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THE UNIVERSITY OF OKLAHOMA GRADUATE COLLEGE

THE ELECTRICAL DECOMPOSITION OF WATER: A CASE STUDY IN CHEMICAL AND ELECTRICAL SCIENCE, 1746-1800

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

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BY

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Norman, Oklahoma
1976

THE ELECTRICAL DECOMPOSITION OF WATER: A CASE STUDY IN CHEMICAL AND ELECTRICAL SCIENCE, 1746-1800

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DISSERTATION COMMITTEE

APPROVED BY

PREFACE

Because one of the theories discussed in this dissertation placed great emphasis on reforming language as a means to reform science, close attention has been paid to the strict quotation of original sources, even when the eighteenth-century term or its spelling varies with the more modern form (for instance, centry instead of sentry). Likewise, foreign words are accented only when they are accented in the original. For this reason the use of <u>sic</u> would be cumbersome and it has been used only where the meaning would not be clear otherwise.

Moreover, no attempt has been made, either in the text or the translation of quotations, to translate eighteenth-century chemical or electrical terminology into modern equivalents. Indeed, if, as Lavoisier believed, language is essential to the concepts it expresses, as to modernize eighteenth-century terminology would be to obscure its historical import. For those desirous of identifying the archaic names of chemical compounds with more modern terminology, consult the table of nomenclature in either Louis-Bernard Guyton de Morveau's Method of Chemical Nomenclature, Proposed by Messrs. De Morveau, Lavoisier, Bertholet, and De Fourcroy To which Is Added, a New System of Chemical Characters, Adapted to the New Nomenclature, by Mess. Hassenfratz and Adet, trans.

James St. John (London: For G. Kearsley, 1788), p. 78 or "Chemistry,"

Encyclopedia Britannica, 3rd ed. (1797), vol. 4, pp. 598-599. Unless otherwise noted, all translations are my own.

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THE ELECTRICAL DECOMPOSITION OF WATER: A CASE STUDY IN CHEMICAL AND ELECTRICAL SCIENCE, 1746-1800

CHAPTER I

CRUCIAL EXPERIMENTS AND THE ELECTRICAL DECOMPOSITION OF WATER

Although the crucial experiment in science has been questioned at least since Pierre Duhem (1861-1916) declared "L' 'Experimentum crucis' est impossible en Physique," the importance historically of the concept of crucial experiment cannot be questioned. The emphasis upon experiment as a means to discover truth may be traced, as it was by Duhem, to the Novum organum scientiarum of Francis Bacon (1561-1626), who in his discussion of the true path to knowledge emphasized experience and identified crucial instances of experiences. According to Bacon:

these <u>Crucial Instances</u> shew the true and inviolable Association of one of these Natures to the Nature sought; and the uncertain and separable Alliance of the other: whereby the Question is decided; the former Nature admitted for the Cause; and the other rejected.

107. These <u>Instances</u> therefore afford great Light, and have a kind of over-ruling Authority; so that the Course of <u>Interpretation</u> will sometimes terminate in them, or be finished by them. Sometimes, indeed, these <u>Crucial Instances</u> occur, or are found, among those already set down; but in general they are new, and expressly and

¹Pierre Duhem, <u>La théorie physique</u>: <u>son objet et sa structure</u>, Bibliothèque de philosophie expérimentale II (Paris: Chevalier & Rivière, 1906), p. 308. "The 'Experimentum crucis' is impossible in physics."

purposely sought and applied, or after due Time and Endeavors, discovered, not without great Diligence and Sagacity.

Thus, to Bacon, experiment in the form of "Crucial Instances . . . new and purposely sought and applied" was the highest form of experience and provided the means to decide between competing explanations of

In the tradition of Bacon's emphasis upon experience, Robert
Boyle (1627-1691) wrote, "I look upon experimental truths as matters of
. . . great concernment to mankind" Boyle believed that:
much may be done towards the improvement of philosophy by a due

much may be done towards the improvement of philosophy by a due consideration of, and reflexion on, the obvious phaenomena of nature, and those things, which are almost in every body's power to know, if he pleases but seriously to heed them; and I make account, that attention alone might quickly furnish us with one

Francis Bacon, Novum Organum Scientiarum: A New Machine for Rebuilding the Sciences; or a Particular Logick for Discovering Arts, and Interpreting the Works of Nature, in The Philosophical Works of Francis Bacon, ed. Peter Shaw, 3 vols. (London: for J. J. and P. Knapton, et al.), vol. 2, p. 493. The passage does not differ significantly in The Philosophical Works of Francis Bacon, ed. with notes by Ellis and Spedding (London: George Routledge and Sons Limited, 1905), p. 343. A Latin edition of 1660, Novum organum scientiarum, 2nd ed. (Amstelaedami, Joannis Ravesteiny, 1660), p. 255, reads: "Instantia Crucis oftendunt consortium unius ex Naturis (quoad Naturam Inquisitam) fidum & indissolubile, alterius autem varium & separabile; unde terminatur quaestio, & recipitur Natura illa prior pro Causa, missa altera & repudiata. Itaque hujusmodi Instantiae sunt maximae lucis, & quasi magnae authoritatis; ita ut Curriculum Interpretationis quandoque in illas definat, & per illas perficiatur. Interdum autem Instantia Crucis illae occurrunt & inveniuntur inter jam pridem notatas; At ut plurimum Novae sunt, e de Industria atque ex Composito quaesitae & applicatae, & diligentia sedula & acri tandem erutae."

³Robert Boyle, A Proemal Essay, Wherein, With Some Considerations Touching Experimental Essays in General, Is Interwoven Such an Introduction to All Those Written by the Author, As Is Necessary to Be Perused for the Better Understanding of Them, in The Works of the Honourable Robert Boyle. To Which Is Prefixed the Life of the Author, [ed. Thomas Birch], 6 vols. (London: For J. & F. Rivington, et al., 1772), vol. 1, p. 299.

half of the history of nature, as well as industry is requisite, by new experiments, to enrich us with the other.

On more than one occasion Boyle appealed to experimentation to either illustrate or confirm his ideas, 5 and in the spirit of Bacon's crucial instance, Boyle believed that one could use experiment to decide between competing theories. 6

An influential model for eighteenth-century natural philosophers was found in the optical writings of Isaac Newton (1642-1727). In a letter published in the 1671/72 Philosophical Transactions, Newton argued that his experiment using two prisms to disperse and recompose light was an "Experimentum Crucis" on the nature of light. 7

In 1749, Benjamin Franklin (1706-1790), who was greatly influenced by Newton's emphasis on experiment, 8 proposed an experiment

⁴<u>Ibid</u>., p. 306.

⁵ Tbid., pp. 301, 302, 303, and Boyle, Some Specimens of an Attempt to Make Chymical Experiments Useful to Tilustrate the Notions of the Corpuscular Philosophy, in Works, vol. 1, p. 356, 359. Boyle, The Sceptical Chymist: or Chymico-Physical Doubts and Paradoxes, Touching the Experiments, Whereby Vulgar Spagyrists Are Wont to Endeavour to Envince Their Salt. Sulphur and Mercury, to be the True Principles of Things, in Works, vol. 1, p. 459.

⁶Boyle, <u>Some Specimens of an Attempt</u>, pp. 355, 356 and Boyle, A Proëmial Essay, pp. 301-302.

⁷ Isaac Newton, "A Letter of Mr. Isaac Newton, Professor of the Mathematicks in the University of Cambridge; Containing His New Theory About Light and Colors: Sent by the Author to the Publisher from Cambridge, Febr. 6, 1671/72; in Order to be Communicated to the R. Society," Philosophical Transactions No. 80 (Feb. 1671/72), p. 3078.

See I. Bernard Cohen, <u>Franklin and Newton: An Inquiry into Speculative Newtonian Experimental Science and Franklin's Work in Electricity as an Example Thereof</u> (Philadelpha: American Philosophical Society, 1956), pp. 317-318.

that he believed would demonstrate conclusively whether electricity and lightning were the same.

21. To determine the question, whether the clouds that contain lightning are electrified or not, I would propose an experiment to be try'd where it may be done conveniently. On top of some high tower or steeple, place a kind of centry box (as in Fig. 9) big enough to contain a man and an electrical stand. From the middle of the stand let an iron rod rise. . . 20 or 30 feet, pointed very sharp on the end. If the electrical stand be kept clean and dry, a man standing on it when such clouds are passing low, might be electrified and afford sparks, the rod drawing fire to him from a cloud. 9

Implicit in Franklin's proposal and in his emphasis on experiment is an acceptance of the crucial role of experiment in science. When Franklin was informed that his experiment had been performed in Europe and the results supported his belief that lightning was electricity, he wrote a description of the Philadelphia or kite experiment 10 and concluded "the sameness of the electric matter with that of lightening [is] completely demonstrated."11

The definition of experiment in three well-known encyclopedias of the eighteenth century also illustrates an emphasis on the role of experiment to demonstrate or discover truth. The Encyclopédie definition of "Expérience" reads "En Physique le mot expérience se dit des épreuves que l'on fait pour découvrir les différentes opérations & le méchanisme de la Nature." The definition of "Experiment" in the first edition of

Benjamin Franklin, Experiments and Observations on Electricity, Made at Philadelphia in America, by Benjamin Franklin, L.L.D. and F.R.S. To Which Are Added, Letters and Papers on Philosophical Subjects, 4th ed. (London: For David Henry, 1769), p. 66.

^{10&}lt;sub>Ibid.</sub>, pp. 111-112.

^{11&}lt;sub>Ibid., p. 112.</sub>

¹² César-Chesneau Dumarsais, "Expérience," Encyclopédie, ou

the Encylopedia Britannica, published in 1771, reads:

EXPERIMENT, in philosophy, is the trial of the result or effect of the applications and motions of certain natural bodies, in order to discover something of their motions and relations, whereby to ascertain some of their phaenomena, or causes.

In addition to the same definition of experiment, the second edition of the Encyclopedia Britannica, published in 1779, included a definition of a term not defined in the first edition, "Experimentum Crucis," and defined it in much the same manner that Bacon defined crucial instance. 14

Ephraim Chambers' Cyclopaedia defined "experiment" as

in <u>Philosophy</u>, a trial of the effect or result of certain applications and motions of natural bodies, in order to discover something of the laws and relations thereof, or to ascertain some phenomenon, or its cause. 15

Chambers' Cyclopaedia also defined "Experimentum Crucis" as "a capital, leading, or decisive experiment." 16

dictionnaire raisonné des sciences, des arts et des métiers, par une societé de gens de lettres, ed. Diderot & d'Alembert (Paris: Chez Briasson et al., 1751-1765), 6:297. "In physics the word experiment refers to the tests one makes in order to discover the different operations and the mechanism of nature."

^{13&}quot;Experiment," Encyclopedia Britannica; or, A Dictionary of Arts and Sciences, Compiled upon a New Plan, 1st ed. (Edinburgh: For A. Bell and C. Macfarquhars, 1771), 2:554.

^{14&}quot;Experimentum Crucis," Encyclopedia Britannica, or, A

Dictionary of Arts, Sciences, &c., 2nd ed. (Edinburgh: For J. Balfour

et al., 1779), 4:2887.

¹⁵ Ephraim Chambers, "Experiment," Cyclopaedia: or, an Universal Dictionary of Arts and Sciences, new ed. with supplement and rev. by Abraham Rees, 4 vols. (Dublin: by John Chambers, 1778-1787), 2:[5G2 verso].

¹⁶ Chambers, "Experimentum crucis," Cyclopaedia, new ed. (1778-1787), 2:[5G2v.].

The concept of experiment in natural philosophy in the eighteenth century was so influential that definitions of experimental philosophy were printed in both French and English encyclopedias. The Encyclopédie reads, "On appelle Philosophie expérimentale, celle qui se sert de la voie des expériences pour découvrir les lois de la Nature."17 The first edition of Encyclopedia Britannica reads, "Experimental Philosophy, that philosophy which proceeds on experiments, which deduces the laws of nature, and the properties and powers of bodies, and their actions upon each other, from sensible experiments and observations." 18 In the second edition, the definition was enlarged to include: "It is not very long since this science has been known to the world Natural Philosophy has been, for these 50 centuries, nothing more than a confused heap of systems " Once experimental natural philosophy was introduced, "the true physics was brought to light Instead The definition of experimental philosophy in Chambers' Cyclopaedia includes the following comment on experiments in the eighteenth century:

<u>experiments</u>, within the last century, are come into such a vogue that nothing will pass in philosophy but what is founded on, or confirmed by, <u>experiment</u>; so that the new philosophy is almost altogether <u>experimental</u>.²⁰

¹⁷ Jean Le Rond d'Alembert, "Expérimental," Encyclopédie, 6:298. "One calls experimental philosophy that which seeks by the way of experiments to discover the laws of nature."

^{18&}lt;sub>"Experimental Philosophy," Encyclopedia Britannica, 1st ed. (1771), 2:554.</sub>

^{19&}quot;Experimental Philosophy," Encyclopedia Britannica, 2nd ed. (1779), 4:2883-2884.

²⁰ Chambers, "Experimental Philosophy," Cyclopaedia, new ed. (1778-1787), 2:[5G2v.].

It was in this tradition of emphasizing experiment as a path to truth and as a means to decide between theories that Antoine-Laurent Lavoisier (1743-1794) sought to convince others of the validity of his new chemical theory. In the preface to his <u>Traité élémentaire de chimie</u> Lavoisier wrote of the errors of traditional chemistry:

Le seul moyen de prévenir ces écarts, consiste à supprimer ou au moins à simplifier autant qu'il est possible le raisonnement, qui est de nous & qui seul peut nous égarer; à le mettre continuellement à l'épreuve de l'expérience; à ne conserver que les faits qui ne sont que des donneés de la nature, & qui ne peuvent nous tromper; à ne chercher la vérité que dans l'enchaînement naturel des expériences & des observations. je me suis imposé la loi de ne procéder jamais que du connu à l'inconnu, de ne déduire aucune conséquence qui ne 21 dérive immédiatement des expériences & des observations. . . .

Thus Lavoisier, as had Newton, signaled his allegiance to the tradition that expérience was the test of theories and the path to the truth. One of the best examples of his reliance on descriptions of expériences to explicate the truth and the mode of deciding between competing theories is found in his "Expériences sur la respiration des animaux." In it Lavoisier argued:

Quelque vraisemblable qu'ait pu paroitre, au premier coup-d'oeil, la théorie de ce célèbre Physicien [Priestley], quelque nombreuses & quelque bien faites que soient les expériences sur lesquelles il a cherché à l'appuyer, j'avoue que je l'ai trouvée en

does not derive immediately from expériences and observations."

contradiction avec un si grand nombre de phénomènes, que je me suis cru en droit de la révoquer en doute: j'ai travaillé en conséquence sur un autre plan, & je me suis trouvé invinciblement conduit, par la suite des mes expériences, à des conséquences toutes opposées aux siennes. 22

The previous examples illustrate the influence of the concept of the crucial experiment upon investigators during the seventeenth and eighteenth centuries. However, several questions must be answered before one can determine the full extent of this influence. What was the role of experiment in deciding between competing theories, in discovering new phenomena, and in forming new theories in eighteenth-century science? A partial answer to these questions and an understanding of the historical significance of "crucial experiments" in eighteenth-century science may be obtained from the examination of a particular series of experiments spanning the last half of the eighteenth century. These experiments centered around the transmission

²²Lavoisier, "Expériences sur la respiration des animaux, et sur les changemens qui arrivent à l'air en passant par leur poumon. Par M. Lavoisier," Histoire de l'Académie Royale des Sciences. Année M.DCCLXXVII. Avec les mémoires de mathématique & de physique, pour la même année, tirés des registres de cette Académie. Mémoires (1780), p. 186. (Mémoires portion of this journal hereinafter referred to as Mémoires de l'Académie des Sciences.) "However likely the theory of this celebrated physicist [Priestley] might have seemed at first glance, however numerous and however well executed the expériences may be on which he seeks to support it, I vow that I have found it to be in contradiction with so great a number of phenomena that I believed myself right to call it into doubt: I have fashioned another plan as a consequence, and I have found myself invincibly led, as a result of my expériences, to consequences completely opposed to his."

²³ For examples of recent discussions of the philosophical implications of the concept of crucial experiments, see Peter K. Machamer, "Feyerabend and Galileo: The Interaction of Theories, and Reinterpretation of Experience," Studies in the History and Philosophy of Science 4 (May 1973):1-46; and Imre Lakatos, "The Role of Crucial Experiments in Science," Studies in the History and Philosophy of Science 4 (Feb. 1974): 309-325. See also Stephen E. Toulmin, "Crucial Experiments: Priestley and Lavoisier," Journal of the History of Ideas 18 (1957):205-220.

of electricity through water and provided and were used to select between two competing chemical theories and between two competing electrical theories as well.

In 1789, the same year that Lavoisier's <u>Traité élémentaire de chimie</u> was published, two Dutch chemists, Adrian Paets van Troostwijk (1752-1837) and Jan Rudolph Deiman (1743-1808), published an account of experiments that they believed demonstated the compound nature of water and thus proved the truth of Lavoisier's new chemical theory. 24 The experiments that they described fit into the eighteenth-century tradition of crucial experiments, for Deiman and Paets van Troostwijk claimed that prior to their experiments there was no convincing basis for deciding between the phlogiston theory and Lavoisier's theory.

Although they considered Lavoisier's explanation of the formation of water from the ignition of two gases plausible, Deiman and Paets van Troostwijk did not consider his explanation conclusively demonstrated.

Quelque persuasives que paroissent les expériences dont M. Lavoisier & la plupart des chimistes françois ont déduit de leur théorie de l'eau, il faut avouer qu'il leur manque encore quelque chose pour être absolument décisives. 25

Adrian Paets van Troostwijk and Jan Rudolph Deiman, "Lettre de Mm. Paets van Troostwyk et Deiman; à M. de La Métherie, sur une manière de décomposer l'eau en air inflammable & en air vital," <u>Observations sur la physique</u>, sur <u>l'histoire naturelle et sur les arts</u> 35 (1789):369-378. (Hereinafter referred to as "Sur une manière de décomposer l'eau." The journal is hereinafter referred to as <u>Observations sur la physique</u>.)

 $²⁵_{\underline{\mathrm{Ibid}}}$, p. 369. "However persuasive the <u>expériences</u> appear that M. Lavoisier and most of the French chemists have deduced from their theory of water, it must be admitted that they still lack something in order to be absolutely decisive."

The Dutch chemists pointed out that the appearance of the two products, acid and water, allowed differing explanations of the process.

En tout cas il semble que les adversaires de la nouvelle théorie peuvent regarder l'eau comme une substance accidentelle avec le même droit que ses défenseurs regardent comme tel l'acide obtenu. 26

Deiman and Paets van Troostwijk believed that the decomposition of water should decide the question of which explanation was correct, but they believed the experiments in which French chemists had used red-hot iron to decompose water to be inconclusive.

La décomposition de l'eau . . . décideroit cette dernière question si elle étoit parfaitement démontrée On n'a réussi jusqu'ici à décomposer l'eau qu'à l'aide du fer, substance dont on obtient par la chaleur seule cet air, qui est supposé être un élément constituant de l'eau. On pourroit donc soupçonner que l'eau ne sert dans cette expérience, qu'à dégager cet air plus facilement & en plus grande quantité du métal qui est disposé lui-même à le fournir . . . Encore cette théorie de la décomposition de l'eau est-elle entièrement fondée sur cette hypothèse, sur laquelle on n'est pas encore généralement d'accord, que la calcination des métaux est due uniquement à leur combinaison avec la base de l'air vital (oxigène). Le fait même, la calcination du métal dans cette experience, ne paroît pas parfaitement constaté. Plusieurs physiciens ont des doutes là-dessus.27

The attempts of Lavoisier to decompose water using red-hot iron

²⁶ Tbid., p. 370. "In any case, it seems that the adversaries of the new theory can regard water as an accidental substance with the same right that its defenders regard similarly the acid obtained."

²⁷ Ibid. "The decomposition of water . . . would decide this question, if it had been perfectly demonstrated. . . . Until now one succeeded in decomposing water only with the aid of iron, [a] substance with which by heat alone one obtains this air, which is supposed to be a constituent element of water. One could, therefore, suppose that water only serves in this experiment to release this air more easily and in greater quantities from the metal which is disposed likewise to furnish it. . . . Moreover, this theory of decomposition of water is entirely founded on this hypothesis, upon which there is still no general agreement, that the calcination of metals is uniquely due to their combination with the base of vital air (oxigène). The fact itself, the calcination of metal in this experiment, does not appear perfectly established. Several physicists have doubts on that."

Deiman and Paets van Troostwijk had once been among those chemists who doubted the decomposition of water. However, they had now changed their minds:

Quoique nous reconnoissions que la nouvelle théorie des chimistes françois sur la nature de l'eau n'a pas été jusqu'ici démontrée à la rigueur, & que nous avons été ci-devant nous-mêmes de sentiment opposé, nous sommes bien loin de vouloir défendre davantage l'ancien système. Au contraire, nous croyons pouvoir contribuer beaucoup à constater la vérité de la nouvelle théorie, puisque nous avons réussi à découvrir un moyen de changer l'eau en même-temps en air inflammable (gaz hydrogène) & en air vital (gaz oxigène), & par conséquent de la décomposer d'une manière qui nous paroit ne pas permettre d'attribuer ces produits à aucune autre substance.²⁸

Deiman and Paets van Troostwijk thus described their discovery as a crucial experiment that would demonstrate the composition of water and the "truth" of Lavoisier's new system of chemistry. Their description of themselves as objective experimenters whose beliefs had been changed by this discovery might fit the eighteenth-century image of the crucial experiment in its ability to lead to the "true nature sought," but it is not an accurate portrayal of what Deiman and Paets van Troostwijk did; the description of their experiments that Deiman and Paets van Troostwijk sent to the editor of Observations sur la physique reveals contrivance and bias instead of accident and objectivity.

have been described in an article by Maurice Daumas and Denis Duveen, "Lavoisier's Relatively Unknown Large-Scale Decomposition and Synthesis of Water, February 27 and 28, 1785," Chymia 5 (1959):113-129.

