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## Genius and the Dogmatization of Error : the Failure of C. L. Berthollet's Attack upon Lavoisier's Acid Theory

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GENIUS AND THE DOGMATIZATION OF ERROR:  
THE FAILURE OF C. L. BERTHOLLET'S ATTACK  
UPON LAVOISIER'S ACID THEORY

In the late eighteenth and early nineteenth centuries Claude-Louis Berthollet vigorously opposed Antoine-Laurent Lavoisier's view that all acidic substances owed their acidity to the presence in them of oxygen, the "acidifying principle". Though Berthollet was one of the most prominent chemists in this period and an early "convert" to Lavoisier's chemistry<sup>1</sup>, and though his opposition was founded upon a wealth of experimental data, his criticisms had but slight impact upon his fellow chemists. The failure of Berthollet's attack is at least in part explicable in terms of Thomas S. Kuhn's model of scientific change<sup>2</sup>.

Lavoisier played a major role in the development of chemical theory and practice often termed the "Chemical Revolution". His contributions to this development include the replacement of phlogistic theories of combustion by his oxygen theory, the inversion of phlogistic ideas on the composition of numerous substances, an emphasis upon quantitative as opposed to qualitative experiments, and the provision of a definition and list of chemical elements which prepared the way for John Dalton. Historians may disagree as to which of these intimately related accomplishments should receive the greatest emphasis, but they generally agree on two basic points: first, chemistry before Lavoisier is somehow very different from chemistry after him; second, it was Lavoisier's genius

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<sup>1</sup> J. R. Partington, *Berthollet and the Antiphlogistic Theory*, "Chymia", 1959, 5, pp. 130—137; cf. H. E. Le Grand, *The Conversion of C. L. Berthollet to Lavoisier's Chemistry*, "Ambix", 1975, 22, pp. 58—70.

<sup>2</sup> T. S. Kuhn, *The Structure of Scientific Revolutions* (International Encyclopedia of Unified Science, vol. 2, no. 2), 2nd ed., University of Chicago Press, 1970.

to provide a new interpretation of familiar data and to present it in a convincing fashion in his textbook, the *Traité Élémentaire de Chimie*. Lavoisier's definition of a chemical element as any substance not yet proved to be compound<sup>3</sup> evidences this genius. He avoided metaphysical discussions about the nature, number, and atomic basis of elements and provided instead both an operational definition and a list of some thirty-three "simple substances"<sup>4</sup>. Neither his definition nor his list resembled those of earlier chemists so, from this point of view, there is a definite break with old ideas. The emphasis upon such discontinuities between "phlogistic" and "oxygen" chemistry has, however, contributed to the neglect of significant continuities and inconsistencies in Lavoisier's system.

Lavoisier's genius was flawed. He opposed a particular "principle", phlogiston, but himself accepted the "principles" form of explanation. That is to say, to the question of why different chemicals exhibited similar properties Lavoisier, like the phlogistic chemists, would reply in compositional terms. The properties of a class of substances were to be explained in terms of the presence in those substances of certain components or "principles". It is true that Lavoisier's "principles" are quite different both qualitatively and quantitatively from phlogistic ones, but this is one area in which Lavoisier's system had important continuities with the older view<sup>5</sup>. He rejected the principle of combustibility but utilized caloric, the principle of heat<sup>6</sup>; azote or nitrogen, the alkalinizing principle<sup>7</sup>; and oxygen, the acidifying principle<sup>8</sup>. This use of principles, moreover, was in certain instances potentially in conflict with his definition of an element.

Lavoisier's *Traité* embodied two criteria for establishing the relative complexity of substances: one provided by his acceptance of "principles"; the other, by his definition of an element. These criteria, when applied to most substances, were mutually consistent. Most acids, for instance, were properly regarded as compounds of oxygen with various "acidifiable bases" such as sulfur, phosphorus, carbon, and nitrogen. These "bases"

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<sup>3</sup> A. L. Lavoisier, *Oeuvres de Lavoisier*, 6 vols., Paris 1862—1893; reference to vol. I, pp. 7—8.

<sup>4</sup> *Ibid.*, vol. 1, p. 135.

<sup>5</sup> M. Fichman discusses other areas of continuity [in:] *French Stahlism and Chemical Studies of Air, 1750—1770*, "Ambix", 1971, 18, pp. 94—122.

<sup>6</sup> R. J. Morris, *Lavoisier and the Caloric Theory*, British J. Hist. Sci., 1972, 6, pp. 1—38. R. Siegfried, *Lavoisier's View of the Gaseous State and its Early Application to Pneumatic Chemistry* "Isis", 1972, 63, pp. 59—78.

<sup>7</sup> H. E. Le Grand, *Determination of the Composition of the Fixed Alkalis 1789—1810*, "Isis", 1974, 65, pp. 59—65.

<sup>8</sup> M. P. Crosland, *Lavoisier's Theory of Acidity*, "Isis", 1973, 64, pp. 306—325. H. E. Le Grand, *Lavoisier's Oxygen Theory of Acidity*, "Annals of Science", 1972, 29, pp. 1—18.

were accordingly listed as simple substances. What of the so-called "undecomposed acids", however: muriatic [HCl]; fluoris [HF], and boracic [H<sub>3</sub>BO<sub>3</sub>]? Lavoisier applied the criterion afforded by his acid theory. Although "undecomposed", these acids were not listed as elemental; rather, the presumed "radicals" or "bases" of these acids appear in his table of simple substances<sup>9</sup>.

At the time the *Traité* was published, such a course of action seemed defensible. Acidic substances, with few exceptions, did contain oxygen and the existence of several acidic metal oxides lend credence to the view that the presence of oxygen in sufficient quantity was not only the necessary but also the sufficient condition for a compound to manifest the properties of an acid. One could take the attitude that it was somehow "wrong" for Lavoisier to extend his concept of acidity to substances not then decomposed or otherwise fully studied. As Kuhn points out, however, imposing such restrictions would effectively end paradigm-directed research. Moreover, the oxygen theory of acidity, though incorrect, had been essential to Lavoisier in his "inversion" of phlogistic notions of composition: a clear instance of a significant scientific advance occurring through an erroneous theoretical commitment<sup>10</sup>.

