussac, Thomson and others, to include not only oxygen, but other highly electronegative elements, such as the halogens and sulfur. Thus one had not only an oxygen family of acids, bases and salts, but a chlorine family, a sulfur family, etc. (21).

Finally, we need to ask the question of where Mitchell got his ideas on the origins of specific properties. Given his emphasis on the emergent, relativistic nature of these properties and their interaction with our organs of sensation, the most obvious source which suggests itself is the writings of the 17th century British philosopher, John Locke, and his famous distinction between primary and secondary qualities (22). Unfortunately, we do not know enough about the details of Mitchell's education to show an explicit influence. In addition, as the recent book by Peter Alexander has shown, most of Locke's ideas on this subject are in reality a popularization of concepts found in the writings of Robert Boyle and are a logical consequence of accepting a mechanical atomic theory of matter - which Mitchell most certainly did (23).

Actually, there are some precedents in the chemical literature of the period which are more likely candidates and which Mitchell would have almost certainly encountered in the course of his chemical training. The most important of these is found in the multi-volume text, *A General System of Chemical Knowledge*, written by Lavoisier's friend and collaborator, Antoine Fourcroy, which had been translated into English by William Nicholson in 1804. In the first volume of this work, Fourcroy offered a list of established laws governing chemical change, the sixth of which reads (24):

Compounds formed by chemical attraction, possess new properties different from those of their component parts.

In commenting on this law, Fourcroy further noted that:

... chemists 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* (italics added).

Likewise, the Scottish chemist, John Murray, gave a detailed discussion of the same law in his 1806 text, a volume also easily accessible to Mitchell, and even cited quantitative data on densities to demonstrate its truth (25). Though the acceptance of this law is tantamount to rejecting the concept of property-bearing principles, it is interesting to note that neither Fourcroy nor Murray carried through with it in the later descriptive sections of their books, where both continued to employ Lavoisier's acidity principle, and it is only Mitchell, as far as I know, who explicitly spelled out its logical consequences for Lavoisier's original system.

While the apparently unique approach of Mitchell to this problem certainly merits the attention of historians, we are still left with our original question of when and why the 19th century chemist abandoned the chemistry of principles, for one cannot seriously maintain that Mitchell had a major impact on his fellow chemists. Though he published, in addition to several textbooks, more than 20 papers on chemical subjects, virtually all of them appeared in obscure medical journals with limited circulations which, like the *Memoirs of the Columbian Chemical Society*, became defunct after only one or two volumes. Likewise, his impact as a teacher of chemistry and as a textbook author was limited to audiences of beginning medical students in the newly-founded medical schools of Ohio and Kentucky, which failed to produce any future generations of chemists to carry on his particular point of view.

A tentative answer to our question can be obtained, however, by briefly considering why the proposition that:

$$\text{properties} = f(\text{composition}) \quad (1)$$

was so important to the 18th century chemist. Read from right to left, this statement can be charitably interpreted as one of the theoretical underpinnings of alchemy. However, long after chemists had ceased to seriously pursue the dreams of the alchemist, this proposition continued to be of importance as read from left to right. For virtually the only way 17th and 18th century chemists could operationally implement the claim that chemistry was the study of the composition of materials was via the premise that the composition of a substance could be directly inferred from its properties. Thus the presence of a sharp taste automatically implied the presence of "salt", insolubility and refractory behavior the presence of "earth", volatility the presence of "air" or "mercury", inflammability the presence of "sulfur", etc.

By changing the meaning of the word "composition" in relation 1 from "nonmaterial, nonisolable principles" to "material, isolable simple substances", and by supplying, via

the law of conservation of mass, a tool which allowed chemists to accurately distinguish between decomposition reactions, on the one hand, and addition and displacement reactions, on the other, Lavoisier supplied the means to circumvent this relation. Composition could now be inferred, not from properties, but via the use of chemical reactions to separate and isolate a species' material components. As the century progressed, the essence of a substance's identity came to be viewed less and less in terms of such properties as inflammability, metallicity or acidity and more and more in terms of mapping its position in the reactivity matrix - that is, in terms of what it could be made from and what it could be converted into. Indeed, though the terms as principle, acid and base, or combustible and supporter, continued to be used into the third and fourth decades of the century, they gradually ceased to imply the necessary existence of certain properties in the substances so labeled (such as sour taste in the case of acids) and became instead indicators of their taxonomic positions in the reactivity matrix. Thus the debates over the nature of acids in the 1830's had little or nothing to do (as so often misrepresented) with the question of whether oxygen or hydrogen was the true acidifying principle; rather they dealt with competing theories of salt formation, which is to say, with competing views of the taxonomic relationships between these substances in the reactivity matrix (e.g., do acid and bases form salts via addition or via displacement reactions ?) (26).