Deiman and Paets van Troostwijk, "Sur une maniere de décomposer 1'eau," p. 370. "Although we realized that the new theory of the French chemists on the nature of water has not hitherto been demonstrated with rigor, and that before this we ourselves had been of the opposite sentiments, we are far from wanting to defend the ancient system. On the contrary, we believe we can contribute much to establishing the truth of the new theory, since we have succeeded in discovering a means of changing water simultaneously into inflammable air (hydrogen gas) and into vital air (oxygen gas), and as a consequence, of decomposing it in a manner which does not appear to us to allow attributing these products to any other substance."

For their examination of the "commotion électrique" or the electric commotion on water, Deiman and Paets van Troostwijk had the assistance of a scientific instrument-maker, John Cuthbertson (1743/5-post 1816) who specialized in electrical instruments. The apparatus that Cuthbertson constructed for them to test the electric commotion on water was relatively simple, consisting of a glass tube one-eighth of an inch in diameter and twelve inches long. One end of the tube was hermetically sealed around a gold wire. The other end of the tube was left open and had a gold wire inserted in the opening. The ends of the wires were five-eighths of an inch apart. This tube was filled with water and then placed on end in a small glass of distilled water with the sealed end up. The gold wires were attached to an electrical machine so that the electric commotion could pass from one wire to the other wire through the water, a distance of five-eighths of an inch.

According to Deiman and Paets van Troostwijk, they initially noticed nothing unusual while passing the electric commotion through the water. However, after they increased the force of the electric commotion, each shock produced an electric spark at the extremities of the wires and each spark produced bubbles of air in the water. As the air from the bubbles collected in the top of the tube, the water gradually receded. When the water level fell below the uppermost wire, an inflammation or ignition took place, and all the air, except for a small residue, disappeared, allowing water to refill the tube. The residue could be successively diminished by repetitions of the experiment. 29

 $^{^{29}\}mathrm{Deiman}$ and Paets van Troostwijk, "Sur une manière de décomposer l'eau," pp. 371-372.

Deiman and Paets van Troostwijk believed that the inflammation indicated the presence (and thus previous production) of hydrogen and oxygen. Anticipating the phlogistic interpretations of their results, they set out to demonstrate experimentally that the electric matter did not contribute to the formation of inflammable air, and, moreover, that the vital air produced did not come from common (or atmospheric) air contained in the water or adhering to the glass tube. In other words, Deiman and Paets van Troostwijk sought to demonstrate that the air produced in the experiment came from the decomposition of water alone. In order to accomplish this demonstration, they tested the effect of the electric commotion on first vitriolic acid and then on nitric acid, using the same apparatus. Although both acids produced air, as had water, no inflammation took place after the level of the acid fell below the uppermost wire.

According to Deiman and Paets van Troostwijk, the air produced in this second experiment could therefore be one of the following components of the acids: either inflammable air or vital air alone, or an acid gas (nitrous air or vitriolic acid air). Because they believed inflammable air to be the only air which would ignite and because they expected enough impurities of common air to support ignition if inflammable air had been produced, Deiman and Paets van Troostwijk ruled out the first possibility immediately.

The results allowed Deiman and Paets van Troostwijk to reject also the possibility of the production of acid air or acid gases since such gases would soon be reabsorbed by their respective acids, while the air produced in their experiment was not thus reabsorbed. By a process

of elimination, they concluded that the air produced was probably oxygen gas. In order to be completely certain, Deiman and Paets van Troostwijk mixed the air produced from the acids with a known quantity of azote. The mixture resulted in a diminution of volume characteristic of a similar mixture of nitrous air and oxygen. The absence of the production of hydrogen from acids allowed the authors of the experiment to infer that the electric spark did not materially contribute to the production of hydrogen, but instead served as an agent capable of separating hydrogen from water or oxygen from acids.

il nous paroît démontré, que la commotion électrique ne fait aucun autre effet sur l'eau, que de disposer la base de l'air inflammable (l'hydrogène) à prendre l'état aériforme, de même qu'elle est cause que dans les acides la base de l'air vital (l'oxigène) prend cet état. Si elle avoit contribué en quelque chose à la formation de l'air inflammable, elle n'auroit pas dégagé des acides, de l'air vital (gaz oxigène) pur, qui en s'unissant au principe inflammable, auroit été détruit: au contraire, elle auroit dû, dans l'hypothèse d'un tel principe, produire de l'air acide vitriolique (gaz acide sulfureux) & de l'air nitreux (gaz acide nitreux). Il paroît, donc qu'on ne peut douter que l'air inflammable (gaz hydrogène) obtenu de l'eau, n'est dû qu'à l'eau seule, & n'en a été une partie constituante. 31

Because the use of water in contact with the atmosphere allowed the possibility of atmospheric air entering into the experiment, Deiman

³⁰ Ibid., p. 372.

^{31 &}lt;u>Ibid.</u>, p. 373. "It appears to us demonstrated, that the electric commotion has no other effect on water, than of disposing the base of the inflammable air (hydrogen) to take the aeriform state; likewise that it is the cause that the base of vital air (oxygen) in acids take this state. If it had contributed in any way to the formation of inflammable air, it would not have released pure vital air from acids, which in uniting to inflammable principle would have been destroyed: On the contrary it would have been obliged in the hypothesis of such a principle to produce vitriolic acid air (sulphurous acid gas) and nitrous air (nitrous acid gas) in the acids. It appears therefore, that one cannot doubt that the inflammable air (hydrogen gas) obtained from water is due only to the water alone and that it has been a constituent part."

and Paets van Troostwijk believed that a change in equipment was necessary to demonstrate that the production of vital air in this experiment could be attributed solely to the decomposition of water. In order to insure that the vital air had not come from a contamination of common air, they first tried to separate the water from the atmosphere with a layer of mercury by using a glass tube bent into an S shape, so that the mercury would rest in the lowest curve of the tube thus sealing the water in the tube from the atmosphere. However, mercury proved unsatisfactory because its weight resisted the evolvement of gas and the displacement of water. Therefore, the use of mercury was discontinued, and the experiments continued with the water exposed to the atmosphere, although the S-shaped tube was retained. Then instead of using mercury to minimize contamination, Deiman and Paets van Troostwijk reduced the surface area of the vessel in which the tube was placed, and thus reduced the amount of water open to the atmosphere. They cleared the water itself of possible air contamination by distillation and by submitting it to a vacuum under Cuthbertson's pneumatic machine (an air pump) in order to draw out any common air contained in solution. Although Deiman and Paets van Troostwijk could not eliminate possible atmospheric contamination of the water, they believed that they could further reduce such contamination by releasing the residue of air which remained in the tube after each inflammation. 32 If the successive inflammations continued even after the water had been successively purged of impurities, then such impurities could not account for the production of vital air.

³² Ibid., pp. 373-374.

Not only did the inflammations continue indefinitely, but with successive trials the residue became successively smaller. Deiman and Paets van Troostwijk reported that after the first inflammation, the residue bubble of air was one-sixteenth of an inch in diameter. They sparked this small bubble again in order to insure that the first ignition was complete. As a result the size of the bubble was reduced by half. 33 After releasing this small residue, Deiman and Paets van Troostwijk began a second production and inflammation of air. The resulting residue was only one-twentieth of an inch in diameter, and a second ignition reduced it again by half. The third production and inflammation of air resulted in a bubble of residue only one-fortieth of an inch in diameter, and it was, in the words of the authors, "très-difficile d'effectuer une seconde inflammation."34 However, by tilting the tube until the small bubble was between the two gold wires, Deiman and Paets van Troostwijk reduced the residue by a second igniton to a bubble approximately one-sixtieth of an inch in diameter that could not be re-ignited. A fourth production and inflammation of air produced a residue bubble approximately one-eightieth of an inch in diameter that could not be re-ignited. 35

The asserted precision of these measurements provided Deiman and Paets van Troostwijk with another strong argument for the decomposition of water by illustrating that impurities played an inconsequential role in the production of the airs from water. Using the first measurement

³³<u>Ibid</u>., p. 375.

³⁴ Ibid., "very difficult to effect a second inflammation."

³⁵ Ibid.

of residue as a base, each successive measurement can be thought of as a fraction of the first one-sixteenth of an inch. Thus, the final residue would only be between one-fifth and two-fifths of one-sixteenth of an inch. In spite of the attention given by the authors to the descriptions of all other aspects of the experiments, including the unsuccessful attempts to use mercury to prevent atmospheric contamination, Deiman and Paets van Troostwijk did not mention how these measurements were made. Although some of these measurements were reported as approximations, the measurement and approximation of such small quantities connotes precision. This connotation of precision provided Deiman and Paets van Troostwijk with an ad populum argument for the decisive nature of their experiments. A table can be constructed from Deiman and Paets van Troostwijk's data that illustrates the reductions in volume they obtained (see Table I).

Having thus demonstrated that impurities presumably could play no important role in the production of vital air and therefore that the vital air must have been produced from a decomposition of water, Deiman and Paets van Troostwijk summarized their case in five points:

- The explosion of the air produced indicated the presence of inflammable air, "seule espèce d'air qui est combustible, & de l'air vital, seule espèce d'air qui peut servir à la combustion."
- The diminishing residue indicated that only two species of air were produced.
- 3. The generation of vital air and the absence of the generation

 $^{^{36}}$ <u>Tbid.</u>, p. 375. "the only species of air which is combustible, & of vital air, the only species of air which can support combustion."

TABLE I

VOLUMES OF RESIDUE BUBBLES COMPUTED FROM DEIMAN
AND PAETS VAN TROOSTWIJK'S FIGURES^a

Inflammation	Bubble Diameter in Inches	Ratio to 1/16 Inch	Volume in Cubic Inches
lst	1/16	1	.000128190
lst re-ignition	1/32	1/2	.000015980
2nd	1/20	4/5	.000065453
2nd re-ignition	1/40	2/5	.000008182
3rd	1/40	2/5	.000008182
3rd re-ignition	1/60	between 1/5 and 2/5	.000002424
4th	1/80	1/5	.000001023

 $^{^{\}mathrm{a}}$ No such table exists in the original article.

of hydrogen from acid indicated that the hydrogen came from water and not from the electric spark.

- 4. Since the residues were diminished, and the inflammations could be continued repeatedly, the vital air was not produced from the limited amount of common air contained in the water.
- 5. Finally, the experiment not only analyzed water, but also synthesized it without the usual acid impurities. According to Lavoisier's new system of chemistry, the acid product occurring in the synthesis of water was due to the impurities in the gases used to synthesize water, while gases produced from water contained no such impurities. 37

Although Deiman and Paets van Troostwijk had presented their case in explicit detail, they found it necessary to conclude their article with a discussion of the problem of acid sometimes produced in the synthesis of water. The authors stated that if the gases used in the synthesis of water were contaminated with azote, another component of common air, the azote might also combine with oxygen and form nitrous air. Nitrous air would then be absorbed by the water to form traces of acid. However, based on the supposition that vital air had a greater affinity for inflammable air than it did for azote, Deiman and Paets van Troostwijk stated that if the quantity of oxygen did not exceed the quantity of hydrogen such impurities would never result. If the quantity of oxygen did exceed that of hydrogen, then the surplus oxygen would unite with the azote impurities and thus give traces of acid. Deiman and Paets van Troostwijk referred to the differing results of Henry Cavendish

³⁷ Ibid., pp. 375-376.

(1731-1810) and Joseph Priestley (1733-1804) to illustrate this last point. 38

Thus in Deiman and Paets van Troostwijk's arguments that their discovery of the electrical production of hydrogen and oxygen from water was a new and conclusive demonstration of the decomposition of water and of the antiphlogistic system, they not only appealed to their experimental techniques and their quantitative experimental findings, but they also (in what may have been a tactic designed to appeal to their reader's biases concerning the nature of experiment and scientific discovery) portrayed themselves as objective experimenters who were forced to revise their theory after having accidentally discovered the "truth."

Despite the authors' indication of their previous phlogistic beliefs, the article itself reflects only a systematic attempt to demonstrate the truth of Lavoisier's new system of chemistry. Neither their experiment nor their conclusion was the "de novo" discovery they had depicted it to be. Prior to Deiman and Paets van Troostwijk's experiments on the electrical decomposition of water, many natural philosophers had tested the electric "commotion" on various substances, including water, and had never concluded that water was decomposed. These investigations and explanations of them invite further examination in detail.

³⁸Ibid., p. 377.

CHAPTER II

EXPLANATIONS OF THE TRANSMISSION OF ELECTRICITY THROUGH WATER PRIOR TO 1786

The earliest examinations of the passage of the "electric commotion" through water were conducted by natural philosophers who were examining the effects of the electric fire on various mediums and the abilities of these mediums to transmit the electric fire. Those natural philosophers conducted their experiments in the context of a chemical and physical theory in which water was, as from the time of Empedocles, one of the elements, and thus indestructible.

More than three decades prior to the publication of Deiman and Paets van Troostwijk's article in <u>Observations sur la physique</u>, Giovanni Battista Beccaria (1716-1781) had published his <u>Dell'elettricismo</u> artificiale, e naturale a systematic examination of the properties of electricity, including a description of a series of experiments on the passage of the "vapore elettrico" through water. In a chapter entitled "in cui si tratta dell'elettricismo per rispetto all'acqua" Beccaria related an experiment in which he had passed the electric vapor through

Giovanni Battista Beccaria, Dell'elettricismo artificiale, e naturale libri due di Giambatista Beccaria (Torino: Nella stampa di Filippo Antonio Campana, 1753), p. 111. (Hereinafter referred to as Elettricismo artificiale, e naturale.) "In which electricity is treated with respect to water."

a thin layer of water on a sheet of glass two lines wide (one line equals 1/12th of an inch) and six inches long. When he connected a "quadro di Franklin" or Franklin square, a device used to store electricity. 2 to the layer of water, Beccaria noted a rattling noise and a visible light. 3 He also transmitted the electric vapor through a small vase of water with a two-inch "aperture" and reported a very weak spark.4 Beccaria then found that a much stronger spark could be produced when he used an ordinary dish filled with water. Beccaria used his own body to measure the intensity of the "commozione." He found that both a noise and sparks were produced when he discharged the Franklin square across large surface areas, whereas only a noise was produced when he discharged it across small surface areas. Associating the presence of a visible spark with intensity, he concluded that the commotion transmitted across large surface areas was stronger than that transmitted across small surface areas and that the strength of the commotion was in proportion to the quantity of water through which the electric vapor was discharged.

E ne' casi, che ho detto, che l'acqua cigola solamente, appena mi sono accorto di alcuna minima commozione; quando l'acqua

²Benjamin Franklin, New Experiments and Observations on Electricity Made in Philadelphia in America by Benjamin Franklin, Esq; and Communicated in Several Letters to Peter Collinson. Esq; of London, F.R.S., 3rd ed. (London: D. Henry and R. Cave, 1760), pp. 25-26, described the use of a glass plate coated with a lead plate to store electrical shocks and mentioned a "battery" constructed of "eleven panes of large sash-glass, arm'd with thin leaden plates. . . ."

Beccaria, Elettricismo artificiale, e naturale, pp. 112-113.

⁴<u>Ibid</u>., p. 113.

⁵Ib1d.

cominiciava a dare scintilla, io cominciava ad avere un qualche leggerissimo scuotimento; e questo cresceva a proporzione che cresceva la scintilla; cioè a proporzione che cresceva la quantità dell'acqua, attraverso a cui scaricava il quadro.

The results were the same when wine was used instead of water. Beccaria also examined "l'acqua chiuta entro lastre" in his experiments. Using a glass tube six inches long and one-third of a line in diameter, filled with water, and sealed at the ends with wax, he connected one end of the tube to the Franklin Square and the other to the conducting arc, but did not "riuscito d'ottenere scintilla attraverso all'acqua così chiusa." After this initial failure, he then inserted a brass wire into each end of the tube. The resulting apparatus allowed the passage of an electric spark through water over an interval of one-third of a line. Beccaria noted that the production of an electric spark in this short interval of water was not only vivid, but also shattered the glass tube.

Ho osservato i sequenti fenomeni. I. Nell'intervallo de' fili occupato da quella poc' acqua (stenta a riuscire l'experienza, se esso intervallo non è minore d'un terzo di linea) scoppia un vivissima scintilla; II. questa scintilla spezza il cannello per la lunghezza dal luogo dell' interruzione per mezzo pollice

 $[\]frac{6}{\text{Ibid}}.$ "and in the cases that I have discussed that the water cracks as $\overline{\text{soon}}$ as I have noticed the least commotion; when water began to take [the] spark I began to see some barely perceptible agitation; and this agitation grew proportionally to the spark; that is, proportionally to the quantity of water through which the square was discharged."

⁷ Ibid., pp. 113-114. "water shut within glass."

 $[\]frac{8_{\mbox{\sc Ibid.}}}{\mbox{\sc Ibid.}}$ "succeed in obtaining a spark across the water thus enclosed."

⁹<u>Thid</u>. "I have observed the following phenomena. I. A very bright spark explodes in the interval of wire occupied by little water. (if the space is not less than a third of a line, the experiment does not easily succeed). II. This spark breaks the tube at a length of a half an inch from the spot of the interruption. . . ."

Beccaria believed that the explosions in this experiment illustrated the relatively great resistance that water offered to the passage of an electric spark because a similar tube containing only atmospheric air offered much less resistance than did the one containing water.

La scintilla elettrica trova una grandissima resistenza in attraversare una piccola parte dell' interiore sostanza dell' acqua.

392. Dico resistenza grande; che essa è certo maggiore della resistanza dell'aria; attraverso all'aria si hanno scintille alla distanza di un pollice, e più; e attraverso all'acqua non le ho mai ottenute pell'intervallo di mezza linea.

Having demonstrated that the resistance of water to the electric spark was greater than that of metals and greater even than that of air,

Beccaria offered the following explanation for the exploding tubes:

Nè però intendo io qui di stabilire, che la scintilla elettrica dilati l'acqua immediamente operando sulle parti di lei propriamente dette; imperciocche essere, pùo essere, che espanda quella non immediatamente, ma per mezzo della dilatazione, che induce nelle particelle d'aria fissa, che sono in gran copia sparse per la sostanza dell'acqua.11

^{10 &}lt;u>Thid.</u>, p. 115. "The electrical spark finds a greater resistance going through a small part of the interior substance of the water. 392. I say a strong resistance because it is higher than the resistance of air; we have sparks at a distance of an inch through air and more, but I have only gotten sparks at an interval of less than half a line through water."

¹¹_Ibid., p. 116. "But nor do I mean herewith to establish that the electric spark expands water immediately, operating on its parts with properly given laws; because it can be that it [the electric spark] expands it [water] non-immediately, rather by means of the dilation which it induces in the particles of fixed air, particles which are abundantly diffused through the water." Because Beccaria mentioned no chemical tests for "aria fissa" or fixed air he was probably referring to elemental air fixed in bodies in much the same manner that Stephen Hales (1677-1671) had discussed the production of a unitary elemental air from various substances. The concept of fixed air as a distinct species of air, as discussed by Joseph Black (1728-1799) was not part of chemical tradition until the latter part of

He suggested that the production of an electric spark in water caused an expansion of the matter of water by exciting and releasing the particles of air fixed in water. Beccaria then demonstrated that bubbles of air were indeed excited by the production of an electric spark just under the surface of the water.

Ma per convincermi più direttamente, che quelle piccole bolle sono eccitate dalla scintilla, empio d'acqua un vasellino di vetro di due pollici nel diametro; poi adatto al solito due fili atti a fare le necessarie comunicazioni, che ambidue dal di fuora del vasellino, ma da parti opposte, salgono sull' orlo di lui, e quindi si ripiegano, e si vengono ad incontrare, e restano in una piccola distanza sotto la superficie dell'acqua; e si fascendo. che per essi fili attraversi il vapore del quadro, osservo constantemente, che la scintilla, la quale al solito, scoppia nella interruzione de' fili, eccita varie assai sensibili bollicelle d'aria, che salgono veloci alla superficie dell'acqua, ed ivi mescolate coll'aria comune spariscono.12

Beccaria's career. See Stephen Hales, <u>Vegetable Staticks: Or, an</u>
Account of Some Statical Experiments on the Sap of 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
(London: for W. and J. Innys and T. Woodward, 1727), pp. 312-317 and
Joseph Black, Experiments Upon the Magnesia Alba, Quick-lime and Other
Alcaline Substances; by Joseph Black, M.D. To Which is Annexed an Essay
on the Cold Produced by Evaporating Fluids; and Some Other Means of
Producing Cold; by William Cullen, M.D. (Edinburgh: for William Creech,
and for J. Murray, and Wallis and Stonehouse, 1777), pp. 69-70. See
also J. R. Partington, A History of Chemistry, 4 vols. (London:
Macmillan & Co., Ltd., 1961-), 3:117, 135-140.

¹² Beccaria, Elettricismo artificiale, e naturale, p. 116.

"But in order to convince myself more directly, that the small bubbles are stimulated by the spark, I filled a small glass vase two inches in diameter with water; then in the usual way I applied two wires to make the necessary communications, from the outside of the small vase, but from opposite parts they ascend on the edge of it, then they are bent so that they approach each other and remain a small distance [apart] under the surface of the water; thus making the vapor of the square go through these wires, I could always observe, that the spark which usually bursts at the point where the wires interrupt, stimulates many very sensible air bubbles, that rise quickly to the surface and disappear mingling with the air."