Claude-Louis Berthollet between 1785 and 1800 collected a considerable body of experimental data which conflicted with Lavoisier's views on acidity. Even in his 1785 paper on dephlogisticated marine acid [chlorine] in which he first adopted Lavoisier's chemistry, he noted properties of that substance which were different from those predicted by Lavoisier's acid theory. He observed that this "acid" in solution had a harsh taste which did not resemble the distinctive sour taste of acids, that it destroyed vegetable colours rather than reddening them, and that no effervescence occurred when it combined with the fixed alkalies, potash [K<sub>2</sub>CO<sub>3</sub>] and soda [Na<sub>2</sub>CO<sub>3</sub>]<sup>11</sup>. These observations led Berthollet in a revised version of this paper to regard this "acid" as almost devoid of acidity, although it supposedly contained more of the "acidifying principle" than the more powerful "common marine acid" [HCl]<sup>12</sup>. Further discrepancies soon appeared.

Berthollet's determination of the composition of prussic acid [HCN] two years later was important to the gelling of his opposition to the oxygen theory of acidity. In a memoir presented in December 1787 he

<sup>9</sup> Lavoisier, *Oeuvres*, vol. 1, p. 135. Similarly, the fixed alkalies, potash [K<sub>2</sub>CO<sub>3</sub>] and soda [Na<sub>2</sub>CO<sub>3</sub>] were omitted due to his conviction that these substances were compounds containing nitrogen, the alkalizing principle.

<sup>10</sup> Kuhn, *Scientific Revolutions*, pp. 100—101.

<sup>11</sup> C. L. Berthollet, *Mémoire sur l'acide marin déphlogistique*, "Observations sur la physique", 1785, 26, pp. 321, 325.

<sup>12</sup> C. L. Berthollet, *op. cit.*, *Mém. Acad. Roy. des Sci.*, 1785 (published 1788), pp. 276—295; reference to pp. 279—280.



concluded from his experiments that prussic acid contained only nitrogen, hydrogen, and carbon<sup>13</sup>. It did not contain oxygen. Louis Clouet's synthesis of prussic acid some four years later by passing ammonia gas [NH<sub>3</sub>] through a porcelain tube containing incandescent carbon provided support for this conclusion<sup>14</sup>. The question remained as to whether or not prussic acid was a true acid. Berthollet was quite definite in his opinion that indeed it was a true acid even though it was quite different in composition from most acids<sup>15</sup>. He would certainly not be in sympathy with Lavoisier's attempts in the *Traité* to imply that prussic acid contained oxygen<sup>16</sup> or to remove prussic acid from the class of acids<sup>17</sup>, thereby eliminating this exception to his acid theory. Berthollet's remarks on the classification of prussic acid suggest that he not only objected to the specific compositional dictates of the oxygen theory of acidity on experimental grounds, but also that as early as 1787 he was beginning to take exception to the accepted belief that the properties of a compound were simply a reflection or a blending of the properties carried by its constituents. Except for a very few chemists such as J. M. d'Arejula, however, the implications of Berthollet's work were unappreciated at this date<sup>18</sup>.

In 1788 he struck at the assumption of Lavoisier's acid theory that the metallic oxides, although not usually themselves regarded as acids, nonetheless acted as acids with respect to the alkalies because of the oxygen the former contained<sup>19</sup>. Berthollet took exception to this view. He admitted that non-acidic metal oxides acted as acids when combined with alkalies. However, he pointed out that those oxides also acted as alkalies when combined with acids. The chemical behaviour of the metallic oxides did not provide support for Lavoisier's acid theory. They should be regarded, he suggested, as "a term which gives birth to two opposite progressions"<sup>20</sup>.

On the basis of his extensive research he forcefully argued in 1789 that while the oxygen theory of acidity might be applicable to most

<sup>13</sup> C. L. Berthollet, *Mémoire sur l'acide Prussique*, Mém. Acad. Roy. des Sci., 1787 (1789), pp. 148—162; reference to p. 159.

<sup>14</sup> L. Clouet, *Mémoire sur la composition de la matière colorante du Bleu de Prusse*, "Annales de Chimie", 1791, 11, pp. 30—35.

<sup>15</sup> Berthollet, *Acide Prussique*, p. 161.

<sup>16</sup> Lavoisier, *Oeuvres*, vol. 1, pp. 93 and 243.

<sup>17</sup> *Ibid.*, vol. 1, p. 243.

<sup>18</sup> J. M. d'Arejula, *Réflexions sur la nouvelle Nomenclature Chimique*, "Observations sur la Physique", 1788, 33, pp. 262—286.

<sup>19</sup> A. L. Lavoisier, *Mémoire sur l'union du Principe oxygène avec le Fer*, Mém. Acad. Roy. des Sci., 1782 (1785), pp. 541—559.

<sup>20</sup> C. L. Berthollet, *Observations sur la combinaison des oxides métalliques avec les alkalis et la chaux*, Mém. Acad. Roy. des Sci., 1788 (1791), pp. 728—741; reference to pp. 728—729.

acids, certain limitations should be placed upon it. He remarked that many of his experiments did not contradict Lavoisier's view on acids and indeed "would serve to confirm it if it were not established on a sufficiently large number of facts." This statement of seeming support for the oxygen theory of acidity was, however, immediately followed by a summary of the experimental evidence in conflict with it. He denied that the presence of oxygen was either the necessary or sufficient condition of acidity on the grounds that some substances such as water contained oxygen yet were not acidic and that some acids such as prussic, muriatic, and fluoric had not been proved to contain oxygen. He also attacked the prevalent theory of composition according to which the properties of a compound were determined solely by that compound's composition. In particular, he attacked the view that acidity must denote the presence of oxygen in a compound since oxygen was the unique acidifying principle or carrier of acidic properties. He noted that substances could be composed of different elements yet exhibit similar properties. Therefore, he cautioned, one should not infer composition merely on the basis of chemical behaviour. If his views were accepted, he continued, muriatic acid would be regarded as a substance the composition of which was unknown: it might not contain oxygen. He stopped short of repudiating the oxy-acid theory, however. He admitted the term "oxygen" or "generator of acids" indicated a property he no longer considered to be general, but that he would continue to employ it because it was well established that many substances, though not all, became acids on combining with this principle and that oxygen could be extracted from most, but not all, acids. Berthollet thus reduced Lavoisier's general theory to a correlation of certain data to which there were a number of exceptions<sup>21</sup>.