Consequently, as suggested earlier, there was no explicit confrontation with the chemistry of principles. It simply faded away, along with the importance of relation 1 as an approach to determining composition. Though Lavoisier failed to deal directly with the issue of principles and properties, he nonetheless provided chemists with the tools that would eventually direct their energies into a more fruitful approach to the problem of composition. By the time the property-composition problem was revived in the second half of the 19th century and correctly reformulated as:

$$\text{properties} = f(\text{composition and structure}) \quad (2)$$

the newer generation of structural organic chemists was no longer aware of the details of the earlier program and, with the accumulated fruits of Lavoisier's approach to composition to build upon, it seemed almost inconceivable that their program was anything other than the completion of his own (27).

In passing, it is of interest to note that there is evidence that it took chemists several decades to learn how to make full use of the implications of Lavoisier's approach to composition and, even to this day, it is misrepresented in both chemistry texts and in the history of science literature. Both sources generally imply that what is involved in analysis is the simple separation of a substance into its component elements. However, as anyone who has practiced classical chemical analysis knows, this is seldom the case. What one actually does is to

synthesize from an unknown substance one or more known compounds, from whose established composition one can infer the composition of the unknown (thus, in classical organic analysis, the unknown is converted into carbon dioxide and water) - a point which was emphasized by Fourcroy as early as 1804 (28). Even the known compounds produced in the analysis may never have been directly decomposed into their elements, but rather have, in turn, compositions inferred in a similar manner via their interconversions into yet other known compounds - the final end set of compounds actually having been directly decomposed into their elements being quite small.

In other words, classical chemical analysis depends on more than the definition of simple substances and the law of conservation of mass provided by Lavoisier. It also requires an empirical knowledge of the interconversions of different materials and an extensive mapping of the reactivity matrix, much of which, as the study of late 18th century analytical chemistry has shown, was done prior to the work of Lavoisier, whose contributions can in many ways be viewed as a set of rules for guiding the chemist through its manifold pathways (29). Indeed, the history of the discovery of new elements clearly shows that use of the reactivity matrix can even allow chemists to infer the existence of new elements through the behavior of their compounds (usually the oxides) without having actually isolated the element itself (30).

Lastly, it is of interest to note that, with the advent of the electronic theory of matter and the instrumentation revolution, modern chemistry has again returned to a left to right reading of relation 2 and direct physical methods of analysis are rapidly replacing the methods of classical chemical analysis. On the other hand, the reading of relation 2 from right to left, which may be interpreted as a form of "molecular engineering" and which is, in some sense, a modern equivalent of the alchemist's dream, still remains very much an open problem for 20th century chemistry.

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 29. J. W. Llana, "A Contribution of Natural History to the Chemical Revolution in France", *Ambix*, **1985**, 32, 71, and H. Cassebaum and G. Kauffman, "The Analytical Concept of a Chemical Element in the Work of Bergman and Scheele," *Ann. Sci.*, **1976**, 33, 447.
 30. See the accounts in M. E. Weeks, *Discovery of the Elements*, 6th ed., J. Chem. Educ., Easton, PA, 1960.
 31. E. Cassirer, *Substance and Function*, Open Court, Chicago, IL, 1923, p. 153.
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- ## A BIOGRAPHICAL CHECKLIST
- The following is a checklist of biographies of Lavoisier in the *Oesper Collection in the History of Chemistry* at the University of Cincinnati. For teachers and practicing chemists looking for brief, accessible introductions, Guerlac (1975), McKie (1952) and Davis are recommended. For more scholarly detail on specific aspects, Guerlac (1961) and Holmes are recommended.
- * A. Bauer, *Lavoisier*, Wein, 1906.
 - * M. Berthelot, *La Révolution Chimique - Lavoisier*, Germer-Baillière, Paris, 1890.
 - * M. Berthelot, *Notice Historique sur Lavoisier*, Académie des Sciences, Paris, 1889.
 - * J. A. Cochrane, *Lavoisier*, Constable, London, 1931.
 - * M. Crosland, *Les Héritiers de Lavoisier*, Palais de la Découverte, Paris, 1968.
 - * C. Cuttlota, *Respiration and the Lavoisier Tradition*, American Philosophical Society, Philadelphia, PA, 1972.
 - * M. Dumas, *Lavoisier*, Gallimard, Paris, 1941.
 - * M. Dumas, *Lavoisier, Théoricien et Expérimentateur*, Presses Universitaires de France, Paris, 1955.
 - * K. S. Davis, *The Cautionary Scientists: Priestley, Lavoisier and the Founding of Modern Chemistry*, Putnam, New York, 1966.