Beccaria was also certain that, in addition to exciting the fixed air in water, the production of an electric spark through water divides the water into minute, insensible particles. ¹³ He believed that such a division was demonstrated by the suspension of a drop of water near the gap in two wires inside a spherical glass container, the top of which had an opening one inch in diameter. When he produced an electric spark in the gap, the inside of the glass became clouded, illustrating the rapid dispersion of water by the force of an electrical spark. ¹⁴

In summary, Beccaria believed that the passage of electric vapor through water excited and released air fixed in the water, divided the water into minute particles, and rapidly dispersed these particles. Thus, although Beccaria had sought to illustrate the effects of water on the passage of electric vapor and especially to demonstrate that water retarded the passage of the electric vapor, his investigations also included a reciprocal examination of the effects of electric vapor on water. He concluded that the division and dispersion of water by the production of an electric spark in it was analogous to the normal evaporation of water, a process that he believed to be a result of electrical causes. 16

Beccaria continued his discussion of the effects of the electric spark on water in later publications. His Elettricismo

¹³IPIG.

¹⁴ Ibid.

¹⁵гыд.

¹⁶ Ibid.

atmosferico, ¹⁷ written in the form of fifteen letters to Giacomo Beccari (1728-1766), included a letter relating the effects of the electric spark on water. Among the experiments that Beccaria related in this letter were some not mentioned in his earlier publication, including the shattering of larger and stronger glass tubes. After varying the strengths of the tubes, he observed that the distances the pieces were scattered were proportional to the strength of the tube:

Una si fatta scintilla eccitata da due quadri di Franklin sottili, e di 400. pollici di superficie, spezza un cannello di vetro grosso due linee, e ne getta i minuzzoli alla distanza di 20. piedi; spezza ancora de' cannelli molto più grossi di otto, e di dieci linee, e ne getta i minuzzoli ad una distanza proporzionale. 18

Beccaria's explanation of the effect of the electric spark on water is stated more succinctly in the sixth letter than it had been in his <u>Electricismo artificiale</u>, <u>e naturale</u>. Moreover, by the time Beccaria had written his letters, he had extended his explanation to deal with the effects of the electric spark on liquids other than water.

73. Siccome una densa, e assai ampia scintilla vibra via con impeto una goccia d'acqua, per cui attraversi così i rarissimi fili del vapor elettrico spinti sull'acqua per l'ordinaria elettricità fanno insensibilmente evaporare e l'acqua, e gli altri liquori. 19

¹⁷Giovanni Battista Beccaria, <u>Elettricismo atmosferico</u>. <u>Lettere di Giambattista Beccaria</u> (Bologna: Colle Ameno, 1758).

^{18 &}lt;u>Ibid.</u>, 74. "A spark like that excited by two thin Franklin squares 400 inches in surface, breaks a glass tube two lines at the thickest part and throws its bits to a distance of twenty feet; it also breaks tubes of a much greater thickness of eight, or ten lines and throws their bits to a proportional distance."

That is, other liquids as well as water could be vaporized by producing an electric spark in them.

Beccaria extended this explanation further to include substances other than liquids when he discussed the production of fixed air by the passage of an electric spark. Although he expected solids to be similarly affected, he was unable to detect any evolution of fixed air from solids:

scintilla a saltare attraverso alla piccola goccia di liquore, che sta di mezzo a detti fili; e così se ne spiega dell'aria, che si vede a salire per l'acqua molto lentamente in forma di bollicelle. 190. L'Analogia mi persuade, che la scintilla elettrica debba spiegare, e mettere in istato di attuale elasticità l'aria fissa contenuta ne' corpi sodi similmente, siccome spiega l'aria fissa contenuta ne' corpi liquidi; ma per ora non ho trovato alcun' esperimento, con cui mostrare ciò ocularmente, vale a dire, non ho trovato maniera di rendere sensibile l'aria, che per via della scintilla elettrica si spiega da' corpi sodi; siccome rendo sensibile l'aria, che si spiega dalli liquori. 20

La boccia si scarica attraverso a due fili; la cera obbliga la

Beccaria published another work in 1772, the <u>Elettricismo</u> artificiale, ²¹ which summarized his previous electrical investigations, especially those of his <u>Elettricismo</u> artificiale, <u>e naturale</u> and his <u>Electtricismo</u> atmosferico, in terms of a new assumption concerning the conduction of the "fuoco eletrico." Beccaria believed that the passage

²⁰ Ibid., p. 82. "The phial discharges the [electric] vapour across two wires; the wax obliges the spark to jump through the small drop of liquid which stands in the middle of the above mentioned wires; and thus some of the air is released, which is seen rising very slowly through the water in the form of small bubbles.

190. Analogy persuades me that the electric spark ought to release, and put in a state of actual elasticity the fixed air contained in solid bodies similarly, as it releases fixed air contained in liquid bodies, but for now I have not found any experiment, with which to demonstrate this [result] visibly, that is, I have not found any way to make the air visible, that is discharged from solid bodies by the electric spark, as I make the air discharged from liquids visible."

²¹ Giovanni Battista Beccaría, Elettricismo artificiale di Giambattista Beccaría ([Torino: Nella Stamperia Reale, 1772]).

of the electric fire though matter actually occurred through the pores found in all matter. On this basis, Beccaria explained the passage of the electric spark through water in terms of two principles:

- The pores of water have less capacity to conduct the electric fire than do those of metal or of air.
- The electric fire separates the particles of water, and scatters them just as ordinary fire would. Because the electric fire acts faster than ordinary fire, it scatters water more quickly.²²

According to Beccaria, the electric fire is passed through long, narrow bodies of water with difficulty because narrow bodies of water contain fewer pores that would facilitate the passage of electricity. Wide bodies of water, such as those contained in ordinary dishes, pass the electric fire with greater ease because their pores are more numerous and less resistant to its passage.

Beccaria believed the rapid evaporation of water could occur any time the quantity of the electric fire exceeded the capacity of the pores in a body of water to transmit it. Therefore, evaporation was most likely to occur in smaller bodies of water. The rapid dispersal of water by the passage of the electric fire through it allowed such transmission to proceed by providing the area and pore capacity necessary for the conduction of the electric fire.²³

Although Beccaria repeatedly alluded in the <u>Elettricismo</u>

<u>artificiale</u> to the action of electric fire on fluids, he did not mention
the production of bubbles of fixed air by the passage of an electric
spark as in his previous works. He did, however, relate several new

²²Ibid., p. 247,

²³ Beccaria, Elettricismo artificiale, p. 255.

experiments. These experiments centered around the construction of an "air cannon" operating on the power of the electric fire to drive fluids rapidly into vapor. The cannon consisted of a wax tube containing a chamber which Beccaria filled with water or wine impregnated with camphor. The wax had conducting wires inserted in it, forming a small interval across the chamber of fluid. The open end of the chamber was stoppered with a lead or wooden ball. The force of the vapor generated by the passage of the electric spark from one wire, through the liquid and to the other wire would drive out the ball and project it distances beyond twenty-five feet. 24

Beccaria explained the production of bubbles and the excitation of air from water, the same phenomena that Deiman and Paets van Troostwijk later reported in the terms of the decomposition of water, as the simultaneous excitation of fixed air from water and the rapid evaporation of water excited by the electric fire. Thus an alternative explanation existed for the Dutch experiment.

Beccaria's experiments received attention in Italy and abroad. In Italy, Carlo Barletti (1735-1800), a one-time disciple of Beccaria, 25 wrote a work defending the one-fluid theory in which he briefly discussed the passage of electricity through water. The apparatus Barletti described for passing electricity through water was very much like the one Beccaria had described for the same purpose. It consisted of a glass tube filled with water and sealed at each end. Barletti inserted a wire in each end

^{24&}lt;u>Tbid., pp. 252-254.</u>

²⁵v. Cappelletti, "Carlo Barletti," <u>Dizionaria biografico degli</u> <u>Italiani, Intituto della Encyclopedia Italiana (Roma: Società Grafica Romano, 1960-), 6:401-404. See also Antonio Pace, <u>Benjamin Franklin and Italy</u> (Philadelphia: American Philosophical Society, 1958), pp. 24, 31-34. Barletti later rejected the one-fluid theory.</u>

leaving an interval between the wires inside the tube. He reported that the passage of the electric fire across this interval broke the tube in an instant. ²⁶

Outside of Italy, Thomas François Dalibard (1730-1799) knew of Beccaria's experiments by 1754. Dalibard had translated Franklin's Experiments and Observations on Electricity into French in 1752 and in the same year had performed the Philadelphia experiment, an experiment suggested by Franklin to determine if lightning and electricity were the same. 27 Beccaria in his first publication on electricity, the Elettricismo artificiale, e naturale, had adopted Franklin's one-fluid theory. In the Elettricismo artificiale, e naturale Beccaria had also included a letter addressed to the leading opponent of Franklin's theory, the Abbé Jean-Antoine Nollet (1700-1770), answering the current objections to Franklin's theory. 28 In 1754, Franklin was notified of this unsolicited defense by Dalibard. Franklin wrote Dalibard the following year, praising Beccaria's Elettricismo artificiale, e naturale.

You desire my opinion of Pere Beccaria's Italian book. I have read it with much pleasure and think it one of the best pieces on the subject, that I have seen in any language. 29

²⁶Carlo Barletti, Nouve sperienze elettriche secondo 1a teoria del Sig. Franklin e le produzioni del P. Beccaria di Carlo Barletti (Milano: Giuseppe Galeazzi, 1771), pp. 43-44.

^{27&}lt;sub>Pierre Hamadjian</sub>, "Thomas François Dalibard," A <u>Dictionary of Scientific Biography</u>, ed. Charles Coulston Gillispie (New York: Charles Scribner's Sons, 1971), 3:535 (hereinafter cited as <u>DSB</u>).

²⁸ Beccaria, Elettricismo artificiale, e naturale, p. 144.

²⁹ Benjamin Franklin, The Writings of Benjamin Franklin, ed. Albert Henry Smyth, 10 vols. (New York: Macmillan, 1907), 4:269.

Franklin's letter to Dalibard was also read at the Royal Society of London on 18 December 1755. Two years later, Franklin had Beccaria's first letter to him, dated 1757, read at the Royal Society of London. Tranklin continued to praise Beccaria and to introduce his works to others. In a letter to Ebenezer Kinnersley (1711-1778), he mentioned Beccaria's experiments concerning the passage of the electric fire through water:

water may be exploded, that is, blown into vapour, whereby a force is generated Water reduced to vapour, is said to occupy 14,000 times its former space.—I have sent a charge through a small glass tube, that has berne it well while empty, but when filled first with water, was shattered to pieces and driven all about the room:—Finding no part of the water on the table, I suspected it to have been reduced to vapour; and was confirmed in that suspicion afterwards, when I had filled a like piece of tube with ink, and laid it on a sheet of clean paper, whereon, after the explosion, I could find neither any moisture nor any sully from the ink. This experiment of the explosion of water . . . I believe was first made by that most ingenious electrician father Beccaria 32

Although he did not mention the production of bubbles or the excitation of air from water as Beccaria had, Franklin did provide a mechanism for

³⁰ Benjamin Franklin, "Extract of a Letter Concerning Electricity, from Mr. B. Franklin to Mons. Delibard, Inclosed in a Letter to Mr. Peter Collinson, F.R.S.," Philosophical Transactions, Giving Some Account of the Present Undertakings, Studies and Labours, of the Ingenious, in Many Considerable Parts of the World 49, Pt. 1 (1755):305. (Hereinafter referred to as Philosophical Transactions.)

³¹ Giovanni Battista Beccaria, "Experiments in Electricity: In a Letter from Father Beccaria, Professor of Experimental Philosophy at Turin, to Benjamin Franklin, L.L.D. F.R.S.," <u>Philosophical Transactions</u> 51, pt. 2 (1760):514. See also Pace, <u>Franklin and Italy</u>, for a detailed account of Franklin's relationship to Beccaria in the third chapter, "A Scientific Friendship: Giambatista Beccaria," pp. 49-70.

Benjamin Franklin, Experiments and Observations on Electricity, 4th ed. (1769), p. 415. Beccaria's Elettricismo artificiale of 1772 mentions Franklin's experiments, pp. 251-252.

the production of a gas from water by the passage of the electric fire, that is, the rapid vaporization of water by the electric fire. Franklin's letter to Dalibard, as well as the one to Kinnersley, was published in 1769 in the fourth edition of Franklin's Experiments and Observations on Electricity, 33 which was subsequently published in a French translation in 1773. 34 Therefore, information about Beccaria's experiment was readily available in French and English through Franklin's writings.

Franklin also aided in introducing the knowledge of Beccaria's electrical experiments, including those concerning water, to Joseph Priestley. In 1766, Priestley was in the process of writing a book on electricity and depended upon Franklin and others to send him books on electricity which could be used as source material. Among the works Priestley requested of Franklin was "Beccaria." Priestley's letter to Franklin, dated 18 April 1766, reminding him to send Beccaria's works, reveals Priestley's estimation of Beccaria's importance.

I wrote to Mr. Price last post, in which I desired him to remind you of your promise to procure me Beccaria's work, which you said you thought you could do of Mr. Delaval. Fearing he might not see you soon, I write to desire you to get it for me, if possible, without loss of time. Otherwise, I must reserve his experiments for an Appendix; for, by the references I meet with to them, I find my book absolutely must not come abroad without them. 36

 $^{^{33}}$ Franklin, Experiments and Observations, pp. 161 and 415, respectively.

³⁴ Benjamin Franklin, <u>Oeuvres de M. Franklin</u>, trans. from 4th ed. by M. Barbeu Dubourg, 2 vols. (Paris: Chez Quillau l'ainé, <u>et al.</u>, 1773).

³⁵ Joseph Priestley, A Scientific Autobiography of Joseph Priestley (1733-1804): Selected Scientific Correspondence, ed. with commentary by Robert E. Schofield (Cambridge, Massachusetts: MIT Press, 1966), p. 30.

^{36&}lt;sub>Ibid., p. 36.</sub>

Thus, Beccaria's electrical experiments were also publicized by Priestley's <u>The History and Present State of Electricity</u>. Published in 1767, it received widespread attention in England and Europe. A second edition of the <u>History</u> was published in 1769, and a third and a fourth edition were published in 1775. It was available in French in 1771 and in German by 1772. 38

Priestley made specific reference in the $\underline{\text{History}}$ to Beccaria's experiments:

SIGNIOR BECCARIA'S experiments on <u>water</u>, showing its imperfection as a conductor, are more surprising than those he made upon air, showing its imperfection in the contrary respect. They prove that water conducts electricity according to its quantity, and that a very small quantity of water makes a very great resistance to the passage of the electric fluid.

HE made tubes, full of water, part of the electric circuit, and observed, that when they were very small, they would not transmit a shock, but that the shock increased as wider tubes were used.

BUT what astonishes us most in Signior Beccaria's experiments with water, is his making the electric spark visible in it, not-withstanding its being a real conductor of electricity. . . .

HE inserted wires, so as nearly to meet, in small tubes filled with water; and, discharging shocks through them, the electric spark was visible between their points, as if no water had been in the place. The tubes were generally broken to pieces, and the fragments driven to a considerable distance. This was evidentally occasioned by the repulsion of the water, and its imcompressibility, it not being able to give way far enough within 15 itself, and the force with which it was repelled being very great.

³⁷ Joseph Priestley, The History and Present State of Electricity, with Original Experiments (London: J. Dodsley et al., 1767).

³⁸ Robert Schofield, "Introduction" to The History and Present State of Electricity with Original Experiments, reprint of the third edition of 1755 [sic], The Sources of Science, No. 18, 2 vols. (London: Johnson Reprint Corp., 1966), 1:xxxix-xliii. See also Thomas Thomson's History of the Royal Society, from Its Institution to the End of the Eighteenth Century (London: for Robert Baldwin, 1812), p. 445, for a not-so-laudatory opinion of Priestley's History.

Priestley, <u>History</u>, pp. 209-210.

Priestley did not confirm Beccaria's conclusion that evaporation was hastened by electricity.

. . . I spread a little water, exceeding thin, upon the surface of a smooth piece of slate; but, though the explosion passed over the surface, with its usual violence, I could not perceive that it had occasioned the least degree of evaporation; which Signior Beccaria found to be the consequence of making the electrical explosion through water in such circumstances. 40

Priestley conducted experiments of his own on the passage of electri-

city through fluids, but he did so in a different context. Included was his investigation of reports that lightning turned certain liquids sour. Since he believed electricity and lightning to be the same, he approached the problem by determining "the effect of the electrical explosion transmitted through various liquors."41 For these experiments Priestley used a glass tube nine inches long and approximately one-fourth of an inch in diameter. The tube was stoppered on one end with sealing wax containing a wire inserted through the wax into the tube. The first fluid Priestley tested was beer, and he wrote, "I began with discharging the explosion of the battery through this tube . . . and observed a considerable quantity of fixed air, or something in the form of bubbles, to ascend in it. . . " Priestley dismissed the bubbles in this first trial by stating that the electricity did not sour the beer, although the escape of so much air could make the beer "grow stale something sooner."42 Red wine, milk, ale, and, finally, syrup of violets were also tried. 43 Priestley did not comment again on the presence or absence of bubbles

⁴⁰Ibid., p. 691.

⁴¹<u>Ibid</u>., p. 724.

⁴²тыд.

^{43&}lt;u>Tbid</u>., pp. 724-725.

in these further experiments, for he was testing the fluids for changes in taste, and thus the phenomenon of bubbles probably was not one of primary concern. 44

The subtle distinction between Beccaria's experiments and Priestley's comments on them is an example of the differences in their theories. These differences were reflected in their approach to the assessment of experimental results. Although Priestley and Beccaria nominally worked within the same larger theoretical structure in both chemistry and electricity, that is, the phlogiston and one-fluid theories, it is clear from Priestley's History that he was unwilling to accept some of the phenomena Beccaria had reported and the "conjectures" Beccaria had offered to explain them. Even when Priestley described the excitation of bubbles from beer by the passage of an electric discharge, a phenomenon that would coincide with Beccaria's description of the effects of the electric spark on fluids, Priestley dismissed the phenomenon without further discussion. The subtle difference in their theoretical approach was also apparent to Beccaria. In the Elettricismo artificiale, he mentioned the fact that Priestley did not notice any evaporation of water when he sent an electric spark through a thin layer of water:

Ora io non so concepire come il signor PRIESTLEY non abbia subordinati allo stesso principio questi grandiosi fatti, che le scintille sopra la faccia di tali corpi sbalzassero a tale sopraggrande distanza, perchè scagliassero nei lunghi tratti gli aliti dell' umido, che esse eccitassero ec.; m' immagino, che una sperienza massimanente lo ha dovuto rendere troppo cauto: che egli non ha potuto accorgersi, che avesse sofferto punto di evaporazione un sottilissimo strato di acqua, per cui avea tradotta la scarica.45

⁴⁴ Ibid.

⁴⁵ Beccaria, Elettricismo artificiale, p. 255. "Now, I do not

Priestley did not accept the idea that electricity could hasten the evaporation of water. In 1767 he explained the effects of the passage of an electric discharge through water in terms of electrical and mechanical concepts, that is, the repulsion of the water caused by the electric discharge and water's mechanical incompressibility. 46 Although Priestley did mention one of the phenomena described by Beccaria and later by Deiman and Paets van Troostwijk, the excitation of bubbles, he did not relate it and could not have related it to the decomposition of water. Breause he knew that water was an element and that air could dissolve in it, the bubbles held no significance for him.

Timothy Lane (1734-1804), in a letter to Benjamin Franklin, read to the Royal Society in 1767, described experiments using electricity to shatter various stone or clay pipes, experiments that led him to test the "electric stroke" on water: "As the . . . experiments succeeded better when the stone or clay were previously dipped in water than before, I was induced to try water only."⁴⁷

understand how Dr. Priestley happened not to perceive the dependence of all those facts, on the principle expressed above; and that sparks were enabled to run to such great distances, along the surface of those bodies, by the vapour which they themselves excited as they passed. I imagine his caution against forming any conjectures of that kind, proceeded from his happening not to perceive any vapour arising from a very thin stratum of water, through which he sent a discharge." This translation is from A Treatise upon Artificial Electricity, in which Are Given Solutions of a Number of Interesting Electrical Phoenomena, Hitherto Unexplained. To Which Is Added an Essay on the Mild and Slow Electricity Which Prevails in the Atmosphere During Serene Weather (London: for J. Nourse, 1776), p. 259.

 $^{^{46}}$ Priestley did later describe the chemical effects of electricity on matter. <u>Infra</u>, p. 66.

⁴⁷Timothy Lane, "Description of an Electrometer Invented by

Like Priestley, Lane devoted his description to the shattering of tubes and the agitation of the water without referring to air bubbles or evaporation, for, Lane was interested primarily in the mechanical effect of the "electric stroke" on water. The agitation that he reported was the most obvious effect, and he did not describe any of the phenomena that Deiman and Paets van Troostwijk found so obvious twenty years later. Perhaps he did not see them, or he saw them and dismissed them as secondary to the agitation, or perhaps they even constituted part of the agitation. Lane used a mechanical explanation of the effects of

Mr. Lane; with an Account of Some Experiments Made by Him with It: In a Letter to Benjamin Franklin L.L.D. F.R.S.," Philosophical Transactions 57(1767);458.

^{48&}lt;u>Ibid</u>., pp. 458-459.

^{49&}lt;u>Ibid</u>., p. 459.

⁵⁰Priestley, <u>History</u>, p. 680.

electricity on water rather than a chemical one because, like Priestley, he did not interpret bubbles as evidence of the decomposition of water.