Berthollet pursued these themes in a series of lectures delivered in 1795. He again acknowledged that oxygen often gave acidic properties to its compounds but decisively rejected any necessary link between acidity and the presence of oxygen. Water contained eighty-five parts of oxygen by weight to fifteen parts of hydrogen, yet water was not acidic. Oxymuriatic acid [chlorine] was presumed to contain more oxygen than muriatic acid yet the former was the weaker acid. One oxide of iron contained one third by weight oxygen yet could not be considered an acid, and more generally all the metals acquired through oxygenation the property of combining with and often neutralizing the acids proper. On the other hand, he observed that no one had been able to discover

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<sup>21</sup> C. L. Berthollet, *Suite des Expériences sur l'Acide sulfureux*, "Annales de Chimie", 1789, 2, pp. 54—72; reference to pp. 67—69.

any trace of oxygen in fluoric, boracic, and muriatic acids. Finally, he cited his research on prussic acid, stating again that it should properly be ranked with the acids but did not contain oxygen. He concluded from this mass of evidence that oxygen could not be considered an element inseparable from acidity<sup>22</sup>.

Berthollet in 1796 added another substance to the list of those which acted as acids but which were not known to contain oxygen. He observed that sulfuretted hydrogen gas [ $\text{H}_2\text{S}$ ] when dissolved in water reddened litmus, combined with and neutralized the alkalies, and exhibited other properties analogous to those of acids. It contained no oxygen. He concluded his reflections upon this newest exception to the oxy-acid theory of Lavoisier on a note of seeming disgust with the lack of response to his continuing criticisms of that theory:

I will not recall all the observations that I have opposed to the opinion of those who claim that acidity is an attribute which pertains only to oxygen; I will merely add that sulfuretted hydrogen contains no oxygen, and that it is very little removed, in its acid properties, from carbonic acid which contains almost seventy-six out of a hundred parts of oxygen<sup>23</sup>.

Berthollet's opposition to the oxygen theory of acidity seemed to waver in 1800 when he announced the constituents of muriatic acid to be hydrogen, nitrogen, and oxygen. Two erroneous observations led him to make this claim: one by Humboldt that muriate of iron [ $\text{FeCl}_2$ ] was formed through the absorption of nitrous gas [ $\text{NO}$ ] by sulfate of iron [ $\text{FeSO}_4$ ], indicating that nitrogen was one constituent of muriatic acid; the other by Cavendish that silver muriate [ $\text{AgCl}$ ] was precipitated from a solution of silver nitrate [ $\text{AgNO}_3$ ] by nitrate of potash [ $\text{KNO}_3$ ]. Berthollet argued that in the latter reaction the potash played no role and therefore muriatic acid was formed of elements present in water and nitric acid. Because of the incombustibility of muriatic acid and its resistance to decomposition, he concluded that if hydrogen and oxygen were two of its constituents, then these two were not present in large quantity. He therefore mistakenly felt himself justified in thinking that muriatic acid was a triple combination of small amounts of oxygen and hydrogen and a large proportion of nitrogen<sup>24</sup>.

This "discovery" might well have weakened Berthollet's criticisms of the inclusiveness of Lavoisier's acid theory, but it did not go unchallenged. In that same year L. N. Vauquelin noted that muriatic acid could

<sup>22</sup> C. L. Berthollet, *Chimie* [in:] *Séances des Écoles Normales*, vol. 6, Paris: 1796, pp. 136–163; reference to pp. 161–163.

<sup>23</sup> C. L. Berthollet, *Observations sur l'hydrogène sulfuré*, read 11 March 1796, "Annales de Chimie", 1798, 25, pp. 233–273; reference to pp. 237–238.

<sup>24</sup> C. L. Berthollet, *Sur la nature de l'acide muriatique*, "Bulletin des Sci. Soc. Philomath.", 1801, 2, pp. 125–127.

not be formed by the action of sulfuretted hydrogen on iron filings, as an anonymous letter had asserted, if these filings were first carefully washed. The obvious inference was that the filings contained some muriates<sup>25</sup>. Berthollet was struck by the applicability of this same precaution to his own experiments. He found that if his reactants were carefully purified of muriates, the procedures described by Cavendish and Humboldt did not result in the formation of muriates<sup>26</sup>. Muriatic acid was thus restored to the status of an exception to the oxygen theory of acidity: there was no proof, direct or indirect, that it contained oxygen.

By 1800 Berthollet had attacked on several experimental fronts the identification of oxygen as the unique acidifying principle. His own research had established that at least two substances, prussic acid and sulfuretted hydrogen, were acidic yet contained no oxygen. Furthermore, he had found that although oxymuriatic acid presumably contained more oxygen than muriatic acid, the latter was the stronger acid. On several occasions he had reminded his fellow chemists that the presence of oxygen had not been detected in muriatic, fluoric, and boracic acids. Finally, he had attacked the converse of Lavoisier's theory: compounds containing oxygen should display some degree of acidity. He not only had mentioned the example of water, but had determined that some metallic oxides were actually amphoteric.

In retrospect, it might seem that the decision for chemists should have been quite simple: experiment contradicted the oxy-acid theory, therefore the theory is incorrect and must be either substantially modified or rejected. Such a view would be naive. No theory which provides a basis for research resolves all of its problems. Indeed, scientists continually confront problems or "puzzles" but are generally successful in providing solutions to them. Scientists do not despair when faced with problems; to the contrary, they are confident that solutions will eventually be forthcoming. Kuhn cogently argues that even problems which resist repeated attempts at solution cannot by themselves falsify a particular theory, for its supporters will devise various articulations and *ad hoc* modifications to eliminate the apparent conflict between theory and fact. A previously accepted theory is rejected only if a suitable alternative theory is available<sup>27</sup>.

Kuhn's analysis of the response of scientists to "counterinstances"

<sup>25</sup> L. N. Vauquelin, *Sur la prétendue formation de l'acide muriatique par l'action de l'hydrogène sulfuré sur le fer*, "Bulletin des Sci. Soc. Philamth.", 1801, 2, pp. 172—173.

<sup>26</sup> C. L. Berthollet, *Observations sur l'action que le sulfure de fer exerce sur le gaz nitreux et sur la formation de l'acide muriatique*, "Annales de Chimie", 1801, 39, pp. 3—17.