Although Priestley did not agree with Beccaria's ideas concerning electricity and evaporation, others did. The Abbé Nollet had described a relationship between electricity and evaporation several years prior to the publication of Beccaria's experiments. Nollet did not perform experiments on the passage of electricity through water, but his experiments did provide Beccaria and others with a potential explanation for the phenomena that Deiman and Paets van Troostwijk would later use to argue that water could be decomposed electrically. In 1747 Nollet communicated his study of the electrification of fluids to Martin Folkes (1690-1754), then President of the Royal Society of London. Part of this letter on the electrification of fluids was read at a meeting of the Royal Society on 11 February 1747/48 and was subsequently published in the Philosophical Transactions. 51 In this letter Nollet related how he had examined the electrification of vessels draining through pipes of various sizes in order to determine if electrification accelerated the exiting fluid. After conducting about one hundred experiments using "Vessels of different Capacities, terminating in Pipes of different Bores, from three Lines Diameter to the Smallest Capillaries."52 he found that the fluid was neither sensibly accelerated nor impeded when the drain pipes were over one line in diameter. However, when the drain pipe was less than one line in diameter, the fluid was somewhat accelerated:

⁵¹ Jean-Antoine Nollet, "Part of a Letter from Abba Nollet, of the Royal Academy of Sciences at Paris, and F.R.S. to Martin Folkes Esq; President of the Same, Concerning Electricity," trans. T. Stack, Philosophical Transactions 45 (1747/48, published in 1749):187.

⁵²Ibid., p. 188.

- 3. If the Tube is a capillary one, from which the Water ought naturally to flow, but only Drop by Drop, the electrified Jet . . . is . . . considerably accelerated; and the smaller the capillary Tube is, the greater in proportion is this Acceleration
- 4. And so great is the Effect of the electrical Virtue, that it drives the Liquid out of a very small capillary Tube, throwhich it had not before the Force to pass, and enables it to run out in Cases, where there would not otherwise have been any Discharge. 53

Inspired by these results, Nollet set out to determine whether the "electrical Virtue might possibly communicate some Motion to the Sap of Vegetables." He found that it did. 54 He electrified for several hours fruits, plants and sponges moistened with water and found them "remarkably lighter than others of the same kind [unelectrified]." 55 Nollet also "electrified Liquors of all sorts in open Vessels; and . . . remarked that the Electrification augmented their Evaporation, in some more, in others less, according to their different Natures." 56

Nollet also presented his results to the Académie Royale des Sciences in 1747, and they were published in the <u>Mémoires de l'Académie Royale de Sciences</u> in 1752.⁵⁷ Whereas Folkes had only summarized Nollet's experiments, the paper Nollet submitted to the Académie was published with complete and detailed results and descriptions of the apparatus used in the experiments. Although there was an inevitable

⁵³<u>Ibid.</u> ⁵⁴<u>Ibid.</u>, p. 189. ⁵⁵_{Ibid.} ⁵⁶_{Ibid.}

Jean-Antoine Nollet, "Eclairissemens sur plusieurs faits concernant l'électricité," Mémoires de l'Académie Royale des Sciences.

Année M.DCCXLVII (published 1752), pp. 207-242. Also briefly summarized in "Sur l'électricité," Histoire de l'Académie Royale des Sciences.

Année M.DCCXLVII. Avec mémoires de mathématique & de physique pour la même année, tirés de registres de cette Académie, (published 1752)

Histoire, pp. 29-30. (Hereinafter referred to as Histoire de l'Académie Royale des Sciences.)

delay in the publication of the Mémoires de l'Académie Royale des Sciences, Nollet's results were available to the public in 1749 when his experiments were privately published under the title Recherches sur les 58 causes particulieres des phénomenes électriques.

The experiments Folkes had described as the electrification of "liquors of all sorts" were set out in tabular form in the Recherches. The tables begin with the electrification of water in glasses about four inches in diameter:

Sur des liqueurs contenues dans des tasses ou capsules de verre, dont l'ouverture avoit 4 pouces de diamétre.

- 4 Onces d'eau de la Seine électrisées pendant cinq heures, ont souffert un déchet de 8 grains.
- 4 Onces de la même eau non électrisées, ont perdu pendant la mêmes tems, par la simple évaporation . . . 3

Différence qu'on peut regarder comme l'effet de l'électricité

Nollet repeated his experiments under varying conditions. He used tin vessels instead of glass and found a difference in evaporation of seven grains between the electrified and non-electrified sample. He

⁵⁸ Jean-Antoine Nollet, Recherches sur les causes particulières des phénoménes électriques, et sur les effets nuisibles ou avantageux qu'on peut en attendre (Paris: Chez les Freres Guerin, 1749). (Hereinafter referred to as Recherches.)

⁵⁹ Ibid. p. 323.

[&]quot;Experiment 12

Upon liquors contained in cups or capsules of glass having an opening of four inches in diameter.

⁴ ounces of Seine water electrified for five hours underwent a loss of 8 grains.

⁴ ounces of the same water not electrified, lost by simple evaporation during the same time . . . 3 [grains] The difference that can be regarded as the effect of electricity 5"

also used vessels with a smaller surface area and found a difference of evaporation of only two grains. Using various liquids in the place of water, Nollet found that the difference in the amount of evaporation varied for each liquid;

Les liqueurs suivantes ayant été éprouvées de même & en pareille quantité, les différences ou les déchets causés par l'électrifisation, ont été:

Pour le vinaigre rouge	2 grains
L'eau chargée de nitre	3
L'urine fraîche	7
Le lait nouveau	4
L'huile d'olives	0
L'esprit de térébenthine	7
L'esprit de vin	8
L'esprit volatil de sel ammoniac	11.
Te mercure	n 60

Nollet then electrified the same liquids isolated from the atmosphere by a layer of mercury. Although he found that a layer of mercury would usually prevent the normal evaporation of fluids, the losses in weight were found to be similar to those of electrified fluids open to the atmosphere. However, the fluids which he covered with layers of both mercury and oil suffered only half the weight loss of previous experiments upon electrification. 61

^{60&}lt;sub>Ibid</sub>., 323-324.

[&]quot;The following liquids have been tested in the same way and in like quantity, the difference or losses caused by electrification were:

for red vinegar 2 grains water charged with nitre fresh urine 7 new milk 4 0 olive oil 7 spirit of turpentine spirit of wine 8 volatile spirit of sal ammoniac 11 mercury

⁶¹ Tbid., pp. 325 and 326, respectively.

Nollet argued from these results that:

l'électricité augmente l'évaporation naturelle des liqueurs, puisque à l'exception du mercure qui est trop pesant, & de l'huile d'olives dont les parties ont trop de viscosité, toutes les autres qui ont été éprouvées, ont souffert des pertes, qu'il n'est guéres possible d'attribuer à d'autre cause qu'à l'électricité.62

Nollet also sought to determine whether electricity affected solid bodies in a like manner. He found that it sometimes did^{63}

Nollet believed his hypothesis (that electricity augmented evaporation) to be consistent with his theory of "effluent" and "affluent" electricity. He called the outward flow effluent matter and the inward flow affluent matter, and in his view, all electrical phenomena could be explained in terms of the simultaneous and opposing currents of a universal electric matter. These currents were a dynamic process of the electric matter entering and leaving all bodies through minute pores. 64

Although Nollet adopted two names for the differing currents of electricity, he believed in only one universal electric matter. In his consideration of the two-fluid theory of Charles-François de Cisternay Dufay (1698-1739) Nollet specifically stated this belief in a universal electric matter:

^{62&}lt;sub>Tbid.</sub>, p. 327. "electricity augments the natural evaporation of liquids, since with the exception of mercury which is too heavy, & of olive oil whose parts are too viscous, all others that have been tested, have suffered losses that it is hardly possible to attribute to any cause other than to electricity."

^{63&}lt;u>Tbid</u>., pp. 333-335.

⁶⁴ Jean-Antoine Nollet, Essai sur l'electricité des corps (Paris: Chez les Freres Guerin, 1746), p. xiv.

Y a-t-il dans la nature deux sortes d'Electricités essentiellement differentes l'une de l'autre?

se sont manifestées depuis, M. Dufay, dis-je, a conclu pour l'affirmative sur la question dont il s'agit. Maintenant bien des raisons tirées de l'expérience, me font pencher fortement pour l'opinion contraire. . . .65

Nollet stated that if two sorts of electric matter did exist, the difference between the two could not be in the nature of their particles nor in their mode of their transmission, but only in the size and shape of their particles. 66

Nollet believed that the pores necessary for effluence and affluence differed in number. Thus, differences in the amounts of effluent matter and affluent matter occurred as a result of the difference in the number of entrance and exit pores:

Si la matiere <u>effluente</u> (a) s'élance par des pores plus rares que ceux par <u>où rentre la matiere <u>affluente</u>, . . . il s'ensuit que celle-ci a moins de vîtesse que celle-lã; puisqu'en supposant que l'une ne fait que remplacer l'autre dans un tems donné il passe de la premiere par un plus petit nombre de pores, un quantité égale à ce qui rentre de la derniere par un plus grand nombre de passages. 67</u>

⁶⁵ Ibid., pp. 117-118. "Are there in nature two sorts of electricity one essentially different from the other?

. . . in a time where one was still quite ignorant of the things which have become obvious since, M. Dufay, I say, concluded for the affirmative of the question which is posed. Now many reasons drawn from experience, incline me strongly to the contrary opinion. . . . "

 $^{^{67}}_{\rm Nollet,\ \underline{Essai},\ p.\ 89.}$ "If the effluent matter (a) escapes through pores more rare than those by which the affluent matter

Nollet explained the augmentation of evaporation, as he did all phenomena associated with electricity, in terms of affluence and effluence, that is, the perpetual motion of a universal electric matter through minute one-way pores. In Nollet's theory, the outward or affluent movement provided a mechanism for attraction and the inward or effluent movement provided one for repulsion. Nollet specifically explained the augmentation of the evaporation of bodies by electrification as a result of effluence. When one electrifies

les corps capable d'évaporation . . . ces mêmes effluences dont nous venons de parler, emportent avec elles les parties superficielles d'une liqueur; ou bien elles chassent hors du corps d'où elles sortent, ce qu'elles trouvent de liquide dans ses pores; ainsi après une électrisation de quelque durée, on trouve un déchet sensible dans le poids.68

An additional theoretical examination of the electrical augmentation of evaporation is found in one of Nollet's many replies to his critics, Lettres sur l'électricité. This work contained an open letter to Beccaria defending the concept of effluent and affluent electricity, a concept Beccaria had attacked. In this letter Nollet used the increased evaporation of non-electrified bodies placed near electrified ones as proof of the existence of an affluent matter.

reenters, . . . it follows that the latter has less velocity than the former, since by supposing that one only replaces the other, in a given time there passes from the first by a smaller number of pores, a quantity equal to that which reenters for the last through a larger number of passages."

⁶⁸ Jean-Antoine Nollet, Leçons de physique expérimentale, 3rd ed., 6 vols. (Paris: Chez Hippolyte-Louis Guerin, & Louis-François Delatour, 1753-1764), 6:448. "the bodies capable of evaporation . . . these same effluences of which we have just spoken, carry away with them the superficial parts of a liquid; or indeed they drive out beyond the body from which they have excited whatever liquid they find in its pores: thus, after an electrification of some time, one finds a sensible loss in weight."

Il s'agit enfin des liqueurs qui s'évaporent plus promptement que de coutume, quand on les tient dans des vases ouverts, & à peu de distance, sous des masses électrisées & dont ou soutient l'Electricité. Vous dites "qu'il peut se faire que la matiere effluente du corps électrique, en passant dans la liqueur, la détermine à s'élever en l'air, ou lui donne une sorte de volatilité." Si je n'avois pas prouvé d'ailleurs, & par des faits très-concluants, qu'il existe réellement une matiere affluente, très-capable d'enlever les parties superficielles de la liqueur en se portant au corps électrisé qu est au-dessus, je la supposerois ici comme une chose vraisemblable; & en opposant mes peut-êtres aux vôtres, je disputerois à armes égales de la préférence que pourroit mériter une supposition sur l'autre. dirois . . . contre la vôtre, que la matiere effluente du corps électrisé, s'élançant contre la surface de la liqueur, ne peut point en détacher les parties pour les faire venir contre sa propre direction; & que se répandant dans la masse liquide & dans le vase non isolé, avec tant de facilité qu' elle n'y laisse aucune marque d'Electricité acquise, il n'est pas naturel de penser qu'elle remonte avec des particules d'eau dans l'air, qui est bien moins perméable pour elle 69

In the context of Nollet's theory, non-electrified fluids evaporate more rapidly when placed near electrified bodies because the affluent matter, in its continual rush toward and into electrified bodies, dislodges

⁶⁹ Jean-Antoine Nollet, Lettres sur l'électricité, dans lesquelles on soutient le principe des effluences & affluences simultanées contre la doctrine de M. Franklin, & contre les nouvelles prétentions des ses partisans, seconde partie (Paris: Chez H. L. Guerin, & L. F. Delatour, 1760), pp. 177-178. "It is finally a question of liquids that evaporate more quickly than normal, when one keeps them in open vases, and at a short distance, under electrified masses and of which one sustains the Electricity. You say 'that it can happen that the effluent matter of an electric body, while passing in the liquid, induces it to rise in(to) the air, or gives it a sort of volatility. If I had not already proven elsewhere, and by very conclusive facts, that there really exists an effluent matter, quite capable of carrying off the superficial parts of the liquid while traveling to the electrified body that is above, I would suppose this as a reasonable thing; and while opposing my perhapses to yours, I would dispute equally equipped for the preference that would merit one supposition over the other. I would say . . . against yours, that the effluent matter of an electrified body in hurling itself against the surface of the liquid, does not at all detach parts in order to make them go against its own direction; and that being diffused in the liquid mass and in the non-isolated vase, with so much ease that it leaves no mark of acquired electricity, it is not natural to think that it rises again with the particles of water into the air, which is much less permeable for it: . . .

particles from the surface of the nearby fluid and carries them into the air. Although Nollet supported his idea that electricity augments evaporation with experiments quite different from those of Beccaria, Lane, Priestley, Franklin, and Barletti, the idea lent itself to the explanation of their experiments. Once it was believed that electricity, in whatever manner, reduced the bulk of fluids by occasioning their increased evaporation, then the idea could be applied, as Beccaria applied it, to explaining the rapid dispersion of water by the passage of the electric fire.

Nollet's assertion that electricity augmented evaporation received widespread attention throughout Europe. Beccaria, who had rejected Nollet's theory of affluence and effluence, accepted and cited his belief that electricity augments evaporation in both the Elettricismo artificiale, e naturale 10 and in the Elettricismo artificiale. 11

Priestley also repeated Nollet's ideas concerning electricity and evaporation in the History, even though he did not accept them. 12 Folkes summary of Nollet's experiments also attracted the attention of other Englishmen, including John Ellicott, F.R.S. (1706?-1772), whose discussion of Nollet's experiments was published in the same volume of the Philosophical Transactions as Folkes' summary of them, 33 and William

⁷⁰ Beccaria, <u>Elettricismo artificiale</u>, <u>e naturale</u>, p. 117.

⁷¹ Beccaria, Elettricismo artificiale, p. 274.

⁷²Priestley, <u>History</u>, pp. 135-144. Priestley rejected the concept of affluence and effluence, pp. 120-121.

⁷³ John Ellicott, "Several Essays Towards Discovering the Laws of Electricity, Communicated to Royal Society by Mr. John Ellicott F.R.S. and Read on the 25th of Feb. 1747. And at Two Meetings Soon After," Philosophical Transactions 45 (1747/48):195-224. Priestley's History also discusses Ellicott's reaction to Nollet's experiments on p. 144.

Watson (1715-1787), who adopted Nollet's theory but later shifted to Franklin's.

Watson made numerous electrical experiments and communicated many of both Nollet's and Franklin's experiments to the Royal Society. 74 His writings published in the various volumes of the Philosophical Transactions were later collected and published separately. 75 Even after he discarded Nollet's theory for Franklin's, Watson continued to correspond with Nollet and to review Nollet's publications favorably. 76 Priestley's History relates Watson's numerous experiments, his theory of "flux" and "aflux," and his switch from Nollet's to Franklin's theory. 77

There were several French natural philosophers who accepted Nollet's ideas. The Abbé Mangin (d. 1772) summarized Nollet's views on

⁷⁴Philip Joseph Hartog, "William Watson," The Dictionary of National Biography from Earliest Times to 1900, 22 vols. (London: Oxford Press, 1937-1938, Reprint of 1917 edition), 20:956-958 (hereinafter cited as DNB.) credited Watson with fifty-eight original articles on electricity and numerous summaries of the works of others.

⁷⁵ William Watson, Experiments and Observations Tending to Illustrate the Nature and Properties of Electricity. In One Letter to Martin Folkes, Esq; President, and Two to the Royal Society (London: for C. Davis, 1746).

Watson, A Sequel to the Experiments and Observations Tending to Illustrate the Nature and Properties of Electricity: Wherein It is Presumed, by a Series of Experiments Expressly for that Purpose, that the Source of the Electrical Power, and Its Manner of Acting Are Demonstrated (London: for C. Davis, 1746).

⁷⁶ See, for instance, William Watson, "An Account of a Treatise in French, Presented to the Royal Society, Intituled, 'Lettres sur l'Electricité, by the Abbé Nollet, Member of the Royal Academy of Sciences, &c. &c. by William Watson, M.D. R.S.S.," Philosophical Transactions 52, Pt. 1 (1761):336-343.

⁷⁷ Priestley, <u>History</u>, p. 90.

electricity and evaporation in a work entitled <u>Histoire génèrale et particuliere de l'électricité</u>. Although Mangin's <u>Histoire génèrale</u> contained his own theory of electricity, it also contained an extensive defense of Nollet's theory. In fact, Mangin incorporated most of Nollet's theory into his own. 79

Other Frenchmen who endorsed or accepted Nollet's hypothesis that electricity augments evaporation in their writings on electricity included Pierre Bertholon (1741-1800)⁸⁰ and Joseph-Aignan Sigaud de La Fond

^{78[1&#}x27;Abbé Mangin], <u>Histoire générale et particuliere de</u> l'électricité, ou ce qu'en ont dit de curieux & d'amusant, d'utile & d'interessant, de réjoüissant & de badin, quelques physiciens de l'Europe, 3 vols. (Paris: Chez Rollin, 1752), 3:4-7. Paul Fleury Mottelay, <u>Bibliographical History of Electricity & Magnetism Chronologically Arranged</u>: Researches into the Domain of the Early Sciences, Especially from the Period of the Revival of Scholasticism, with Biographical and Other Accounts of the Most Distinguished Natural Philosophers Throughout the Middle Ages (London: Charles Griffin and Co., Ltd., 1922), p. 455 (Hereinafter cited as Bibliographical History) credits the Histoire générale to "Guerin," but J. C. Poggendorff, Biographisch-literarisches Handwörterbuch zur Geschichte der exacten Wissenschaften enthaltend Nachweisungen über Lebensverhält nisse und Leistungen von Mathematikern, Astronomen, Physikern, Mineralogen, Geologen usw. aller Völkerund Zeiten, 2 vols. (Leipzig: Johann Ambrosius Berth, 1863 reprinted Ann Arbor, Michigan: Edwards Brothers, Inc., 1945) 2:33 lists Mangin as the author. Joseph-Marie Quérard's <u>La France littéraire, ou dictionnaire bibliograph</u>ique des savants, historiens et gens de lettres de la France, ainsi que des littérateurs étrangers qui ont écrit in français, plus particulièrement pendant les XVIII et XIX siècles, 10 vols. (Paris: Chez Firmin Didot, 1837-1839), 5:489 credits this work to Mangin and Firmin Didot, 1837-1839), 5:489 credits this work to Mangin and notes "Cet ouvrage a été attribué mal à propos, à l'avocat Guer, dans la France littéraire de 1769," The Catalogue général des livres imprimés de la Bibliothèque Nationale-auteurs, 220 vols. (Paris: Imprimerie Nationale, 1824) 105:120, concurs in crediting Mangin as the author of the <u>Histoire générale</u>. Therefore Mangin rather than Guérin was most probably the author.

^{79 [}Mangin], <u>Histoire générale</u>, 3:4-7 and 2:37-46 outlines Nollet's theory; the recitation of the theories of others are most often followed by Nollet's responses to them. Mangin's own theory may be found in 2:113-180.

⁸⁰ Louis Dulieu, "Pierre Bertholon," DSB., 2:282 gives 1741-1800, while Poggendorff, 1:167-168 gives only +. 1799.

(1740-1810). 81 Bertholon cited and accepted Nollet's hypothesis in a work entitled De l'electricité du corps humain. 82 Sigaud de La Fond, a prolific writer on chemical, physical, and electrical subjects, wrote in his Traité de l'electricité of 1771:

l'Abbé Nollet . . . a examiné scrupuleusement l'évaporation de différentes liqueurs, qu'il pénétroit abondamment de fluide électrique, & c'est avec l'appareil qu'il imagina pour cet effet (a), [(a) is a footnote which reads "Recherc. sur l'Elect. pag. 320] qui m'a paru aussi simple que commode, que j'ai répété plusieurs des ses expériences, & que j'en ai fait quantité d'autres, qui ne servent qu'à confirmer ce que ce célebre Physicien a avancé à cet égard.83

Sigaud also mentioned Nollet's hypothesis that electricity augments evaporation in two of his other works, <u>Elémens</u> <u>de physique théorique</u> <u>et expérimentale</u>, first published in 1777, ⁸⁴ and <u>Précis historique</u>

⁸¹ Poggendorff, 2:927 and Index biographique des membres et corespondants de l'Académie des Sciences du 22 décembre 1666 au 15 novembre 1954, p. 471; both have Joseph-Aignan, while Nouvelle biographie générale depuis les temps les plus reculés jusqu'à nos jours, avec les renseignements bibliographiques et l'indication des sources à consulter, ed. Hoeffer, 46 Vols. (Paris: Didot Frères, 1855-1866), 43:966 (Hereinafter cited as NBG.) gives Jean-Réné.

⁸²Pierre Bertholon, <u>De l'électricité du corps humain dans</u>
<u>l'état de santé et de maladie</u> (Paris: Chez P. F. Didot le jeune, 1780),
pp. 158, 165-166, 202, 205-206.