<sup>27</sup> Kuhn, *Scientific Revolutions*, pp. 77—80.

provides useful insights into the reception of Berthollet's work relative to acidity. He had provided not just one, but several counterinstances or anomalies in the context of Lavoisier's acid theory. The acid theory was, however, only one aspect of a larger system of chemistry that was proving quite successful in accounting for chemical phenomena. Although, in retrospect, the oxygen theory of acidity was not a crucial part of this larger system which Lavoisier created, it had been crucial to him in the early stages of its erection and he had committed himself to it in the *Traité* and elsewhere. The "new chemistry" and the oxygen theory of acidity were thus historically, though not logically, linked together in the minds of Berthollet's contemporaries. Berthollet, moreover, had attacked Lavoisier's acid theory without proposing a replacement. When, in 1803 in his *Essai de Statique Chimique*, he did propose an alternative, it was ignored — for good reasons — by the overwhelming majority of chemists<sup>28</sup>. Ironically, Berthollet in proposing his new acid theory undercut many of his earlier experiment-based objections to that of Lavoisier. He withdrew his argument based upon the properties of oxymuriatic acid, for instance, and eliminated prussic acid from the class of acids<sup>29</sup>. If Kuhn's structures be correct, Berthollet's criticisms should have had only a marginal impact upon his fellow chemists. The experimental results reported by him might be questioned or reinterpreted, the oxygen theory of acidity might be articulated, or various *ad hoc* modifications might be employed, but the theory itself would not be rejected.

An inspection of the chemical literature of the period confirms this prediction. The community of chemists, regardless of nationality, almost unanimously held fast in their publications between 1790 and 1810 to Lavoisier's acid theory<sup>30</sup>. This is particularly evident in the numerous textbooks and popularizations of the new chemistry which appeared at the turn of the century<sup>31</sup>. Many chemists and popularizers simply took no notice of Berthollet's objections. Others mentioned his experiments but took exception to his conclusions. Still others accepted both his

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<sup>28</sup> For an account of Berthollet's acid theory and its reception, see H. E. Le Grand, *Claude-Louis Berthollet's Essai de Statique Chimique and Acidity*, "Isis", 1975 (forthcoming).

<sup>29</sup> C. L. Berthollet, *Essai de Statique Chimique*, 2 vols., Paris 1803; reference to vol. 2, pp. 9, 254, and 269–270.

<sup>30</sup> Excluded from consideration in this study were chemists who were not considered members of the chemical community between 1790 and 1810; i.e. those such as Joseph Priestley, Friedrich Albert Carl Gren, John R. Coxe, and Antoine Grimoald Monnet who never accepted Lavoisier's system, much less his acid theory.

<sup>31</sup> While such works of necessity do not reflect the frontiers of the research enterprise, they do serve as a sensitive indicator of shared assumptions and as such are quite valuable in a study of this character.

experimental work and his interpretation of it but, at the same time, continued to express confidence in oxygen as the acidifying principle.

Jean Antoine Claude Chaptal, a physician and professor of chemistry at Montpellier, expressed complete confidence in the validity of the oxygen theory of acidity. His textbooks, which "were much read, show originality, and are still pleasant to read"<sup>32</sup>, incorporated not only current ideas but also conclusions drawn from his own research. Although his work with acids was concerned chiefly with improved processes for their production in quantity, he was also interested in compositional problems<sup>33</sup>. In regard to Lavoisier's acid theory he wrote: "There seems to be no doubt that the bodies we have agreed to call *acids* are the combination of oxygen with elementary substances." He claimed that the analysis of nearly all the acids of which the constituents were known had positively established this truth<sup>34</sup>. As for the undecomposed acids, he acknowledged that oxymuriatic acid was less acidic than muriatic, but he regarded both of them — and, by implication, boracic and muriatic — as containing oxygen<sup>35</sup>. This generally uncritical attitude toward the oxy-acid theory was shared by many noted chemists, popularizers, and enthusiastic amateurs. Mathurin Jacques Brisson, a professor of physics with an interest in chemistry; Pierre August Adet, an editor of the *Annales de Chimie* and author of an elementary chemistry text; Edmonde Jean Baptiste Bouillon la Grange, professor at the École de Pharmacie who published his lectures in textbook form; Thomas Garnett, lecturer on chemistry at the Royal Institution; Johann Bartholomäus Trommsdorff; and Sigismund Friedrich Hermbstädt, an early "convert" to Lavoisier's chemistry and professor at Berlin, were among the many professionals who shared Chaptal's outlook toward Lavoisier's theory and took little notice of Berthollet's experiments relative to acidity<sup>36</sup>. They were echoed in this view by numerous popularizers and authors of textbooks and

<sup>32</sup> J. R. Partington, *A History of Chemistry*, 4 vols. Macmillan and So. Ltd., London 1960, 1961, 1962, 1964; reference to vol. 3, p. 557.

<sup>33</sup> See, e.g., Le Grand, *Fixed Alkalis*, p. 60.

<sup>34</sup> J. A. E. Chaptal, *Éléments de Chymie*, 3 vols., Montpellier 1790; reference to vol. I, pp. 164—171. The same viewpoint is expressed in the 3rd ed., 3 vols., Paris 1796; reference to vol. I, pp. 171—172 and 176 and in the 4th ed., Paris 1804.

<sup>35</sup> *Ibid.*, Paris 1796, vol. I, pp. 320—321.

<sup>36</sup> Brisson, *Éléments ou principes physico-chimiques*, 4 vols., Paris 1800; 2nd ed., 4 vols., Paris 1803.

Adet, *Leçons élémentaires de chimie à l'usage des Lycées*, Paris 1804.

Bouillon la Grange, *Manuel d'un cours de chimie, ou principes élémentaires théoriques et pratiques de cette science*, 3 vols., Paris 1799; 3rd ed., 3 vols., Paris 1802.

Garnett, *Outline of a Course of Lectures*, London 1801.

Trommsdorff, *Systematisches Handbuch der gesammten Chemie zur Erleichterung des Selbststudiums dieser Wissenschaft*, 8 vols., Gotha and Erfurt 1800—1807.

Herbstädt, *Systematischer Grundriss der allgemeinen Experimental-Chemie*, 2nd ed., 2 vols., Berlin 1800—1801.



handbooks who did little if any research themselves but who communicated accepted chemical ideas to the lay public<sup>37</sup>.