⁸³ Joseph Aignan Sigaud de La Fond, Traité de l'électricité, dans lequel on expose, & on démontre par expérience, toutes les découvertes électriques, faites jusqu'à ce jour, pour servir de suite aux Leçons de physique du même auteur (Paris: Chez des Ventes de la Doué, 1771), pp. 366-367. "The Abbe Nollet . . . has scrupulously examined the evaporation of different liquors, that he has abundantly impregnated with the electric fluid, and it is with the apparatus that he had conceived for this effect(a), which appeared to me as simple as [it was] convenient, that I repeated several of his experiments, and I have made a quantity of others, that only serve to confirm what this celebrated physicist has advanced in this respect."

⁸⁴ Joseph-Aignan Sigaud de La Fond, Elémens de physique théorique et expérimentale, pour servir de suite à la description &

et expérimentale des phénomènes électriques, first published in 1781.85

Jacques-Mathurin Brisson (1723-1806) also cited Nollet's experiments on electricity and evaporation. In a French translation of Priestley's <u>History</u> to which Brisson added a commentary that defended and expounded Nollet's electrical theory. One of Brisson's notes was in reply to Priestley's comments regarding Nollet's experiments on evaporation. Priestley had stated that Nollet's experiments had by no means satisfied all English philosophers, and he had suggested that Nollet's defense of his theory of affluence and effluence was fraught

usage d'un cabinet de physique expérimentale, 4 vols. (Paris: Chez P. Fr. Gueffier, 1777), 4:475. Second edition published in 1787.

⁸⁵ Joseph Aignan Sigaud de La Fond, <u>Précis historique et expérimental des phénomènes [sic] électriques, depuis l'origine de cette découverte jusqu'a ce jour (Paris: Rue et Hôtel Serpente, 1781), p. 620. Second edition published in 1785. The title of the second edition differs in that <u>phénomènes</u> differently. The <u>Traité de l'électricité</u>'s second edition was published in 1776 (Paris: Chez Laporte).</u>

⁸⁶ Brisson could well be expected to mention Nollet's experiments because Brisson was Nollet's assistant. Prior to 1768 Brisson had been engaged in the study of natural history as the protegé of Réne-Antonie Ferchault de Réaumur (1683-1757) and as caretaker of Réaumur's collection of specimens. After Réaumur's death, the collection was absorbed into the Cabinet du Roi. Because there had been a heated rivalry between Réaumur and George-Louis Leclerc, Comte de Buffon (1707-1789) and because Buffon controlled the Cabinet du Roi, it has been argued that Brisson could no longer use the specimens necessary to his pursuit of natural history. Brisson (perhaps on Nollet's advice) turned to the study of physics. René Taton, "Jacques-Mathurin Brisson," DSB., 2:473-475. See also Jean Torlais, Un physicien au siècle des lumières: L'Abbè Nollet 1700-1770. (Paris: Sipuco, [1954], pp. 236-238.

⁸⁷ Joseph Priestley, <u>Histoire de l'électricité traduite de l'Anglois de Joseph Priestley avec des notes critiques</u>, 3 vols. (Paris: Chez Herissant le fils, 1771). This edition has often been attributed to Brisson. See, for instance, <u>DSB</u>., 2:474 or Torlais, <u>Nollet</u>, p. 236.

with errors. 88 Brisson replied to this criticism by pointing out that Priestley had not supported his allegation of errors with examples, 89 and furthermore, that Priestley favored his fellow Englishmen over the French. 90 Brisson also stated that Nollet did not reply to Ellicott's article in the Philosophical Transactions criticizing Nollet's experiments on electrification and evaporation because Nollet did not know of Ellicott's article. Brisson's explanation of Nollet's silence on the matter is more than plausible, if one considers that Nollet hatibually replied to criticisms of his experiments and theories made by other natural philosophers. 91

Commenting on Priestley's account of Beccaria's exploding tube experiment, Brisson rejected Priestley's explanation that the explosions of the tubes were caused by "the repulsion of the water and by its incompressibility." Instead, Brisson invoked Nollet's concept of affluence and effluence in his explanation of the phenomenon: "La vraie cause de cet effet est le mouvement rétrograde des deux courants de matiere électrique, causé par leur percussion mutuelle dans l'explosion."92

⁸⁸ Priestley, <u>History</u>, p. 143, or Priestley, <u>Histoire</u>, p. 267.

⁸⁹ Brisson in Priestley, <u>Histoire</u>, p. 267.

 $⁹⁰_{\underline{\text{Tbid}}}$., p. 227 (Brisson had referred on 267 to previous note no. 33).

⁹¹ Supra, pp. 45-47.

 $⁹²_{\overline{\text{Did}}}$, 382, note 55. "The true cause of this effect is the retrograde movement of the two currents of electric matter, caused by their mutual percussion in the explosion."

In his <u>Traité élementaire</u> published in 1789, Brisson again cited Nollet's experiments and explained the hypothesis that electricity augments evaporation in the context of the theory of affluences and effluences.

Nollet's experiments also attracted the attention of Jan Krtitel Bohac (1724-1768). In 1751 Bohac (or Bohadsch) sent the Royal Society a thesis that he had presented to the faculty of the University of Prague for a medical degree. William Watson read to the Royal Society on 23 January 1752 a summary of "Bohadsch's" thesis on the utility of electricity in medicine. ⁹⁴ The work contained extensive discussions of the effects of electricity on liquid and solid bodies; ⁹⁵ however, the experiments and tables of results used by Bohadsch on the subject were plagiarized from Nollet's description of his experiments in the Recherches. Even Watson, who prefaced his summary of Bohadsch's thesis with praise for Bohadsch, noted that Bohadsch had committed

a slight plagiarism . . . without quoting his author, he has translated from the French into Latin the tables above mention'd,

⁹³Jacques-Mathurin Brisson, <u>Traité élémentaire ou principes</u>
de physique, fondés sur les connoissances les plus certaines, tant
anciennes que modernes, <u>& confirmés par l'expérience</u>, 3 vols. (Paris:
De l'Imprimerie de Moutard, 1789), 3:329, 458.

⁹⁴ Jan Krtitel Bohác, "An Account of Dr. Bohadsch's Treatise, Communicated to the Royal Society, Intituled, Dissertatio philosophicomedica de utilitate electrisationis in curandis morbis, Printed at Prague, 1751: Extracted and Translated from the Latin by Mr. Wm. Watson, F.R.S.," Philosophical Transactions 47 (1751-1752, published 1753): 345-359.

^{95&}lt;u>Tbid.</u>, see pp. 345-358 for these discussions. See also Jan Krtitel Bohác, <u>Dissertatio de utilitate electrisationis in arte medica seu in curandis morbus quam pro suprema doctoratus medici laurea defendit <u>Joannes Bohadsch. Anno 1751</u>. in <u>Dissertationes medicae selectiores pragenses</u>, vol. 1, ed. by Josephus Thaddaeus Klinkosch (Prague et Dredae: Apud Georgium Conradium Walther, 1775-1793), pp. 2-24.</u>

as well as his experiments, proving that electricity forwards vegetation, from . . . the Abbe Nollet's treatise, intitled, Recherches sur les causes particulieres des phenomenons electriques. 96

Watson was understating the matter. Bohadsch's plagiarism was extensive; however, few eighteenth-century writers, including Nollet, appear to have been disturbed by it. 97

Bohadsch's experiments were reported in such later works on electricity as Priestley's <u>History</u>, Dalibard's <u>Histoire abregée de</u>

<u>l'électricité</u> which was a short historical introduction to Franklin's
<u>Expériments et observations</u>, and Bertholon's <u>De l'électricité du corps</u>

<u>humain</u>. Priestley's <u>History</u> mentioned only Bohadsch's medical experiments, ⁹⁸ while Dalibard cited Bohadsch's evaporation experiments as well as his medical experiments. ⁹⁹ In contrast, Dalibard did not mention

Nollet in his <u>Histoire abregée de l'électricité</u>. ¹⁰⁰

⁹⁶ Watson, in "An Account of Dr. Bohadsch's Treatise," p. 351.

⁹⁷ In order to detect Bohadsch's extensive plagiarism, compare the following: Bohadsch's list of results for the electrification of fluids, pp. 346-347 of Watson's summary with Nollet's Recherches, p. 324. Bohadsch's results for the electrification of solids, p. 348, with Nollet's Recherches, pp. 333-335; Bohadsch's experiments on the evaporation of water river, pp. 346-347, with Nollet's Recherches, pp. 324-325; and Bohadsch's conclusions, pp. 347-348, with Nollet's Recherches, pp. 327-328. I have used Watson's summary of Bohadsch's results because Watson's summary is accurate and because the Philosophical Transactions are more readily available. The same comparison can be made with Bohadsch's De utilitate electrisationis in arte medica, pp. 5, 7, and 6, respectively.

⁹⁸ Priestley, History, p. 409.

⁹⁹Dalibard, <u>Histoire abregée de l'électricité</u>, in <u>Expériences</u>
et observations sur l'électricité faites à <u>Philadelphie</u> en <u>Ame'rique</u>
par M. Benjamin Franklin; & communiquées dans plusieurs lettres à
M. P. Collinson de la Société Royale de Londres (Paris: Chez Durand,
1752), pp. liv-lv.

^{100 &}lt;u>Ibid</u>., pp. 1-1xx.

Quoique les expériences & les observations dont cette Thèse est remplie, n'aient pas toutes le mérite de la nouveauté, elles sont trop interèssantes par leur objet, & par l'ordre dans lequel elles sont rapportées, pour ne pas trouver place dans cette histoire. 101

Bertholon, who had also accepted Nollet's hypothesis that electricity augments evaporation, referred to Bohadsch without mention of plagiarism. 102 Other than Watson, the only natural philosopher who called attention to the plagiarism was the Abbé Mangin. 103

In addition to Nollet's belief that electrification hastened evaporation, Benjamin Franklin believed that the evaporation of sea water was produced by electrification and explained the process in terms of his one theory fluid. Thus there was a prevalent conception concerning the role of electrification on fluids that did serve as a means to understand the dispersal of water by the passage of electricity.

One of the most systematic examinations of the passage of electricity through water is that of Henry Cavendish, whose experiments

¹⁰¹_<u>Ibid.</u>, pp. liv-lv. "Although the experiments and observations which fill this thesis do not have all the merit of being new, they are too interesting through their object and through the order in which they are reported, not to find a place in this history."

Bertholon, <u>De l'électricité du corps humain</u>, pp. 199-200 and 281.

¹⁰³ Mangin's analysis of the plagiarism was less charitable than was Watson's: On distingue aisement dans cet écrit une affectation singuliere de s'approprier toutes les expériences de M. 1'Abbé Nollet sur la végétation, la transpiration, & c. par le moyen de s'approprier 1'électricité: expériences encore qui sont assez infidélement rendues. Mangin, <u>Histoire générale</u>, 1:166-167. "One easily distinguishes in this writing a singular affectation of appropriating all the experiments of M. the Abbé Nollet concerning vegetation, transpiration, etc. [made] by the meams of electricity. Experiments moveover which are indeed rather unfaithfully rendered."

Franklin, Experiments and Observations on Electricity, 4th ed. (1769), pp. 40-43.

remained unpublished and virtually unknown for a century. Cavendish, unlike Deiman and Paets van Troostwijk, confined his experiments to testing the effect of the electric shock on various substances, including water. Beginning in November of 1773, Cavendish experimentally compared the conducting power of iron wire to salt water, and that of sea water to distilled water. Only an excerpt from Cavendish's journal of experiments can portray faithfully his attempt to measure and quantify the relationship between the passage of electricity and the substances conducting it:

In order to compare the conducting power of iron wire and salt water, the shock of two jars had its choice whether it would pass through 2540 inches of nealed iron wire, 12 feet of which weighed 14.2 grains, or through my body

It was found that when the straw electrometer separated to 1 ± 0 , I just felt shock in my wrists, and when it separated to 2 ± 0 , I felt a pretty brisk one in them but not higher up.

I then gave the shock its choice whether it would pass through my body, or 5.1 inches of a column of a saturated solution of sea salt contained in a glass tube, 1 inch of which holds 9.12 grains of fresh water, the wires running into the salt water being fastened to brass wires as before.

I found the shock to be just the same as before, and found too that increasing the length of the column of salt water not more than $\frac{1}{4}$ of an inch made a sensible difference in the strength of the shock.

Therefore the electricity meets with the same resistance in passing through 2540 inches of wire whose base is

$$\frac{\frac{1}{2}}{78 \times 144} = \frac{1}{79}$$
 as through 5.1 inches of salt water whose base is 9.12.

Therefore, if the resistance is as the 1.08 power of the velocity, the resistance of iron wire is 607,000 times less than that of a column of salt water of the same diameter.

577] <u>Comparison of conducting powers of saturated solution of sea salt and distilled water.</u>

The shock of 1 jar charged till the straw electrometer separated to $1+0\frac{1}{2}$, discharged through a column of $\binom{.8}{1.0}$ inches of a mixture of saturated solution of sea salt with 99 of distilled water in tube 6, was $\binom{\text{greater}}{\text{less}}$ than when it was discharged through $35\frac{1}{2}$ inches of saturated solution of sea salt in tube 2.

By a former experiment, the shock passed through $^{.87}_{1.35}$ } of the mixed water was { greater than through $^{40}_{2}$ of saturated solution.

By a mean, the resistance of one inch of the mixed water is equal to that of 38 of the saturated solution, therefore allowing for the different bases of the tubes, the resistance of the mixed water is 39 times greater than that of the saturated solution.

The shock of two jars, charged to 4 + 0, and discharged through $\begin{array}{c} .55 \\ 1.8 \end{array}$ of distilled water in tube 5, was { greater than when it was discharged through 23½ of the abovementioned mixed water in tube 8.

By a former experiment, the shock passed through $\{2,0\}$ of distilled water was $\{1 \text{ ess} \}$ than through $23\frac{1}{2}$ of the mixed.

By the mean, the resistance of 1.3 of distilled water = that of $23\frac{1}{2}$ of the mixed. 10.9 inches of tube 5 in the place where used holds 120 grains of φ , or 37 inches holds 408 grains, which is the same as tube 8: therefore the resistance of distilled water is 18 times greater than that of mixed, or 702 times greater than that of a saturated solution of sea salt. 105

Cavendish resumed his experiments on water in 1776 and again made detailed comparisons of the conductivity of salt water, fresh water, and distilled water. He also compared the conductivity of water with

Henry Cavendish, The Scientific Papers of the Honourable Henry Cavendish. F.R.S., Vol. 1: The Electrical Researches, ed. by James Clerk Maxwell (Cambridge: University Press, 1921), pp. 285-287. Cavendish's notebook was not published until 1879.

boiled water in order to determine if water purged of its air exhibited any change in its ability to conduct an electric shock. Cavendish made extensive comparisons of the conductivity of various salt solutions as well. 106

In his experiments on water, Cavendish never referred to any of the phenomena reported by so many other investigators, that is, augmented evaporation, agitation, shattering of the tube or vessel, or the generation of bubbles. In performing these experiments, Cavendish was not interested in such phenomena; he was only interested in the relative conductivity of water. Even if Cavendish saw these phenomena without recording them, they presumably could not have indicated to him that water was being decomposed, for to Cavendish water was an element and hence could not be decomposed. 107

Thus when Deiman and Paets van Troostwijk reported in 1789 that they had "réussi à découvrir un moyen de changer l'eau en même-temps en air inflammable (gaz hydrogène) & en air vital (gaz oxigène)" thereby providing new and persuasive arguments for Lavoisier's system of chemistry, they were once again tilling already familiar experimental ground. Prior to 1789, there had been numerous experiments examining the effects of electricity on water or the effects of water on the conduction of

¹⁰⁶ Ibid., pp. 311-322.

¹⁰⁷ In 1773 when Cavendish performed these experiments, no one had suggested that water was a compound of hydrogen and oxygen. Lavoisier did not do so until 1783. Even in 1784, after Cavendish had announced that the ignition of a mixture of phlogisticated and dephlogisticated air produced water, he did not refer to water as a compound and probably did not believe it to be one. In his "Experiments on Air," Philosophical Transactions 74(1784):137, Cavendish mentioned the possibility that inflammable air was a compound of phlogiston and water.

electricity. Most of these experiments were reported and discussed in books. journals, and in private correspondence by Franklin, Beccaria, Barletti, Priestley, Noilet, Sigaud de La Fond, Dalibard, Lane, Bohadsch, Mangin, Brisson, Folkes, Watson, Ellicott, Bertholon, and others. Some of these experiments, such as Cavendish's, remained unpublished and unknown, Many discussions of these experiments contained a description of one or more of the phenomena, that is, bubbles, agitation, diminution of the bulk of the water, or the shattering of the tube, mentioned by Deiman and Paets van Troostwijk's. But, because these experiments were conducted in the context of a theory in which both water and air were elements, the explanations of these experiments were not in the terms of the decomposition of water, but rather in the terms of the mechanical or electrical effects of electricity on water. Thus the agitation and diminishment of water associated with the passage of electricity through water was explained, when noted, in various fashions, One could, as Franklin did, appeal to the electric fire's ability to rapidly vaporize water in much the same way that fire vaporizes water, or one could, as Priestley did, appeal to electricity's ability to make water violently self-repulsive. If one accepted Nollet's theory of affluent and effluent electricity, then one could, as Brisson did, explain the agitation of the water by suggesting that it was a result of the retrograde movement of one of the two currents of electric matter causing the percussion of the two. One could, as Lane did, merely state the effects of the electric stroke on water without further explanation, or one could, as Priestley did, mention the phenomena occasioned by the passage of the

electric discharge through fluids, such as the excitation of bubbles from beer, and then ignore them, believing them to be incidental.

The theory proposed by Beccaria, that electricity hastens evaporation, depended on the mechanical ability of electricity to divide water into minute insensible particles and on its ability to excite and release fixed air from water. This view was based on another idea introduced by Nollet and prevalent in the latter half of the eighteenth century: electrification hastens the insensible evaporation of fluids. Even if one rejected Nollet's theoretical explanation of the phenomena, as Beccaria did, the idea that electrification hastens evaporation lent itself to the explanation of the effects of the passage of the electric fire through fluids.

The phenomena associated with the passage of electricity through water had been discussed and explained in the way one would have expected them to have been—in terms of contemporary theories. Usually they were considered in terms of such electrical theories as Nollet's theory of effluent and affluent electric matter or Franklin's one-fluid theory. Sometimes the phenomena connected with the passage of electricity through water were not discussed or explained, but merely stated. In either case, the interpreted results of such experiments were dictated by the theories of the experimenter, especially by the belief accepted by a majority of European natural philosophers from 1750 to 1790, that water was an element.

Deiman and Paets van Troostwijk's work illustrates this same feature of scientific investigation. They did not just perform a traditional and oft-repeated experiment and then adopt a new theory.

Instead, they had adopted a new theoretical stance quite different from that of those natural philosophers before them who had discussed the passage of electricity through water. Deiman and Paets van Troostwijk were able to interpret the well-known phenomena associated with the passage of electricity through water as a demonstration of the validity of Lavoisier's chemical theory because they already accepted that theory. Unlike most of their predecessors, they believed that water was a compound.

CHAPTER III

THE IDENTIFICATION OF ELECTRICITY AS PHLOGISTON AND THE BACKGROUND TO DEIMAN AND PAETS VAN TROOSTWIJK'S EXPERIMENTS

Deiman and Paets van Troostwijk had not accidentally discovered the decomposition of water: they had sought it. Their search took the form of a re-evaluation of experiments that had been conducted within a theoretical framework which held the decomposition of water impossible. However, they were not the first to re-evaluate the passage of electricity through water. Similar experiments were performed in the context of Lavoisier's new chemical theory in 1786 by Martinus van Marum (1750-1837). Van Marum, a friend and colleague of Deiman and Paets van Troostwijk, used these experiments to argue that since water could be decomposed electrically, Lavoisier's concept of water as a compound was true.

Even prior to his conversion to Lavoisier's anti-phlogistic system, Van Marum had been interested in the role of electricity in chemistry. In 1778 he had written a prize-winning essay on phlogisticated and dephlogisticated air for a competition sponsored by Teyler's Tweede Genootschap, the second of two foundations created from the estate of

J. G. de Bruijn, "Teyler's Tweede Genootschap," Martinus Van Marum: Life and Work, ed. by R. J. Forbes, Hollandsche Maatschappij der Wetenschappen, 5 vols. completed (Haarlem: H. D. Tjeenk Willink & Zoon, 1969-), 3:22-32. The second foundation was created for cultural and scientific inquiry, the first for theological work.

a rich Haarlem merchant, Pieter Teyler van der Hulst (1702-1778).

Van Marum won election to Teyler's Tweede Genootschap in 1779, and in four years he became director of the natural history and physics cabinets of the museum sponsored by the society. Van Marum's experiments using the great electrical machine constructed for Teyler's Museum by the same John Cuthbertson who later constructed the apparatus Deiman and Paets van Troostwijk used in their experiments on water, gained Van Marum recognition throughout the European scientific community. In these experiments he was often assisted by Deiman and Paets van Troostwijk.

Van Marum's interest in the chemical aspects of electrical phenomena originated from his belief that electricity and phlogiston were the same. During the latter half of the eighteenth century an increasing interest in electrical phenomena resulted in the discovery of new phenomena which natural philosophers attempted to explain by means of existing physical theory. One set of these new phenomena was the electrical calcination of metals and the electrical production or "revivification" of metals from calxes. The effort to bring this set of phenomena into the context of eighteenty-century physical theory led to the association of electricity with elemental fire because of their similarities and to the identification of electricity with phlogiston. The association of electricity with fire and the identification of the electric fire with phlogiston illustrates a widespread and pervasive

² Infra, pp. 85-86, 106-107 and G. C. Gerrits, Grote Nederlanders bij de Opbouw der Natuurwetenschappen, Leiden: E. G. Brill, 1948, pp. 210-226. See also T. H. Levere, "Martinus van Marum and the Introduction of Lavoisier's Chemistry into the Netherlands," Martinus van Marum: Life and Work, 1:158-163.

problem in eighteenth-century science: how to define the role of fire in chemical phenomena.

Beccaria discussed similarities between electricity and fire as early as 1758. Beccaria's ideas on the subject were influenced by the writings of Benjamin Franklin, who had treated the electric fire as if it were similar to common fire. Franklin, in the first edition of his Experiments and Observations on Electricity, published in 1751, discussed the similar effects of electricity and fire on water, noting that both electric fire and common fire are present in all bodies. Beccaria believed that one of the most significant similarities between electric fire and common fire was each one's ability to calcine metals and to revivify metals from their calxes. According to Beccaria, electricity calcines metals by driving off their phlogiston, and it revivifies metals by driving surface residues of phlogiston back into the calx.

The role Beccaria assigned to electricity with regard to fire was similar to Georg Ernst Stahl's (1660-1734) conception of the relationship between fire and phlogiston: Beccaria regarded electricity,

³Beccaria, <u>Elettricismo atmosferico</u>, p. 247.

Franklin in a letter dated 1749 had discussed electricity as if it were similar to common fire. See Franklin, Experiments and Observations, 4th ed. (1769), pp. 40, 50. The letter was published in English in 1751 and was available in a French edition of Franklin's works in 1752. Franklin was in turn influenced by the writings of Boerhaave and S'Gravesande. See I. Bernard Cohen's Franklin and Newton: pp. 230-239.

⁵Beccaria, <u>Elettricismo artificiale</u>, pp. 302, 309. For an English translation see Beccaria, <u>Treatise on Artificial Electricity</u>, pp. 304, 312.

like fire, as an agent capable of impressing or releasing phlogiston.
In France, Stahl's ideas had been modified in the teachings of Guillaume-François Rouelle (1703-1770) so that phlogiston was no longer considered as a principle activated by fire; rather, phlogiston was identified with the matter of fire itself. In England, Priestley also modified Stahl's ideas of phlogiston in that he considered phlogiston as a substance not associated with heat and capable of activating fire rather than being activated by it. Because his conception of phlogiston differed from Beccaria's, Priestley pointed out, in his History and Present State of Electricity, that the phlogiston necessary for the electrical revivification of metals from calxes in Beccaria's experiments must have come from the metallic conductors, a source external to the calx.

In this case of revivifications, he [Beccaria] always observed streaks of black beyond the coloured metalic stains, owing, as he imagined, to the phlogiston driven thither from the parts that were vitrified, when the other part revivified the calx. Probably, the phlogiston which revivified the calces was in that black dust, which the electric shock will throw from metals. . . .

It was Priestley's view that electricity calcined metals by depriving them of their phlogiston. He could not tolerate any suggestion that electricity alone could revivify calxes. 10 because he was reluctant

See James Robert Morris, Jr., "Eighteenth-Century Theories of the Nature of Heat (Ph.D. dissertation, University of Oklahoma, 1965), pp. 39,747 Rhoda Rappaport, "Rouelle and Stahl--The Phlogistic Revolution in France," Chymia 7(1961):73-102.

⁸ Morris, "Eighteenth-Century Theories of Heat," pp. 81-83, 185.

Priestley, <u>History</u>, p. 294.

¹⁰ Ibid., pp. 681-683.

to believe that the same agent could accomplish two opposing chemical actions, namely that electricity could both calcine a metal and revivity a calx (reconstitute the calx into a metal again).

Subsequently, Priestley changed his mind on the subject. While relating experiments on common air in his Experiments and Observations on Different Kinds of Air, he mentioned that he had been "led to consider the electric matter as phlogiston, or something containing phlogiston. . . ."

He also added in a footnote an apology to Beccaria:

Here it becomes me to ask pardon of that excellent philosopher Father Beccaria of Turin, for conjecturing that the phlogiston, with which he revivified metals, did not come from the electric matter itself, but from what was discharged from other pieces of metal with which he made the experiment. See History of Electricity, p. 277, & c. This revivification of metals by electricity completes the proof of the electric matter being, or containing phlogiston. 12

The phenomena of electrical calcination and revivification of metals from metallic calxes thus lent itself to the consideration of electricity in a new light. In the first place the calcination of metals and the revivification of metals from calxes were chemical operations. Second that which Beccaria did in his experiments was most accurately described as chemistry:

According to the 1771 Encyclopedia Britannica,

THE word ELECTRICITY signififies . . . the effects of a very subtile fluid matter, different in its properties from every other fluid

Joseph Priestley, Experiments and Observations on Different Kinds of Air, 2nd ed. "corrected" (London: for J. Johnson, 1775), p. 192.

^{12&}lt;sub>Ibid., p. 193,</sub>

As we are entirely ignorant of the Nature of the electric fluid, it is impossible to define it but by its principal properties: that of repelling and attracting light bodies is one of the most remarkable. 13

Beccaria's examination of the effects of electricity on matter brought electricity into consideration for its ability

which is the 1771 Encyclopedia Britannica's definition of chemistry. In other words, Beccaria's discussion of the electrical calcination of metals and the revivification of metals from calxes led to a consideration of the chemical properties of electricity to a degree others had not carried it. Before Beccaria's experiments, electricity had most often been examined <u>qua</u> electricity, not <u>qua</u> an electric fire exhibiting chemical properties.

The definition of chemistry found in the 1779 edition of the Encyclopedia Britannica emphasizes the role of heat in chemistry:

Chemistry May be defined, [as] The study of such phenomena or properties of bodies as are discovered by variously mixing them together, and by exposing them to different degrees of heat, alone, or in mixture, with a view to the enlargement of our knowledge in nature. . . . It is the study of the effects of heat and mixture upon all bodies. 15

Beccaria's assumption of the similarities of electric fire and common fire allowed him to replace common fire with the electric fire as a heat-providing agent in chemical operations. 16

^{13&}quot;Electricity," Encyclopaedia Britannica (1st ed., 1771) 2:471.

^{14&}quot;Chemistry," Encyclopaedia Britannica (1st ed., 1771) 2:66.

^{15&}quot;Chemistry," Encyclopaedia Britannica (2nd ed. revised, 1779) 3:1804.

¹⁶ Beccaria, Elettricismo artificiale, pp. 3, 65, 110-111.

Without being aware of Beccaria's experiments or of Priestley's comments on them, Nicolas-Christiern de Thy, le Comte de Milly (1728-1784) wrote an article on the reduction of metallic calces to metal by the electric fire. De Milly, an officer who had quit the cavalry to devote himself to the "sciences," 17 identified the electric fire with phlogiston. In the terms of the contemporary phlogiston theory, the production of calx from metal required the addition of phlogiston. If the electric fire could produce metals from calxes, it must, like fire, provide phlogiston to the calx. 18

After his article was published in <u>Observations sur la physique</u>, de Milly received a letter from Giussepe Angelo Saluzzio, Conte de Menusiglio (1734-1810), President of the Royal Society of Turin¹⁹ and a former pupil of Beccaria, informing him of Beccaria's same experiments performed and published some sixteen years earlier. As a result, de Milly wrote a letter to the editors of <u>Observations sur la physique</u>, explaining his ignorance of Beccaria's experiments and pointing out that

¹⁷Marie-Jean-Nicolas Caritat Marquis de Condorcet, "Eloge de
M. Le Comte de Milly," Histoire de l'Académie Royale des Sciences.
Année M.DCCLXXXIV., pp. 64-69.

¹⁸ Nicolas-Christiern de Thy, le Comte de Milly, "Mémoire sur la réduction des chaux métalliques, par le feu électrique, lu à l'Académie des Sciences de Paris, le 20 Mai 1774; par le Compte de Milly," Observations sur la physique 4(1774):148. In spite of the title of this article, there is no record in either the <u>Histoire</u> or the Mémoires de l'Académie Royale des Sciences of de Milly's memoir having been presented in 1774. Moreover, discussions of de Milly's experiments published after 1774 refer to only de Milly's article in Observations sur la physique.

¹⁹ Poggendorff, 2:743-744. Saluzzio, or "le Comte de Saluces," as de Milly called him, later published his own article on the reduction of calxes in the Mémoires de la Société Royale de Turin 3(1788).

while the experiment was not original, his argument, that the electric fire and phlogiston were identical, was original. 20

Actually, his conclusion was not as original as he had thought; Amié-Henri Paulian (1722-1800), a Jesuit teacher of physics at Avignon, had identified electricity with the element of fire fixed in matter in his <u>Dictionnaire</u> de physique, first published in 1761. ²¹ Paulian's identification of electricity with the elemental fire fixed in matter was, in any case, not too different from de Milly's identification of phlogiston with electricity, once one associated phlogiston with the element of fire fixed in matter. Although Paulian cited no experiments

 $²⁰_{
m Nicolas-Christiern}$ de Thy, le Comte de Milly, "Lettre adressée à l'auteur de ce recueil. Par M. le Comte de Milly, "Observations sur la physique 4(1774):318. Like de Milly, Lavoisier also had Beccaria's experiments on calcination drawn to his attention. An extract of Lavoisier's experiments on the calcination of metals in sealed containers was published in the same year as de Milly's articles on the revivification of calxes. Lavoisier requested that the editor of Observations sur la physique print after the synopsis of his experiments a letter from Beccaria dated 12 November 1774. This letter pointed out that Lavoisier's calcination experiments duplicated experiments that Beccaria had performed sixteen years earlier. Beccaria had noted that in his experiments there was no significant weight increase and very little calcination in proportion to the size of the sealed flask. Since he believed that phlogiston could not enter the sealed flask and thus very little calcination would occur, Beccaria's results were consistent with the phlogiston theory. Lavoisier agreed with and lauded Beccaria's results but argued instead that the small weight increase had occurred through calcination resulting from the fixing to the metal of the limited amount of air contained in the sealed flask. See Antoine-Laurent Lavoisier, "Mémoire sur la calcination des métaux dans les vaisseaux fermés, & sur la cause de l'augmentation de poids qu'ils acquierent pendant cette opération; lu par M. Lavoisier, de l'Académie Royale des Sciences à la séance publique de la même Académie, le 12 Novembre 1774," Observations sur la physique 4(1774):448-451. Lavoisier, "Lettre ecrite à l'auteur de ce recueil; par M. Lavoisier, de l'Académie des Sciences, après lui avoir envoyé le mémoire qu'on vient de lire," Observations sur la physique 4(1774):452-453.

^{21&}lt;sub>Ami</sub>é Henri Paulian, <u>Dictionnaire de physique</u>, 3 vols., 1st ed. (Avignon: Chez Louis Chambeau, 1761), 2:106.

in his <u>Dictionnaire</u> for his identification of electricity with elemental fire, he did so in a later work, <u>L'Electricité soumise a un nouvel examen</u>, published in 1768.²²

De Milly's identification of the electric fire with phlogiston was rejected by some phlogiston chemists, such as Brisson and Louis-Claude Cadet de Gassicourt (1731-1799), who attacked de Milly's hypothesis in a memoir, read to the Académie des Sciences on 15 November, 1775.

Using some of the same experiments performed by Beccaria and de Milly, they sought to show that the metal produced when the "fluide électrique" was passed through metallic calxes resulted from fusion to the calx of the wires conducting the electric fluid rather than from a revivification of the calx. In order to demonstrate that the metal was produced from the conducting wire, Brisson and Cadet repeated each experiment twice, first using wires of tin, then wires of gold. They used gold for a comparison because they believed that fused gold could not be mistaken for any other metal. Mentioning the same black powder that Priestley reported, Cadet and Brisson summarized:

le fluide électrique, auquel on connoît très-bien la propriété de faire fondre & de calciner les métaux, n'a en aucune façon celle de revivifier les chaux métalliques. En effet la foudre,

Paulian, L'Electricité soumise a un nouvel examen, dans différentes lettres addressées à M. l'Abbé Nollet, et dans quelques questions de physique, présentées sous la forme scholastique: le tout, selon une théorie nouvelle, appuyée sur les expériences les plus incontestables (Avignon: Chez la Veuve Girard & Franç. Sequin, 1768), p. 107.

²³ Jacques-Mathurin Brisson and Louis-Claude Cadet de Gassicourt, "Mémoire sur l'action du fluide électrique, sur les chaux métalliques. Par M.rs Brisson & Cadet," Mémoires de l'Académie Royale des Sciences. Année M.DCCLXXV (published in 1778), pp. 243-244.

que tout le monde sait être une électricté en grand, a souvent fait fondre ou calciné les métaux: jamais elle n'en a revivifié les chaux. 24

Cadet and Brisson were convinced that electricity could calcine metals and never revivify calxes. Like Priestley, they rejected ascribing two opposing processes to the same agency.

Another phlogiston adherent, Joseph-Aignan Sigaud de la Fond, accepted de Milly's identification of the electric fire with phlogiston. He also repeated de Milly's experiments and published a synopsis of these in <u>Observations sur la physique</u> in the same year that de Milly's article appeared. According to the synopsis:

le procédé de M. Sigaud de la Fond ne laisse aucun scrupule & fait voir manifestement que ces sortes de révivifications sont totalement dues à la matiere électrique que fait ici fonction de phlogistique.²⁵

In his repetition of de Milly's experiment, Sigaud de la Fond had enclosed a metallic calx in a glass tube two inches long and about two lines in diameter. The conducting wires were inserted through the ends of the tube. Using this apparatus

une seule explosion révivifie une portion plus ou moins grande de la chaux métallique; & si on veut en révivifier une plus grande

^{24&}lt;u>Ibid.</u>, p. 254. "The electric fluid is very well known to have the property of melting and calcining metals, has in no way that of revivifying metallic calxes. Indeed lightning, which everyone knows to be electricity on a large scale, has often melted or calcined metals: never has it revivified their calxes.

²⁵[Sigaud de la Fond?], "Nouvelles experiences de l'electricité," Observations sur la physique 4(1774):444. The articles discusses Sigaud de la Fond in third person while the index gives his name as author. "the procedure of M. Sigaud de la Fond leaves no qualms & causes one to see clearly that these sorts of revivifications are due totally to the electric matter which has here the function of phlogiston."

quantité, il ne s'agit que de répéter plusieurs fois de suite l'expérience. . . 26

Sigaud de la Fond also referred briefly to the ability of electricity to revivify calxes in his <u>Elémens de physique</u>. Although he mentioned that electricity was responsible for the opposite effect, the calcination of metals, Sigaud de la Fond did not doubt that the two opposing processes were both caused by the electric discharge:

L'or fin prend ici une couleur purpurine. . . . Il se convertit donc en une espece de chaux métallique. . . , une seconde . étincelle . . . revivifie le métal: & c'est de cette maniere qu'on peut revivifier presque toutes les chaux métalliques, comme P. <u>Beccaria</u> l'a originaiment [sic] découvert en Italie, comme M. le Comte de <u>Milly</u> . . . l'a démontre en 1774, & comme nous le démontrerions encore ici, 27

Sigaud de la Fond discussed the matter in greater detail in his <u>Précis historique</u>, prefacing his discussions of de Milly's article on the electrical revivification of calxes with the remark "l'électricité, sans le concours de tout agent ultérieur, sans aucun autre intermède, produit le même effet [as phlogiston]..."

^{26 &}lt;u>Thid.</u>, p. 445. "a single explosion revivifies a more or less great portion of the metallic calx; and if one wants to revivify a greater quantity, it is only a matter of repeating the experience several times in a row. . . ."

²⁷ Sigaud de la Fond, Elémens de physique, 1st ed. (1777), 4:437 or 2nd ed. (1787), 4:423. "The gold takes here a purple color. . . . It is therefore converted to a species of metallic calx. . ., a second spark . . . revivifies the metal: and it is in this way that one can revivify almost all the metallic calxes, as P. Beccaria originally discovered in Italy, as M. le Comte de Milly . . has demonstrated in 1774, & as we would demonstrate again here. . . .

²⁸ Sigaud de la Fond, <u>Précis historique</u>, 1st ed. (1781), p. 612 or 2nd ed. (1785), p. 516. "electricity without the aid of any ulterior agent, without any other intermediary, produces the same effect [as phlogiston]. . . "

The acceptance of the identification of phlogiston with electricity was by no means universal. In the first edition of his Complete Treatise of Electricity Tiberius Cavallo (1749-1809) pointed out that natural philosophers had been known to identify the electric fluid with fire and thus to even call it the electric fire. However, Cavallo believed electricity to be a fluid "sui generis, i.e., different from all other known fluids." Cavallo accepted the existence of phlogiston, a principle of active fire transferable from one body to an another, as being "beyond a doubt," but he saw little resemblance between the electric fluid and phlogiston:

In the first place if they were both the same thing, they should always be together, and whenever such a quantity of fire exists, there the same quantity of electric fluid should be found, but this is contrary to experiments . . . Secondly fire penetrates every known substance . . , whereas the electric fluid pervades only Conductors. Thirdly the electric fluid goes through a very long Conductor in a space of time almost instantaneous, but fire is very slowly propagated. I might enumerate several other improprieties attending this hypothesis of the sameness of fire, and of the electric fluid, but those already mentioned, are, I think, sufficient to induce my reader to suppose otherwise. 31

Cavallo went on in his discussion of the nature of electricity specifically to reject Priestley's conclusion that the electric fluid was phlogiston and to suggest an explanation for the electrical revivification that Priestley would have accepted in 1767; that is, the phlogiston necessary for the revivification of calxes did not come from

Tiberius Cavallo, A Complete Treatise of Electricity in Theory and Practice; with Original Experiments. By Tiberius Cavallo (London: for Edward and Charles Dilly, 1777), p. 110.

^{30 &}lt;u>Tbid.</u>, pp. 111-112.

^{31&}lt;u>Ibid</u>., pp. 112-113.

the electric fluid but "either from the surface of the Conductors, between which the explosion is taken, or from particles of heterogeneous matter floating in that air, in which the explosion is made." Although the <u>Complete Treatise</u> was published in several editions, Cavallo did not change his discussion of the nature of the electric fluid in these later editions. 32

As an alternative to identifying electricity as phlogiston, Cavallo cited the views of William Henly (fl. 1775).

Mr. Henly, in consequence of several very interesting experiments, that he has lately made, supposes that, although the electric fluid be neither phlogiston nor fire, yet that it is a modification of that element, which, while in quiescent state, is called Phlogiston, and when violently agitated is called Fire. ³³

According to Cavallo, Henly's belief that "the phlogiston, the electric fluid, and fire, are only different modifications of the very same element . . . " had "a great deal of probability."³⁴

³²_Ibid., pp. 113-114. His discussion of the electric field is found on pp. 112-122 of the 1st vol. of each edition. Cavallo, A Complete Treatise on Electricity, in Theory and Practice; with Original Experiments. By Tiberius Cavallo, F.R.S., 2nd ed. "with Considerable Additions and Alterations," 2 vols. (London: C. Dilly and J. Bowen, 1782). Cavallo, A Complete Treatise on Electricity, in Theory and Practice; With Original Experiments. By Tiberius Cavallo, F.R.S., 3rd ed. "Containing the Practice of Medical Electricity besides other Additions and Alterations, 2 vols. (London: for C. Dilly, 1786). Cavallo, A Complete Treatise on Electricity, in Theory and Practice; With Original Experiments. By Tiberius Cavallo, F.R.S., 4th ed. "Containing the Practice of Medical Electricity, Besides Other Additions and Alterations. The Third Volume is Entirely New, and Contains the Discoveries and Improvements Made Since the Third Edition," 3 vols. (London: for C. Dilly, 1795).

^{33&}lt;sub>Cavallo</sub>, <u>Complete Treatise</u>, 1st ed. (1777), p. 115. Robert Edward Anderson in "William Henley," <u>DNB</u>, 9:421 refers to Henly as "Henley or Henly." For convenience the form Henly's contemporaries used has been adopted.

³⁴Cavallo, Complete Treatise, pp. 116-117.

Henly, in a paper read to the Royal Society of London and published in the same year as Cavallo's <u>Complete Treatise</u>, related how he had always "considered electricity as a fluid <u>sui generis</u>" and had, therefore, avoided the term electric fire. However, he had begun to believe that electricity might be considered as "elementary fire, inherent in all bodies" and he asked, "is there not a high degree of probability in the supposition, that light, fire, phlogiston and electricity, are only different modifications of one and the same principle?" Henly cited experiments that he had made with Cavallo and George Adams (1750-1795), and he appealed to the authority of Priestley, Booerhaave, and Stahl to further support his arguments. 37

While experimenting with Adams on the electrification produced by the cooling of molten chocolate, Henly had noticed that after the chocolate dried to a powder it lost its electrification and that when oil was added to the powder the chocolate became re-electrified. He explained:

The large proportion of phlogiston in oil is well known; and as the addition of oil to the chocolate completely restored its electricity when lost, is not this an indication of a great affinity at least between phlogiston and the electric fluid, if indeed they not be the same thing: 38

³⁵ William Henly, "Experiments and Observations in Electricity," Philosophical Transactions 67, Pt. 1(1777):130.

³⁶ Ibid., p. 135.

^{37 &}lt;u>Ibid</u>., p. 143.

^{38&}lt;sub>Ibid.</sub>, pp. 96-97.

Perhaps one of the most significant steps in the examination of the relationship of chemical and electrical phenomena came as a result of an article by the Baron Reth de Servières (f1. 1777), one of the more obscure personages in the history of science. Servières has been identified as the Officer of the Regiment of the Orleans Cavalry, correspondent to l'Ancienne Société Royale des Sciences de Montpellier and to the Société Royale de Agriculture de Paris, Corresponding Associate of the Société Patriot de Hesse, President of the Bureau de Consultation des Arts et Métiers, member of la Société Royale de Suede, and author of Observations sur le thermometer (Vesoul, 1777) and other publications. 39

In a short article printed in 1778 in <u>Observations sur la</u>

<u>physique</u>, Servières suggested a program of experiments designed to discover if the electric matter and phlogiston were identical, as de Milly had asserted. Although Servières did not indicate that he had performed or intended to perform these experiments himself, his proposal emphasized the chemical implications of the attempt to identify electricity and phlogiston. Servières wrote:

M. le Comte de <u>Milly</u>, dans un beau Mémoire lu à l'Académie des Sciences de Paris, le 20 Mai 1774, rendit compte d'une suite d'expériences qu'il avoit faites, & montra des choux métalliques, dont il avoit fait la réduction par le feu électrique. De cette réduction il concluoit que la matiere électrique est identique ou

Ouérard, La France littéraire, 9:93. Also Catalogue général des livres imprimés de la Bibliothèque Nationale-auteurs, 171:279.