Antoine Francois Fourcroy is rather typical of those who took cognizance of Berthollet's experiments but rejected his conclusions drawn from them. In the massive *Système des connaissances chimiques* he presented an orthodox account of the oxygen theory of acidity<sup>38</sup>. On the basis of some experiments he carried out with L. N. Vauquelin, he believed prussic acid to contain oxygen<sup>39</sup>. In the instance of sulfuretted hydrogen he accepted Berthollet's characterization of it as a compound of sulfur and hydrogen which possessed the properties of an acid, but he did not mention any connection between this and the oxygen theory of acidity<sup>40</sup>. His discussion of muriatic acid is quite interesting. He suggests that it could properly be ranked among the simple substances as it had not been decomposed. His own opinion, however, is that muriatic acid is a compound of some unknown "radical" and oxygen in which the affinity of the "radical" for oxygen is extremely strong, though he admits that this is a "pure hypothesis"<sup>41</sup>. John Murray in his textbook expressed himself in terms very similar to those of Fourcroy, though he was more confident concerning the undecomposed acids which he had "little hesitation" in proclaiming compounds of oxygen<sup>42</sup>. Popularizers such as William Nisbet and Frederick Accum; Arthur and Charles Roguson Aikin, authors of a popular but quite derivative chemical dictionary; and amateurs such as the lawyer Charles-Louis Cadet-Gassicourt followed the lead of chemists such as Fourcroy in either failing to see the implications of or casting doubt upon Berthollet's experiment-based objections to Lavoisier's acid theory<sup>43</sup>.

<sup>37</sup> Such derivative writers include the following: W. S. Jacobs, *The Student's Chemical Pocket Companion*, Philadelphia 1807; J. Parkinson, *The Chemical Pocket-Book or Memoranda Chemica*, Dublin 1801; 2nd ed., London 1801, 3rd ed., London 1803; R. Heron, *Elements of Chemistry*, London 1800; A. Fabulet, *Nouveaux Éléments théorique et pratique de Chimie*, Paris 1802; P. P. Alyon, *Cours Élémentaire de Chimie théorique et pratique*, 2 vols., Paris 1799; Skrimshire, *A Series of Popular Chemical Essays*, 2 vols., London 1802; 2nd ed., London 1804.

<sup>38</sup> 10 vols., Paris 1801; reference especially to vol. 2, pp. 27—31.

<sup>39</sup> *Ibid.*, vol. 9, pp. 89—92. Fourcroy and Vauquelin supposed prussic acid contained oxygen on the basis of several experiments of dubious validity. Cf. Fourcroy and Vauquelin, *Copie De quelques Découvertes Chimiques*, "Annales de Chimie", 1790, 6, pp. 177—182. Thought their experiments were far less elegant in this instance than Berthollet's, their conclusions were more acceptable since they were in agreement with the prevailing theory and their research was frequently cited by other authors; e.g., T. Thomson, *A System of Chemistry*, 2nd ed., 4 vols., London 1804; reference to vol. 2, p. 183.

<sup>40</sup> Fourcroy, *Système*, vol. 2, pp. 192—193.

<sup>41</sup> *Ibid.*, vol. 2, pp. 107—108.

<sup>42</sup> J. Murray, *Elements of Chemistry*, 2 vols., Edinburgh 1801; reference to vol. 1, pp. 296 and 310 and vol. 2, p. 355.

<sup>43</sup> Nisbet, *A General Dictionary of Chemistry*, London 1806; e.g., pp. 3 and 220. Accum, *A System of Theoretical and Practical Chemistry*, 2 vols., London 1803;



Jane Haldimand Marcet is in a class by herself not only in regard to the great success met by her numerous popularizations but also on account of her perceptiveness concerning the implications of both the experimental evidence assembled by Berthollet and Lavoisier's elemental definition. Her *Conversations on Chemistry* went through some eighteen English editions, numerous pirated American editions, two French editions, and remains today an excellent introduction to early nineteenth-century chemistry<sup>44</sup>. Her remarks concerning the undecomposed acids are particularly revealing. Speaking as "Mrs. B.", she replies to the question of "Caroline", the tyro, as to why these acids should not by Lavoisier's definition be listed as elements: "Analogy affords us so strong a proof of the compound nature of the undecomposed acids, that I could never reconcile myself to classing them with the simple bodies..."<sup>45</sup>. She thus accepted the compositional view entailed by Lavoisier's theory of acidity rather than his definition of an element. Of all the evidence ranged against that theory, only the behaviour of prussic acid seemed to be a cause for concern. She accepted the analysis of it as an acidic compound formed of only carbon, hydrogen, and nitrogen. The implications of this for the oxy-acid theory are the subject of the following:

Caroline. But this does not accord with the system of oxygen being the indispensable principle of acidity?

Mrs. B. It is true; and this circumstance, together with others of the same kind, has led several chemists to suspect that oxygen may not be the sole generator of acids, and that acidity may possibly depend rather on the arrangement than on the presence of any particular principles.

Caroline. I do not like that idea. For if it were founded, all our theory of chemistry must be erroneous.

Mrs. B. The objection is yet so new and unconfirmed by common experience, that I confess I do not feel inclined to distrust the general doctrine of acidification which we have hitherto adopted<sup>46</sup>.

Her attitude, like that of the chemists on whom she drew, is quite normal from a Kuhnian perspective. Even significant discrepancies need not

e.g. vol. 1, pp. 137, 184, 261, 327, 333, 343 and vol. 2, p. 260. The Aikins, *A Dictionary of Chemistry and Mineralogy*, 2 vols., London 1807; e.g., vol. 1, pp. 10—12 and vol. 2, pp. 114—116. Cadet-Gassicout, *Dictionnaire de Chimie*, 4 vols., Paris 1803; e.g., vol. 1, pp. 13—14 and 18—19.

<sup>44</sup> The following editions have been consulted: London 1807 and 1809, Philadelphia 1806, and New Haven, Conn. 1814. These editions are mutually consistent excepting the addition of material relating to the decomposition of soda and potash to the London 1809 and subsequent editions. It should be noted that much of Marcet's information on chemistry came through her attendance at Humphry Davy's lectures in the Royal Institution.

<sup>45</sup> *Conversations on Chemistry*, Philadelphia 1806, pp. 246—247; 2 vols., London 1807, vol. 2, pp. 18—19. For comments on acidity generally, see Philadelphia, pp. 244—252 and London, vol. 2, pp. 15—23.

<sup>46</sup> *Ibid.*, Philadelphia, pp. 380—381; London, vol. 2, pp. 230—231.

attract great attention. Scientists might well believe that even very stubborn problems will eventually be solved within the existing theory. Moreover, with respect to Lavoisier's chemistry, there were other problems available, so that chemists could, as it were, put the question of acidity "on the back shelf"<sup>47</sup>. Few indeed were the chemists and popularizers who expressed concern before 1810 regarding the oxygen theory of acidity.

Only a very few chemical writers were sufficiently impressed by the type of evidence adduced by Berthollet to express dissatisfaction with Lavoisier's acid theory between 1790 and 1810. The reservations and objections of these chemists and popularizers are in the nature of minority view, to be sure, but they serve to underline further Kuhn's point that scientists will not abandon a particular theory unless there is an alternative. Samuel Parkes in the first edition of his highly popular *Chemical Catechism*<sup>48</sup> acknowledged that Lavoisier's acid theory was applicable to most acids, but also noted Berthollet's objections<sup>49</sup>. He was more critical of the oxy-acid theory in the edition of 1807. He added to his earlier remarks on the properties of sulfuretted hydrogen the following comment: "As sulphuretted hydrogen gas in formed without oxygen, and yet possesses strong acid properties, it seems to overthrow the doctrine of Lavoisier..."<sup>50</sup>. He did not, however, go on to repudiate that theory. Richard Chenevix, who carried out a number of compositional studies, referred to the properties of prussic acid and sulfuretted hydrogen and to the behaviour of muriatic acid to support his contention that serious flaws were discernible in this "law of the French chemistry." Rather than opting for an abandonment of that "law", however, he suggested only that the whole question of acidity and oxygen be subjected to further study, though he himself offered no new data on this issue<sup>51</sup>. Martin Heinrich Klaproth, one of the more noted analytical chemists of the period, summarized many of the experimental arguments against the oxygen theory of acidity such as the non-acidity of water and the acidity of prussic acid and sulfuretted hydrogen. He recognized the superiority of Lavoisier's definition of an element to his acid theory for determining composition, and on that basis questioned the extension of the acid theory to the undecomposed acids. In fact, he placed Lavoisier's acid theory squarely within the "principles" tradition of

<sup>47</sup> Kuhn, *Scientific Revolutions*, p. 81.

<sup>48</sup> 9 editions between 1806 and 1819, 12 editions in all.

<sup>49</sup> *A Chemical Catechism for the Use of Young People*, London 1806; e.g., pp. 218, 226 and 243.

<sup>50</sup> *A Chemical Catechism*, 2nd ed., London 1807, p. 308 n.

<sup>51</sup> R. Chenevix, *Observations and Experiments upon oxygenized and hyperoxygenized muriatic Acid; and upon some Combinations of the muriatic Acid in its three States*, Philosophical Transactions 1802, pp. 126—167; reference to pp. 165—166.

chemical explanation. He closed his discussion by warning "it cannot be concluded that if a substance is acidic, it must contain some oxygen"<sup>52</sup>. Despite the critical tone of his discussion, however, he did not specifically suggest the abandonment of Lavoisier's theory. The remarks of William Henry typify the difficulties besetting those chemists who heeded the body of research contradicting the compositional dictates of the oxy-acid theory. He agreed that prussic acid and sulfuretted hydrogen possessed some of the characteristics of acids, but then stated: "All the acids, which have hitherto been decomposed, agree in containing oxygen, which has been considered as the general principle of acidity"<sup>53</sup>. The connection between acidity and oxygen required qualification, he acknowledged, in light of Davy's discovery of oxygen in the fixed alkalis<sup>54</sup> but he closed with the ambiguous comment: "Notwithstanding this limitation...many of the most remarkable qualities of the acids depend on their containing oxygen"<sup>55</sup>.

Thomas Thomson's animadversions on acidity strengthen further the argument that the lack of a suitable alternative theory was a significant obstacle to the abandonment of Lavoisier's. Thomson's *System of Chemistry* of 1802 reveals his keen awareness of the flaws of Lavoisier's view. After referring to the experimental results conflicting with it, he quite precisely summarized the dilemma which faced those chemists who accepted oxygen as the acidifying principle:

If we lay it down as an axiom that oxygen is the acidifying principle, we must either include among acids a great number of bodies which have not the smallest resemblance to those substances which are at present reckoned acids, or exclude from the class several bodies which have the properties of acids in perfection. The class of acids being perfectly arbitrary, there cannot be such a thing as an acidifying principle in the most extensive sense of the word<sup>56</sup>.

Thomson sought to escape this dilemma in 1804. He repeated his earlier criticisms of the oxygen theory of acidity<sup>57</sup> and offered as an operational alternative a reclassification of acids into three groups: products of combustion<sup>58</sup>, supporters of combustion<sup>59</sup>, and combustible acids, the

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<sup>52</sup> M. H. Kaproth and F. B. Wolff, *Chemisches Wörterbuch*, vol. I, Berlin 1807, pp. 24, 25.

<sup>53</sup> W. Henry, *The Elements of Experimental Chemistry*, 6th ed. (of An Epitome of Chemistry), 2 vols., London 1810; reference to vol. 1, p. 396.

<sup>54</sup> Davy's discovery of oxygen in potash and soda occasioned surprisingly little comment with respect to Lavoisier's acid theory. For a brief study see Le Grand, *Fixed Alkalis*, pp. 63—65.

<sup>55</sup> Henry, *Elements*, vol. 1, pp. 309.

<sup>56</sup> T. Thomson, *A System of Chemistry*, 4 vols., Edinburgh 1802; reference to vol. 2, pp. 3—5.

<sup>57</sup> T. Thomson, *A System of Chemistry*, 2nd ed., 4 vols., London 1804; reference to vol. 2, pp. 2—5.

<sup>58</sup> *Ibid.*, vol. 2, p. 7.