Servières had twelve articles printed in Observations sur la physique. See Observations sur la physique 29(1786):471. See also Oeuvres de Lavoisier: Correspondance, ed. with notes by René Fric, in progress, 3 vols. completed as of 1975 (Paris: Albin Michel, 1955-), 3:694-696.

phlogistique. Sa conclusion paroît très-juste; car deux effets semblables supposent nécessairement une seule & même cause. La matière électrique ne sera bien connue, que lorsqu'elle aura été soumise aux expériences & à l'analyse des Chymistes. J'ose donc les inviter à courir une nouvelle carrière, qui peut mener à des découvertes aussi neuves qu'utiles. Parmi un très-grand nombre d'expériences qu'on pourroit tenter pour découvrir l'identité ou la non-identité du feu électrique avec le phlogistique, je n'en proposerai que trois, dont le résultat seroit décisif. 40

The experiments Servières suggested were the following:

- 1. Combining the electric fire with vitriolic acid.
- Combining the electric fire with nitre.
- 3. Combining the acid of marine salt with the electric fire. 41

 He expected, in accordance with phlogiston theory, that if the electricity contained phlogiston, its combination with vitriolic acid would yield sulfur, its combination with nitre would decompose the nitre, and its combination with marine acid would yield phosphorus. 42 Servières was explicitly concerned with investigations of a possible relationship between chemical and electrical phenomena.

Le Baron Reth de Servières, "Projet de quelques expériences chymico-électriques; par M. le Baron de Servières," Observations sur la physique 13, Supplément (1778):150. "M. le Comte de Milly, in a fine memoir read to the Academy of Sciences of Paris on 20 May 1774 gave an account of a series of experiments that he had made and showed metal calxes that had been reduced by the electric fire. From this reduction he concluded that the electric matter is identical to phlogiston. His conclusion appears quite right; because two similar effects necessarily imply one and the same cause. The electric matter will not be well known until it is submitted to the experiments and analysis of chemists. I dare therefore to invite them to take a new course which can lead to new as well as useful discoveries. Among a great number of experiments which could be attempted to discover the identity of non-identity of the electric fluid with phlogiston I will propose only three, the result of which would be decisive."

^{41 &}lt;u>Ibid</u>., p. 151.

⁴² For a summary of the phlogistication of these substances see "Chemistry," Encyclopaedia Britannica, 1st ed. (1771), 2:72-74, 119-120, 123.

The chemical role of electricity attracted the attention of others who sought to identify electricity with phlogiston. Sigaud de la Fond extended the examination of chemical properties of the electric fire by asserting that in addition to producing the same effects as phlogiston, electricity contained a chemical agent similar in its effects to acid. In his demonstration of the acidic effects of electricity, Sigaud de la Fond utilized a glass tube four to five inches long and two lines in diameter. After stopping one end of the tube with wax, he inserted a wire through the wax. When the open end of the tube was immersed in a solution of tournesol or of tincture of violets, and the electrical discharge was passed through the tube, a red color indicative of acidity appeared within the solution. The air space at the top of the tube was also diminished by two or three lines.

Franz Karl Achard (1753-1821) also associated electricity and phlogiston and examined the chemical properties of electricity. Achard, born of French protestant émigrés, was a protegé of Andreas Sigismund Marggraf (1709-1782) and later became Director of the Class of Physics at the Berlin Academy. He displayed an interest in the effects of electricity on matter in 1783 with an article exploring the analogy between heat and electricity. One of the points of analogy Achard mentioned was that "l'électricité positive accélère l'évaporation aussibien que l'électricité négative; ce qui forme un troisième point d'analogie entre

⁴³ Joseph-Aignan Sigaud de la Fond, <u>Précis historique</u>, pp. 618-619.

⁴⁴ J. B. Gough, "Franz Karl Achard," <u>DSB</u>, 1:44-45.

les effets de la chaleur & de l'électricité." In 1784 Achard published an examination of the electric fluid that stemmed from the program of experiments suggested by Servières. He pointed out in this memoir that some authors had identified the electric spark with acid or believed it to contain an acid because of the biting effect it had on the tongue and because the passage of the electric discharge often produced a smell similar to that of "phosphore," a substance that he believed to be a compound of acid united to phlogiston. 46 Achard therefore devised an experiment to test the acidity of the electric spark. He used a tube one-half an inch in diameter and three or four inches long, corked on both ends, with wires of tin inserted through the opposing corks. After filling the tube with tournesol infusion, he sent 2,000 successive electric discharges through the infusion over a distance of one line between the wires. Achard did not observe in the tournesol solution a color change that would indicate acidity. He then replaced the tournesol with volatile alkali and noted that after 4,000 discharges no neutral salts had appeared. He believed his experiments supported de Milly's hypothesis and noted

⁴⁵Franz Karl Achard, "Mémoire sur l'analogie qui se trouve entre la production & les effets de l'électricité & de la chaleur, de même qu'entre la propriété des corps de conduire le fluide électrique & de recevoir la chaleur; avec la description d'un instrument nouveau, propre à mesurer la quantité de fluide électrique que peuvent conduire des corps de différente nature, placés dans les mêmes circonstances; par M. Achard," Observations sur la physique 22 (1783):248. "Positive electricity accelerates evaporation as well as does negative electricity; which forms a third point of analogy between the effects of heat and of electricity."

⁴⁶ Franz Karl Achard, "Mémoire renfermant le récit de plusieurs expériences électriques faites dans différentes vues; par M. Achard," Observations sur la physique 25(1784):430. See also Sigaud de la Fond, Dictionnaire de physique (1781), 3:578.

que dans l'inflammation du fluide électrique, il ne sépare aucun acide, & qu'il ne peut par conséquent pas être mis dans la classe des substances sulfureuses; ce qui est très favorable à l'opinion du Comte de Milli. . . . 47

Achard's experimental findings contradicted those of Sigaud de la Fond, who had already experimentally determined to his own satisfaction that the electric spark produced acidic effects. Achard agreed with Sigaud de la Fond in identifying electricity with phlogiston, but, unlike Sigaud de la Fond, he believed that if the electric fluid did exhibit acidic effects, such effects would be contradictory to the identification of electricity with phlogiston. Fortunately for Achard, who believed the electric fluid and phlogiston to be the same, he did not find the electric spark to have any acid effects. Moreover, he argued that not only the reduction of calxes but "la décomposition & la phlogistication de l'air commun & de l'air déphlogistiqué" by the electric spark also furnished proof of de Milly's assertion that the electric spark produces phlogiston. 48 The action of the electric spark on dephlogisticated and vital air had been discussed by other chemists. Priestley had shown as early as 1771 that both common air and dephlogisticated air were sensibly altered by electrical discharges. According to Priestley, the passage of electrical discharges through vital or common air changed the

⁴⁷ Achard, "Mémoire renfermant le récit de plusieurs expériences," pp. 430-431. "that in the inflammation of the electric fluid, it separates out no acid, & consequently it cannot be put in the class of sulphur-containing substances; which is very favorable to the opinion of the Comte de Milli..."

 $^{{}^{\}mbox{48}}\underline{\mbox{1bid.}},$ p. 431. "the decomposition and phlogistication of common and dephlogisticated air."

purity of these airs and diminished or nullified their ability to support respiration or a flame. 49

Although Achard mentioned Servières' articles, he did not conduct the program of experiments that Servières had devised because he did not consider Servières' experiments to be a decisive test in identifying the electric spark. The only experiment proposed by Servières that Achard may have attempted was the passage of the electric discharge through nitre. Without indicating that he conducted such an experiment, Achard pointed out that nitre in fusion is alkalized by the electric discharge, an "effet que peut uniquement produire le phlogistique.

Cette expérience est une des trois que le Baron de Servières propose.
..."50

Rather than follow Servières' proposal of testing the electric discharge on vitriolic acid, Achard chose instead to test it on dry Glauber's Salt: "le phlogistique, à cause de sa grande affinité avec l'acide vitriolique, décompose les sels neutres qui contiennent cet acide: . . ."⁵¹

⁴⁹ Priestley, Experiments and Observations on Different Kinds of Air, p. 181.

⁵⁰ Achard, "Mémoire renfermant le récit de plusieurs expériences," p. 431. "effect that phlogiston can uniquely produce. This experiment is one of the three that the Baron de Servières proposes. . . ."

⁵¹_<u>Ibid.</u>, p. 431. "phlogiston because of its great affinity with vitriolic acid, decomposes neutral salts that contain this acid." Glauber's salt is a product of a reaction between vitriolic acid and caustic alkali. Under certain conditions Glauber's Salt can be decomposed to produce vitriolic acid..

Achard believed that the acid in the salt would combine with the electric fire and form a "soufre artificiel." However, the salt did not decompose in the least. 52

Achard rejected Servières' assumption that phosphoric acid and marine acid were the same. Since no one had yet been able to obtain phlogisticated marine acid, Achard believed that even if the passage of the electric discharge through marine acid yielded phosphorus,

cette expérience ne peut pas servir de preuve; car dans le cas même où la matière électrique ne différeroit en rien du phlogistique, il est très-certain qu'elle ne feroit éprouver aucun changement à l'acide marin. 53

Consequently, Achard rejected Servières third proposal, the passing of the electric discharge through marine acid.

The identification of electricity with phlogiston posed a possible conflict with the ideas of Cavendish, ⁵⁴ Priestley, ⁵⁵ James Watt (1736-1819) ⁵⁶ and Richard Kirwan (1733-1812), ⁵⁷ who, beginning with

⁵² Tbid., "artificial sulfur."

⁵³<u>Thid</u>. "This experiment cannot serve as proof; because even in the case where electric matter would not differ in any way from phlogiston, it is very certain that it would not cause any change in the marine acid."

⁵⁴ Henry Cavendish, "Experiments on Air," Philosophical Transactions 74(1784):137.

Joseph Priestley, "Experiments Relating to Phlogiston, and the Seeming Conversion of Water into Air, By Joseph Priestley, L.L.D. F.R.S.; Communicated by Sir Joseph Banks, Bart. P.R.S.," <u>Philosophical Transactions</u> 73(1783):402. Priestley did not indicate in this paper whether he had rejected the identification of electricity with phlogiston.

James Watt, "Thoughts on the Constituent Parts of Water and of Dephlogisticated Air; with an Account of Some Experiments on that Subject. In a Letter from Mr. James Watt, Engineer, to Mr. De Luc, F.R.S.," Philosophical Transactions 74(1784):330.

 $^{^{57}}$ Richard Kirwan, "Continuation of the Experiments and

Kirwan in 1782, had identified phlogiston with inflammable air.

Furthermore, there were variations in opinion even among those natural philosophers who identified phlogiston with electricity. For instance, Felice Fontana (1730-1805), professor of physics at Pisa, described electricity in his Opuscules physiques et chymiques as "une vraie flamme ou substance en combustion." Although Fontana noted that: "L'électricité produit . . . sur 1'air commun tous les mêmes effets que produit le phlogistique ou la flamme actuelle," he did not consider the electric matter to be "un principe simple." Instead Fontana thought that electricity as well as

les autres substances lumineuses comme les phosphores.... seroient réduites à un même principe; ensorte que la famille des corps combustibles & inflammables comprendroit un plus grand nombre de substances qu'auparavant. 61

Fontana believed inflammable air to be a compound containing phlogiston. 62 He discussed several chemical effects of electricity. They were:

Observations on the Specific Gravities and Attractive Powers of Various Saline Substances. By Richard Kirwan, Esq. F.R.S.," Philosophica1
Transactions 72(1782):196-197.

⁵⁸ Felice Fontana, Opuscules physiques et chymiques de M. F. Fontana, trans. by M. Gibelin (Paris: Chez Nyon 1'ainé, 1784), p. 151.

 $^{^{59}\}underline{\text{Tbid}}.$ "electricity produces . . . on common air all the same effects as phlogiston or an actual flame would."

⁶⁰ Ibid., p. 150, "a simple principle."

 $⁶¹_{\overline{\text{Lbid}}}$, p. 152. "the other luminous substances such as the phosphorouses . . . would be reduced to a single principle; so that the family of combustible and inflammable bodies would include a greater number substances than previously."

 $^{^{62}\}underline{\text{Tbid}}$, p. 146. "L'air inflammable a sûrement le phlogistique au nombre de ses parties constituantes. . . ."

- 1. Electricity is always accompanied by the odor of sulfur.
- 2. Electricity diminishes respirable air.
- 3. Electricity reddens tournesol.
- 4. Electricity precipitates chalk in calcareous earth.
- 5. Electricity crystallizes caustic vegetable salts.

Moreover, he pointed out that three of these effects

opinions.

du tournesol, de la chaux, & des sels caustiques, n'ont jamais lieu lorsqu'on se sert d'air phlogistiqué, & ils cessent dans 63 l'air commun dès qu'il a acquis la nature d'air phlogistiqué.

Therefore, two important differences exist between the chemical

properties attributed to electricity by Achard and by Fontana:

1. Fontana believed that the electric discharge had an acidic effect;

Achard did not. They cited different experiments to support their

2. Fontana believed that the electric discharge diminishes respirable air; Achard had not considered the effect of the electric discharge on air. Fontana was interested in the effect of the electric discharge on air because he was interested in chemical changes occurring in respiration.

Fontana, unlike Achard, cited no specific experiments in his Opuscules to demonstrate his description of the chemical effects of electricity.

^{63 &}lt;u>Thid.</u>, p. 151. "on tournesol, on chalk, and on the caustic salts, never take place in phlogisticated air, and they cease in common air when it has acquired the nature of phlogisticated air."

⁶⁴ Fontana himself is a subject worthy of study. If one compares the account of him in Poggendorff, 1:767-768 to that of Luigi Belloni in the DSB, 5:55-57, it is difficult to believe at first glance that the articles do not refer to two different Fontanas.

Less than a year after the publication of Achard's article,

Van Marum published an account of his own electrical and chemical experiments. Among these was an examination of the calcination of metals and of the revivification of metal calxes by the passage of an electrical discharge. Van Marum had at his disposal the great static electric generator built for Teyler's Museum by John Cuthbertson, probably the largest and most powerful static electric generator then in existence, and he intended to answer once and for all any questions concerning the effects of electric discharge on metals and their calxes:

Ce sujet m'a paru depuis longtems être d'une grande conséquence, puisque si la revivification des métaux se fait véritablement par la décharge électrique, elle nous apprend à connoître d'une manière très décisive la nature de la matière électrique. Les expériments, qui j'ai faits auparavant à cet égard, n'ont jamais été satisfaisants, et ils m'ont depuis longtems fait désirer de décider cette question par le moyen d'une force plus grande, que celle qu'on a employée jusqu'ici. La batterie, que j'ai décrite, me procurant l'occasion, que je désirois, je priai Mr. Paets van Trooswyk de faire ces expériments avec moi. 65

Van Marum approached these experiments from a phlogistic point of view. In fact, in 1780 he had won an essay contest sponsored by Teyler's Tweede Genootschap on the topic of phlogisticated and

⁶⁵ Martinus Van Marum, "Description d'une très-grande machine électrique, placée dans le Muséum de Teyler a Haarlem, et des expériments faits par le moyen de cette machine," Verhandelingen, uitgegeeven door Teyler's Tweede Genootschap 3(1785):184. (Hereinafter referred to as Verh TTG.) "This subject has appeared to me for a long time to be of great consequence, since if the revivification of metals is really effected by the electrical discharge, it leads us to know in a very decisive manner the nature of the electric matter. The experiments that I have made previously concerning this matter had never been satisfying, and they have made me want for a long time to decide this question by means of a greater force than that which has been used until now. The battery that I have described, furnishing me the opportunity that I had wanted, I asked Mr. Paets van Troostyk to make these experiments with me,"

dephlogisticated air. 66 Three years later, he and Paets van Troostwijk won another gold medal, this time from the Bataasch Genootschap of Rotterdam. 67 for a practical chemical essay based on the phlogiston theory.

Van Marum's examination of the effects of electricity on metals and metallic calxes was first published simultaneously in French and Dutch in 1785 in the <u>Verhandelingen</u> of Teyler's Tweede Genootschap. 68

The article containing these experiments, "Description d'une très-grande machine électrique," was also published in German translation in 1786. 69

After mentioning the experiments of Beccaria, de Milly, and the contradicting results of Brisson and Cadet, 70 Van Marum outlined his own experiments that he believed would allow the question to be resolved decisively. In order to forestall any objections that the results were affected by metallic contamination, Van Marum and Paets van Troostwijk 71

⁶⁶ Martinus Van Marum, "Natuurkundige Verhandling ter beandwoording van't voorstel by Teylers Tweede Genootschap uitgeschreeven over de gephlogisteerde en gedephlogisteerde luchten," Verh. TTG. 1(1781).

⁶⁷Martinus Van Marum and Adrian Paets van Troostwijk, "Welke is de aart van de verschillende, schadelijke en verstikkende Uitdampingen van Moersassen, Modderpoelen, Secreeten, Riolen, Gast- of Ziekenen Gevangenhuizen, Mijnen, Putten, Graven, Wijn- en Bierkelders, doove Koolen etc? En Welke zijn de beste middelen en tegengiften om de schadelijkheid dier Uitdampingen, naar haaren verschillenden aart, te verbeteren, en de verstiken te redden?" (Antwoord), Verhandling Bataafsch Genootschap Proefondery. Wijsbegeerte 8(1787):1-61.

⁶⁸ Recto in French, verso in Dutch. <u>Supra</u>, p. 85, note 65.

⁶⁹ Martinus van Marum, Beschriebung einer ungemein grossen
Electrictrisier-Maschine und der damit im Teylerschen Museum zu Haarlem
angestelten Versuche durch Martinus van Marum, (Leipzig: im Schwickertschen Verlage, 1786), pp. 37-38.

 $^{^{70}\}mathrm{Marum},$ "Description d'une très-grande machine électrique," pp. 182-184.

⁷¹<u>Ibid</u>., 184-186.

used non-metallic conductors (moistened cloth) to bring an electric discharge to the calx. Convinced that his experiments were conclusive,

Van Marum aruged:

La revivification des métaux par la décharge électrique étant mis, par nos expériences, au dessus de toute contradiction, on peut donc régarder comme une vérité bien fondée, qu'il se trouve une grande analogie entre la matière électrique et le phlogiston. La chimie nous apprend, que les chaux des métaux ne peuvent être en aucune manière revivifiées ou changées en métaux, que seulement, quand on leur fournit du phlogiston. Comme nous avons fait nos expériences de manière . . . que c'est donc seulement par la matière électrique, qu'elles sont revivifiées, il est donc évident, que cette revivification démontre: que la matière électrique est ou le phlogiston même, ou qu'elle contient au moins beaucoup de ce principe. /2

After relating experiments on the electric calcination of various metals, he discussed the "seemingly" inconsistent results in a footnote:

(a) Quand on compare cette calcination des fils de métal avec les expériments précédents faits sur la revivification des chaux métalliques, il semble que ces expériences se contredisent, en les considérant superficiellement, puisque la même cause paroit produire des effets contraires. Mais on doit se rapeller ici, comment le feu produit de même ces deux effets contraires sur les métaux et sur leurs chaux. Ce sont les differentes circonstances, qui donnent occasion, que la matière électrique aussi bien que le feu peuvent produire des effets contraires sur ces substances.

⁷² Ibid., 190. "The revivification of metals by the electric discharge being put, by our experiments, beyond all contradiction, one can therefore regard as a well-founded truth, that there is a great analogy between the electric matter and phlogiston. Chemistry teaches us, that the calxes of metals cannot be revivified or changed into metal in any other way than when they are furnished with phlogiston. As we have made our experiments in such a way. . . . that it is therefore only by the electric matter that they are revivified, it is therefore evident, that this revivification demonstrates: that the electric matter is either phlogiston itself, or that it at least contains much of this principle."

 $⁷³_{\underline{\text{Ibid.}}}$, 200. "When one compares this calcination of metal wires with the preceding experiments made on the revivification of

Van Marum also noted that his electrical experiments on dephlogisticated air presented an apparent contradiction to the conception of electricity as phlogiston. That is, he believed that the electric matter should also impart phlogiston to atmospheric air, but was unable to confirm this belief by experiment. Therefore Van Marum admitted that his "expériments sur l'air déphlogistiqué paroissent être contraires à cette ecpérience . . " However, he believed this contradiction to be illusory and stated that he hoped to prove it thus in his next treatment of the subject. 74

In 1785, Jean-Claude de Lamétherie (1743-1817), editor of the Observations sur la physique, published an account of Van Marum's experiments on calxes. Lamétherie had already identified electricity as phlogiston in 1784. That is, in his Essai sur l'air pur, Lamétherie identified electricity as a species of inflammable air and he had identified inflammable air as the "vrai phlogistique de Stahl." In Lamétherie's account of Van Marum's experiments, Lamétherie wrote, "J'ai, je crois, assez bien prouvé dans mon Essai analytique sur l'air pur, & c., que la matière électrique étoit une espèce d'air inflammable.

metallic calxes, it seems that these experiments are contradictory, in considering them superficially, since the same cause appears to produce contrary effects. But one should recall here, how fire produces likewise these two contrary effects on metals and on their calxes. These are different circumstances, which give opportunity, that the electric matter as well as fire can produce contrary effects on these substances; . . . "

^{74 &}lt;u>Tbid.</u>, p. 190. "experiments on dephlogisticated air appear to be contrary to this experiment."

⁷⁵ Jean-Claude de Lamétherie, Essai analytique sur l'air pur, et les différentes espèces d'air (Paris: Rue et Hotel Serpente, 1784), pp. 169-170, 69.