<sup>59</sup> *Ibid.*, vol. 2, p. 56.

latter class being subdivided into four "orders"<sup>60</sup>. He claimed that Lavoisier's theory applied to the first two classes and to the first three of the four "orders" of the third class, and to one of the three acids in the fourth "order", leaving only prussic acid and sulfuretted hydrogen as "anomalous" acids. In 1807, still uncomfortable with Lavoisier's theory, he offered another operational alternative: Berthollet's definition of an acid as simply that which combines with and neutralizes an alkali<sup>61</sup>. He did not, however, go on to accept either Berthollet's theory of acidity or his general system of chemical activity of which it was a part. Berthollet's definition was useful, for it avoided the compositional entanglements of Lavoisier's acid theory, but the theory of acidity based upon that definition was for Thomson not an acceptable alternative<sup>62</sup>.

As of 1810, then, several chemists expressed considerable concern as to the validity of the oxygen theory of acidity but stopped short of rejecting it completely. One might conjecture that for them, the objections of Berthollet and the discovery of oxygen in the fixed alkalies by Davy had produced a "crisis state", but as yet there was no satisfactory alternative to Lavoisier's acid theory<sup>63</sup>. The next decade, however, witnessed not only the accumulation of additional evidence incompatible with the oxygen theory of acidity, but also the appearance of an acceptable alternative theory.

Humphry Davy's work on muriatic acid and chlorine has often been pointed to as the final nail in the coffin of the oxygen theory of acidity, but this is a somewhat simplistic view. Davy, perhaps more than any other chemist of the day, saw the value of Lavoisier's definition of an element and used it to attack what he regarded as the flaws in Lavoisier's system such as the oxygen theory of acidity, about which his doubts may date to as early as 1799<sup>64</sup>. His elegant experiments led him

<sup>60</sup> *Ibid.*, vol. 2, p. 111.

<sup>61</sup> T. Thomson, *A System of Chemistry*, 3rd ed., 5 vols., Edinburgh 1807; reference to vol. 2, p. 155. Cf., Berthollet, *Statique Chimique*, vol. I, p. 73.

<sup>62</sup> Principally because of the connection of Berthollet's system with indefinite proportions and the seeming impossibility of reconciling it with Dalton's new atomic theory.

<sup>63</sup> On criterion of a "crisis state" as defined by Kuhn is the appearance of numerous articulations and *ad hoc* modifications of the accepted theory in order to eliminate apparent inconsistencies between theory and fact (Kuhn, *Scientific Revolutions*, p. 78). Though the period after 1810 is noteworthy for such attempts, the appearance of not only Berthollet's acid theory but also that of Amedeo Avogadro (*Idées sur l'acidité et l'alcalinité*, "Journal de Physique", 1809, 59, pp. 142—148) as well as classification schemes such as that of Thomson suggest the existence of a "crisis state" in acid theory for some chemists prior to 1810.

<sup>64</sup> See, for example, J. A. Paris, *The Life of Humphry Davy*, 2 vols., London 1831; reference to vol. 1, p. 49. J. Davy, *Memoirs of the Life of Sir Humphry Davy* (vol. 1 of The Collected Works of Humphry Davy, ed. John Davy, 9 vols., London 1839—1840), p. 33. R. Siegfried, Introduction to the facsimile ed. of Davy's *Collected Works*, Johnson Reprint, New York: 1972 and *The Mind of Humphry Davy*, "Proceedings of the Royal Institution of Great Britain", 1968, 43 (200), pp. 1—21.

to regard oxymuriatic acid, by Lavoisier's own elemental definition, as a simple body, chlorine, and to regard muriatic acid as a compound of hydrogen and chlorine<sup>65</sup>. Two further "counterinstances" were provided by his work on iodine and hydroionic acid [HL]<sup>66</sup> and by that of J. L. Gay-Lussac on cyanogen [C<sub>2</sub>N<sub>2</sub>] and prussic acid which confirmed Berthollet's earlier analysis<sup>67</sup>. This array of fresh experimental evidence was not, however, sufficient per se to cause chemists to abandon immediately Lavoisier's acid theory. What to one man might seem an anomaly or even a "counterinstance" may well seem to another to be a difficult, though not insoluble, problem. John Murray, fearing that Davy's work would lead directly "to the subversion of the established chemical system, and to an entire revolution in some of the most important doctrines of the sciences"<sup>68</sup> attempted to refute Davy's conclusions<sup>69</sup>. Another writer, identified only as "F.D.", was concerned lest the recent discoveries result in the "too inconsiderate rejection of a theory, beautiful on account of its unity and implicity"<sup>70</sup>. J. J. Berzelius strenuously opposed Davy's opinion until shortly before 1822<sup>71</sup>. Generally, however, the debate between the critics and supporters of the oxy-acid theory was neither particularly acrimonious nor protracted<sup>72</sup>. It may be that many chemists simply set aside the whole matter in favor of more promising lines of research such as those associated with Daltonian atomism.

Those who, influenced by the new discoveries, did abandon Lavoisier's theory simultaneously espoused an alternative. Henry, perhaps influenced by Murray's speculations, inclined to the view that acidity sometimes depended on oxygen, sometimes on hydrogen, and in other cases on the "combined operations" of hydrogen and oxygen<sup>73</sup>. Gay-Lussac, in his

<sup>65</sup> H. Davy, *Researches on the Oxymuriatic Acid, its Nature and Combinations; and on Elements of the Muriatic Acid.*, Collected Works, vol. 5, pp. 284—311. See also H. E. Le Grand, *Ideas on the Composition of Muriatic Acid and their Revelance to the Oxygen Theory of Acidity*, "Annals of Science", 1974, 31, pp. 213—225.

<sup>66</sup> H. Davy, *Some Experiments and Observations on a New Substance which becomes a Violet-Coloured Gas by Heat, and Further Experiments and Observations on Iodine*, Collected Works, vol. 5, pp. 437—456, and 457—477.

<sup>67</sup> J. L. Gay-Lussac, *Recherches sur l'acide prussique*, "Annales de Chimie", 1815, 95, pp. 135—231.

<sup>68</sup> J. Murray, *Observations and Experiments on the Nature of Oximuriatic Acid*, "Nicholson's Journal", 1811, 28, pp. 132—152; quote from p. 133.

<sup>69</sup> Cf. W. Henry, *The Elements of Experimental Chemistry* 7th ed., 2 vols., London 1815, vol. 1, p. 266.

<sup>70</sup> F. D. *On the Production of Hyperoximuriate of Potash, considered with respect to Mr. Davy's Ideas of the Nature of Oximuriatic Acid*, "Nicholson's Journal", 1811, 28, pp. 313—314.

<sup>71</sup> J. J. Berzelius, *On the Nature of Muriatic Acid*, "Thomson's Annals of Philosophy", 1813, 1, pp. 254—260, J. R. Partington, *History*, vol. 4, pp. 143 and 168.

<sup>72</sup> For a very brief account of the controversy, see Partington, *History*, vol. 4, pp. 55—56.

<sup>73</sup> W. Henry, *The Elements of Experimental Chemistry*, 8th ed., 2 vols., London 1818; reference to vol. 1, pp. 276—278.

own paper on iodine, argued that while oxygen was the most usual acidifying principle, on occasion chlorine, iodine, sulfur, and nitrogen could act as acidifying agents while hydrogen acted as an alkalizing principle<sup>74</sup>. Thomson in 1817 took the following stand: "Lavoisier's hypothesis can now have few or no supporters and the opinion of Berthollet, respecting the nature of acidity, promises fairest to be the true one"<sup>75</sup>. Davy himself suggested in 1810 that chlorine could be regarded as "a peculiar acidifying and dissolving principle" which could form an acid upon combination with hydrogen<sup>76</sup>. This suggestion could be interpreted as a minor modification of Lavoisier's "principles" approach. Subsequently, however, he put forth the vague notion that acidity "seems to depend upon peculiar combinations of matter, and not only any peculiar elementary principle"<sup>77</sup>. None of these theories and articulations were, at the time, fully satisfactory, though many chemists adopted one or another of them. By 1815 it seems clear that a "crisis state" with regard to acidity existed for many chemists.

From this confusion gradually emerged a theory which preserved a role for oxygen in acid formation but which also answered the experiment-based objections to the view that oxygen was the unique acid-former. The new explanation of acidity is foreshadowed by Davy's electrochemical speculations. In 1808 Davy associated electrical states with chemical properties, noting that "acids are uniformly negative, alkalies positive; and inflammable substances highly positive; and as I have found, acid matters when positively electrified, and alkaline matters when negatively electrified, seemed to lose all their peculiar properties and powers of combination"<sup>78</sup>. Davy's description of iodine, chlorine, and fluorine, together with oxygen, as electronegative "undercompounded bodies" which can form acids is additionally suggestive<sup>79</sup>. Other chemists, most notably J. J. Berzelius, went on to erect a comprehensive theory of chemical activity which, as one ramification, replaced Lavoisier's acid

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<sup>74</sup> J. L. Gay-Lussac, *Mémoire sur l'iode*, "Annales de Chimie", 1814, 91, pp. 1—160; reference to pp. 133—159. Of interest is Davy's rebuttal: *On the Analogies Between the Undecomposed Substances, and on the Constitution of Acids*, Collected Works, vol. 5, pp. 510—516.

<sup>75</sup> T. Thomson, *A System of Chemistry*, 5th ed., 4 vols., London, 1817; reference to vol. 2, p. 72.

<sup>76</sup> Davy, *Researches on the Oxymuriatic Acid*, p. 297.

<sup>77</sup> Davy, *Violet-Coloured Gas*, p. 456. See further on this point R. Siegfried, *Sir Humphry Davy on the Nature of the Diamond*, "Isis", 1966, 57, pp. 325—335 and especially Trevor H. Levere, *Affinity and Matter: Elements of Chemical Philosophy 1800—1865*, Clarendon Press, Oxford 1971, pp. 23—67.

<sup>78</sup> H. Davy, *Electro-Chemical Research on the Decomposition of the Earths; with Observations on the Metals Obtained from the Alkaline Earths, and the Amalgam Procured from Ammonia*, Collected Works, vol. 5, pp. 102—139; reference to p. 137.

<sup>79</sup> Davy, *Violet-Coloured Gas*, pp. 453—456.



theory<sup>80</sup>. Oxygen in the new view continued to be of major importance. It was the most electronegative element. Consequently, in a number of its combinations its electronegativity was not fully "saturated" and these compounds were acidic. In the instance of water and most of the metal oxides, however, the electropositivity of hydrogen and the metals was sufficient to offset the electronegativity of oxygen and these compounds were not acidic. Finally, other electronegative substances such as sulfur, chlorine, iodine, fluorine, and, in some schemes, nitrogen could form acidic compounds provided their electronegativity were not saturated on combining. Thomas Thomson succinctly phrased the new theory some years after its establishment: "Acids are compounds of electro-negative bodies and a base, and in them the electro-negative electrocity continues to predominate"<sup>81</sup>. The new electrochemical theory of acidity thus reinterpreted the role of oxygen in the formation of many acids, provided a rationale for the non-acidity of some oxygen compounds, and, finally, accounted for the properties of those acids which did not contain oxygen. The theory that oxygen was the unique acid-former was at last replaced.

This brief study indicates the value of Kuhn's schema of scientific change and provides a further illustration of the conservative character of paradigm-directed science. The acceptance of Lavoisier's ingenious system, so successful in some areas of chemistry, led to a rather dogmatic adherence to his erroneous acid theory on the part of most of his followers even in the face of what would appear to be numerous "counterinstances" adduced by Berthollet. In accord with Kuhn's model, this adherence is faithfully reflected in the textbooks of the time. Beginning particularly with Davy's discovery of oxygen in the fixed alkalies and culminating with his research on chlorine and iodine, as well as that of Gay-Lussac on cyanogen, a growing sense of "crisis" was manifested in the proliferation of competing acid theories and modifications of the oxy-acid theory. Finally, the oxygen theory of acidity gave way to a wholly new electrochemical theory of chemical activity, including acidity — a theory which still gave pride of place in acidity to oxygen, but which also accounted for the anomalies confronting the older theory. In conclusion, though there are aspects of Kuhn's scheme which are contestable, in broad outline it provides a useful tool for the analysis of not only major theoretical shifts such as the "Copernican Revolution" but also of shifts within a small area of a particular science such as acidity theory.

<sup>80</sup> Useful discussions of these electrochemical developments include Colin A. Russell, *The Electrochemical Theory of Berzelius*, "Annals of Science", 1963, 19, pp. 117—145; his introduction to J. J. Berzelius, *Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité*, Johnson Reprint, New York 1972; and Levere, *Affinity and Matter*, pp. 140—157.

<sup>81</sup> T. Thomson, *The History of Chemistry*, 2 vols., London 1831; reference to vol. 2, p. 270.