⁷⁶ Lametherie in Martinus Van Marum, "Description d'une très-trande

Thus Beccaria's association of electricity with common fire through their ability to release or impress phlogiston mechanically had been changed. Natural philosophers such as Van Marum, Priestley, de Milly, and others identified electricity with phlogiston, the fixed fire in matter, because they were impressed by the chemical ability of electricity to phlogisticate calxes and common air. The attempts to explain new phenomena with existing theory were accompanied by and in part themselves stimulated an increase in the chemical examination of the diverse effects of electricity. Although this examination began with the study of the effects of electricity on metals and calxes, it was extended to studying the effects of electricity on acids, bases, salts, and indicators, as well.

The usage of the electrical production of metal from calx as an instance demonstrating that electricity was phlogiston required the examination of the chemical action of electricity on other substances and the explanation of this action in a manner consistent with the phlogiston theory. Therefore, Lamétherie, Van Marum, and others made such an examination and found the effects of electricity qua phlogiston to be consistent.

Although the identification of electricity with phlogiston satisfied Van Marum, it did not satisfy other natural philosophers. Some rejected it outright; others requested that Van Marum demonstrate it with further experiments. For instance, Cavallo included a synopsis of Van

machine électrique placée dans le Museum de Teyler, à Haerlem, & des expériences faites par le moyen de cette machine; par Martin Van-Marum, . . . Extrait," Observations sur la physique 27(1785):154. "I have, I believe, proved rather well in my Analytic Essay on Pure Air etc. that the electric matter is a species of inflammable air."

Marum's "Description d'une très-grande machine électrique" as an appendix to the third edition of his own <u>Complete Treatise on Electricity</u>, published in 1786. Although Cavallo's synopsis included descriptions of Van Marum's experiments on gases and on the electric calcination and revivification of metals, Cavallo did not mention Van Marum's identification of the electric matter with phlogiston. This tead, Cavallo commented, "It appears that the electric shock produced both these apparently contradictory effects." Cavallo also left unchanged his chapter containing the argument that the electric fluid is not phlogiston. The same and the electric fluid is not phlogiston.

Van Marum maintained an extensive correspondence with other natural philosophers of his time and often used this correspondence to transmit news of his current researches or to ask for suggestions or comments about his experiments. 80 Priestley was one of those receiving a copy of Van Marum's "Description d'une très-grande machine électrique." In response, Priestley sent Van Marum a list of experiments suggested by William Withering (1741-1799):

- 1. Burn diamonds by electricity.
- Try its effect upon lime water, and upon perfectly caustic fixed alkali.
- Will the phlogiston of electric matter blacken concentrated vitriolic acid?
- 4. Will it phlogisticate the acid of phosphorus?

Tiberius Cavallo, <u>A Complete Treatise on Electricity</u>, 3rd ed., 2 vols. (London: J. Dilly, 1786), Vol. 2, pp. 273-286.

⁷⁸Ibid., 2:285.

⁷⁹<u>Ibid.</u>, 1:112-122.

⁸⁰ See R. J. Forbes, "Correspondence of Van Marum," Martinus Van Marum: Life and Work, 1:361-375.

⁸¹ Priestley, A Scientific Autobiography, pp. 245-246.

Withering's first four suggestions were concerned with determining the similarities of electricity with respect to common fire, acids, and phlogiston. If diamonds could be burned by electricity, then electricity would display a similarity to common fire; if the effect of an electric discharge on lime water and caustic fixed alkali was a neutralization, then electricity would display acidic qualities; if electricity blackened concentrated vitriolic acid and phlogisticated the acid of phosphorous, then electricity would contain or would be phlogiston. Thus Withering's judgment was similar to that of others, such as Beccaria, de Milly, Servières, and Achard, all of whom had sought to examine the nature of electricity chemically within the framework of the phlogiston theory.

Van Marum had also sent a description of his experiments to Alessandro Volta (1745-1827). In a letter to Van Marum dated 8 March 1786, Volta indicated that he had received Van Marum's experiments and suggested that he repeat on a larger scale some experiments already performed by Cavendish:

Vous aurez vu dans un memoire de Mr. Cavendish que l'étincelle électrique change en acide nitreux un mélange d'air dephlogistiqué et d'air phlogistiqué dans la proportion si je me rappelle bien de 3. parties du premier et de 5. du dernier. Vous pouvez faire cette expérience en grand. 82

Volta suggested in a second letter of 26 June 1786 that Van Marum test

⁸² Alessandro Volta, Le opere di Alessandro Volta, Edizione nazionale sotto gli auspici della Reale Accademia dei Lincei e del Reale Istituto Lombardo di Scienze e Lettere, 7 Vols.; (Milano: Ulrico Hoepli, 1918-1929), Vol. 4, p. 67. Hereinafter referred to as Opere, Edizione nazionale.) "You will have seen in a memoir of Mr. Cavendish that the electric spark changes into nitrous acid a mixture of dephlogisticated air and phlogisticated air in the proportion if I recall well of 3 parts of the 1st and 5 of the last. You can do that experiment on a large scale."

the electric spark for acidic effects. 83 Thus after Van Marum had provided a crucial instance, an experiment that he believed would serve to demonstrate that tlectricity was phlogiston, he had been asked to perform further experiments in order to determine if the identification of electricity with phlogiston was consistent with phlogiston theory. Even though he performed the experiments suggested by his correspondents, including Priestley, his results were not published until 1795, almost ten years later. Upon the publication of these results, Van Marum wrote:

il étoit probable, que la grande force de notre machine pût aussi servir à la décomposition de quelques autres substances. . . . Plusieurs Physiciens éclairés ont été de cet avis, et ils m'ont nommé plusieurs substances liquides et non liquides, sur les quelles ils désiroient qu'on essayât l'action des rayons de notre machine. Quoique la plupart de ces expériences n'ayent pas donné des phénomènes très remarquables, je donnerai cependant . . . les résultats de toutes les expériences, qu'on a désirées à cet égard.

After relating these experiments Van Marum added:

Les résultats des expériences, que je viens de décrire dans ce chapitre, ne m'ont point animé de les pousser plus loin. J'en fais seulement mention pour satisfaire aux désirs de ceux, qui étoient curieux de savoir, si ces expériences, faites avec la grande force de notre machine, pouvoient produire quelque phénomène instructif⁸⁵

^{83&}lt;sub>Ibid., p. 69</sub>.

Martinus Van Marum, "Seconde continuation des expériences faites par le moyen de la machine électrique teylerienne par Martinus Van Marum," Verh. TTG 9(1795):124. "It was probable that the great force of our machine could serve also in the decomposition of other substances. . . . Several enlightened physicists have been of this opinion, and they have named to me several substances, liquid and non-liquid, that they desired to be tested by the action of the rays of our machine. Although most of these experiments have not given very remarkable phenomena, I will, however, give . . . the results of all these experiments, that they have desired in this respect."

⁸⁵ Ibid., p. 136. "The results of the experiments that I have just described in this chapter, do not at all inspire me to continue them any further. I mention them only to satisfy the wishes of those, who were curious to know if these experiments made with the great force of our machine, could produce any instructive phenomenon."

Although these experiments might have been of interest to someone who accepted the phlogiston theory as had Van Marum when he wrote of his "Description d'une très-grande machine électrique," Van Marum no longer found them instructive, because in 1785 he rejected the phlogiston theory that he had so vigorously defended and adopted instead the new chemical system of Lavoisier,

According to Van Marum and his biographers he was persuaded to abandon the phlogiston theory during a trip to Paris in 1785 or shortly thereafter. While in Paris he had met Lavoisier, Claude-Louis, Comte Berthollet (1748-1822), and Gaspard Monge (1746-1818). Monge especially had sought to convert him to Lavoisier's new chemical theory. Van Marum wrote in a 1787 publication:

Dezelfde moeyelkheid van een verouderd begrip afteleggen heeft ook my langen tyd van het aanneemen der voorgestelde leer te rug gehouden, zo dat zelf de eerste leezing der schriften van M. LAVOISIER, die in de Memoires van 1774 tot 1780 geplaatst zyn, my omtrent de Stahliannsche leer niet eens aan 't wankelen heeft kunnen brengen. De daar in voorgestelde leer, toen in't geheel niet met myne begrippen kunnede strooken, kwam my als eene ongerymde nieuwigheid voor, tot dat ik in 1785, te Parys zynde, door verscheiden uitkomsten van proefneemingen, welken zommigen Academisten my geliefden, onder het oog te brengen, getroffen, omtrent de oude leer begon in twyffel te geraaken, en hier door vervolgens tot een nauwkeuriger onderzoek der zaake gebracht wierd. O

Martin Van Marum, "Premiere continuation des expériences faites par le moyen de la machine électrique teylerienne," Verh. TTG 4(1787):265. Although the Verh. TTG were published verso in Dutch and recto in French, this quotation comes from Van Marum's summary of Lavoisier's theory, the only part of this volume printed solely in Dutch; "The same difficulty of rejecting an obsolete idea delayed for a long time my accepting the proposed doctrine, so that my first reading of the writings of Mr. Lavoisier, in the Mémoires from 1774-1780, did not shake mine concerning the Stahlian theory. The proposed doctrine at that time, not in accord with my ideas struck me as an absurd novelty, until in Paris in 1785 I began to be touched by doubt concerning the old theory, through the diverse results of experiments which some Academicians put before my eyes."

Eleven years later he said:

Lorsque j'étois à Paris in 1785, j'eus l'avantage de converser avec les célèbres Fondateurs de la chimie moderne, LAVOISIER, MONGE et BERTHOLLET, qui voulurent bien avoir la complaisance de m'entretenir sur les principes fondamentaux de la nouvelle chimie, et de me fair voir quelques unes des expériences les plus décisives, et peu connuës dans ce tems là. Quoique j'eusse publié peu de jours avant mon départ d'ici la théorie de quelques nouvelles expériences électriques, entièrement fondée sur le systême du phlogistique, & que je fusse par conséquent très disposé à me tenir à un systême, que je venois de reconnoître, suivant le commun accord, pour une vérité bien fondée: je sentis, cependant l'évidence et la force de leurs argumens, fondés entièrement sur des faits, qu'ils mirent sous mes yeux; je commençai bien tôt à revoquer en doute le système du phlogistique. . . .87

This last account of Van Marum's conversion to the new chemistry is confirmed by Van Marum's diary of his trip to Paris in 1785. His terse entries in this diary reveal that Van Marum was as much swayed by the charm of Lavoisier and Monge as he was by their arguments for the new chemical system. Van Marum introduced himself to Monge on 17 July 1785, eleven days after his arrival in Paris, and during their first meeting Monge began to discuss Lavoisier's chemical theory. Van Marum wrote that he liked Monge very much. 88 They met again on the 25th and

⁸⁷Martinus Van Marum, Description de quelques appareils chimiques nouveaux ou perfectionnés de la Fondation Teylerienne, et des expériences faites avec ce appareils (Haarlem: Chez Jean Jacques Beets, 1798), iii. "When I was in Paris in 1785, I had the advantage of speaking with the celebrated founders of modern chemistry, Lavoisier, Monge, and Berthollet, who were obliging enough to converse with me on the fundamental principles of the new chemistry, and to show me some of the most decisive experiments, little known at that time. Whereas I had [just] published a few days before my departure the theory of several new electrical experiments, entirely based on the phlogistic system, and I was, consequently, very disposed to hold fast to a system which I had just recognized, following the common accord, to be a well founded truth: However, I felt the force of their arguments founded entirely on the facts that they put before my eyes; I very soon began to doubt the phlogistic system. . . ."

⁸⁸Marum, "Journal physique de mon sejour à Paris 1785,"
Martinus Van Marum: Life and Work, 2:37, 225.

30th of July to discuss the new chemistry and Van Marum was sufficiently interested that he made notes from these three discussions. 89 Unfortunately, it is not known whether these notes still exist. 90

On the 18th of July Van Marum met Lavoisier, and Lavoisier asked him to dine. 91 Two days later at the Académie des Sciences, Lavoisier brought before the assembly Van Marum's recently published account of the experiments made with the great electrical machine at Teyler's Museum and proposed that a committee be appointed to report on these interesting experiments. After this meeting Van Marum was invited to have lemonade(!) with Monge, Lavoisier, and others at the house of Jean-Baptiste-Gaspard Bernard de Saron (1730-1794), president of the parlement of Paris. 92

So by the time Van Marum met Berthollet to discuss chemistry on the 1st of August, ⁹³ he had been subjected to a combination of social and scientific attention that would flatter most men. Perhaps the <u>coup de grâce</u> came on the 6th of August at the Académie des Sciences, when Monge and Jean-Baptiste Le Roy (1720-1800) reported to the assembly on Van Marum's electrical experiments. Van Marum's diary entry for that day reveals that he was indeed pleased with the Académie's reception of his experiments. ⁹⁴ He found himself charmed, flattered, and impressed by the

⁸⁹<u>Ibid</u>., 2:43, 45 or 230, 232.

^{90&}lt;sub>Ibid</sub>., 2:12.

⁹¹ Ibid., 2:32, 225.

^{92&}lt;u>Ibid., 2:38-39, 227.</u>

⁹³ Ibid., 2:49, 233.

^{94&}lt;u>Ibid</u>., 2:49, 236.

attentions of the proponents of the new chemistry. Presumably their acute judgment of electrical experiments impressed him as well.

In 1787 a sequel to Van Marum's "Description d'une très-grande machine électrique" was published. This sequel described the experiments performed in 1786, including the electrical calcination of metals and the electrical revivification of metal calxes. These he explained in the context of Lavoisier's new chemical system. Although he had not considered the phlogistic explanation of the calcination of metals and the revivification of calxes by the passage of an electric discharge as being inconsistent in 1785, he now believed these phenomena to be a crucial instance that phlogiston theory could not explain.

J'avoue, que quand on veut soutenir l'hypothêse du phlogistique, on peut remarquer sur ce que j'ai avancé, que les phénomènes des calcinations des metaux sont également expliquables suivant l'hypothêse de Stahl. Quand on considere pourtant la réduction des chaux metalliques, et l'explication qu'on en doit donner suivant la susdite hypothêse, alors cette hypothêse ne peut être considerée, selon moi, comme vraisemblable: car suivant cette hypothêse la decharge électrique feroit que dans un cas le metal perdroit son phlogistique, pendant que dans un autre cas au contraire, quand le decharge est conduite par la chaux d'un metal au lieu de l'être par le metal même, elle restitueroit au metal le phlogistique perdu; on suppose donc suivant ce systême, que la même cause produit dans différentes circonstances des effets, qui sont diamétralement opposés, ce qui est certainement contradictoire. 95

⁹⁵ Martinus Van Marum, "Premieme continuation des expériences," pp. 110-112. "I admit that if one wants to support the phlogiston hypothesis, one can remark on what I have advanced, that the phenomena of the calcinations of metals are equally explicable according to the hypothesis of Stahl. When one considers however the reduction of metallic calxes and the explanation that one should give it according to the above-mentioned hypothesis, then this hypothesis cannot be considered, in my opinion, as plausible: because according to this hypothesis the electric discharge would in one case cause the metal to lose its phlogiston, whereas in the other case to the contrary, when the electric discharge is conducted by the calx of the metal instead of the metal itself, it restores to the metal the lost phlogiston; one supposes

Van Marum thus labeled a position absurd and inconsistent that he had defended as being consistent only a few years earlier. Although he claimed the phlogiston theory was contradictory because it explained opposing processes in terms of the same cause, he was aware that Lavoisier's theory might also be accused of the same inconsistency. For the new theory ascribed two opposing processes, calcination or the fixing of air in metal, and revivification or the release or air from calxes, to the same cause, electricity. Van Marum anticipated this objection:

Je prevois ici une objection, qui a quelque apparence, mais qui n'est pas pourtant bien fondée. On fait peut-être sur ce nouveau systeme cette remarque, que suivant ce systeme la chaleur fait que dans un cas le principe d'air pur s'unit avec le metal, et que dans un autre cas au contraire le metal perd ce principe, qui s'y étoit uni, et que suivant ce systême on attribue par consequent à la même cause des effets, qui sont diamétralement opposés, de la même maniere, que je l'ai indiqué à l'égard de hypothèse de Stahl. Cette objection s'évanouit pourtant tout à-fait, quand on considere, que quoique la chaleur cause ces susdits effets différents sur les metaux, c.a.d. l'union et la separation du principe d'air pur, il y faut pourtant des degrés de chaleur sort différents, et que par consequent les causes différent vraiment beaucoup.96

therefore according to this system, that the same cause produces in different circumstances, effects which are diametrically opposed, which is certainly contradictory."

Van Marum offered additional experiments illustrating the plausibility of Lavoisier's theory in explaining phenomena. According to Lavoisier's oxidation theory, vital or dephlogisticated air was necessary for calcination. Consequently, Van Marum attempted to calcine metal wires removed from any contact with vital air. Using an atmosphere of phlogisticated air, he found that the electric discharge would not calcine metals in the absence of vital air. 97 Van Marum also calcined metal wires in pure air and in saltpeter air explaining that saltpeter air contained vital air and was therefore conducive to calcination. 98 Although he believed that these airs contained the essence of air necessary to calcination, a phlogiston theorist might say with equal justification that since these airs were devoid of phlogiston, they readily received phlogiston from metals and were conducive to calcination. So, in the same publication Van Marum turned his attention to the calcination of metals in water:

Expériences sur la calcination de metaux dans l'Eau.

Ces expériences m'ont paru pouvoir fournir de nouvelles preuves concernant le nouveau système de calcination, comme aussi à l'égard de la composition de l'eau...

He found that metal wire could be calcined under water even though the

⁹⁷ Ib<u>id</u>., 124.

^{98&}lt;sub>Ibid.</sub>, 130-132.

^{99&}lt;sub>Ibid</sub>., 134.

[&]quot;Experiments concerning the Calcination of Metals in Water.

[&]quot;These experiments appeared to me to be able to furnish new proofs concerning the new system of calcination as well as with regard to the composition of water. . . "

water blocked its access to atmospheric, vital air. Believing that water was decomposed by the passage of an electrical discharge and that this decomposition provided the vital air necessary for calcination, Van Marum argued that the calcination of metals in water could not be satisfactorily explained by phlogistic theory. He believed that he had found a crucial demonstration of the truth of Lavoisier's new theory:

Cette calcination des metaux dans l'eau ne s'accorde nullement avec l'hypothêse de $\underline{\text{Stahl}}$, qui suppose, que les metaux se calcinent par l'émission de leur phlogistique: puisque l'eau, suivant cette même hypothêse ne reçoit pas le phlogistique ou ne le peut reçevoir que tres difficilement. 100

If the electrical calcination of metals occurred in water because water was decomposed, Van Marum expected phlogisticated air, the other constituent of water according to Lavoisier's theory, to be produced. According to Van Marum, it was. He frequently observed bubbles rising in the water during calcination. He attempted to collect the air generated and to test it, but found this to be a difficult task. First Van Marum inverted a glass vessel over the wire and tried to collect the air generated in the vessel. The electric discharge shattered the vessel. He then tried to collect the generated air in a glass cylinder used normally for exploding gases. "Mais quoique le verre de ce cylindre eût à peu-près partout l'épaisseurde 3/4 de pouce, il fut pourtant brisé par la secousse de l'eau, causée par la decharge." Finally, Van Marum

^{100 &}lt;u>Ibid.</u>, 136-318. "Thic calcination of metals in water is not at all in accordance with Stahl's hypothesis, which supposes, that the metals calcine by the emission of their phlogiston: since, according to this hypothesis water either does not accept phlogiston or only does so with great difficulty."

 $^{101 \}frac{1}{1 \, \mathrm{bid}}$. 140. "But although the glass of this cylinder was approximately 3/4 of an inch thick on all sides, it was, nevertheless, broken by the commotion of the water, caused by the discharge."

immersed the wire in water at a depth of about eight inches, covered all but the center of the wire with wooden tubes, and inverted a glazed stone basin over the wire. He collected only about one-half of a cubic inch of gas. Believing this amount to be entirely too much to have come from the decomposition of water and finding that he could not ignite it, Van Marum concluded that it was atmospheric or common air released from the water by the passage of the electric discharge. Hoping that this air had now been driven out, he repeated the experiment using the same water and produced a much smaller amount of air, Van Marum again repeated the experiment obtaining even less air. He found this final production of air to be inflammable. 103

Although Van Marum collected inflammable air from the electrical calcination of tin, his attempts to ignite air produced from the calcination of lead were in vain. He was not daunted by this somewhat limited success and decided to conduct any further experiments in water "qui a perdu par ébullition l'air." He postponed a repetition of these experiments "jusqu'à une saison plus favorable à cause de la difficulté de charger la batterie parfaitement dans cette automne, dont l'air est généralement humide. . . "105 He argued that

^{102&}lt;u>Ibid</u>., 142-144.

^{103&}lt;sub>Ibid.</sub>, 146-148.

¹⁰⁴ Tbid., 148. "which has lost air through boiling."

^{105 &}lt;u>Ibid</u>. "to a more favorable season because of the difficulty in charging the battery perfectly this autumn, when the air is generally humid.

la derniere expérience ne nous a pas paru douteuse.

Ces expériences sur la calcination des metaux dans l'eau ne s'accordent donc pas seulement tres bien avec le nouveau systême de calcination, mais elles fournissent de plus une nouvelle preuve, qui démontre, que l'eau est composée des principes de l'air pur et de l'air inflammable. 106

Whereas Van Marum's explanation of the phenomena surrounding the calcination of metals and the revivification of calxes in various gases could be explained in an equally satisfactory manner in the terms of phlogiston theory, the calcination of metals under water had not been explained or even performed by proponents of the phlogiston theory. Van Marum had examined the calcination of metals under water because antiphlogistic theory emphasizes the role of oxygen in calcination. He was attempting to illustrate that calcination did not take place in the absence of air, that is, under water. There had been no special reason to examine the calcination of metals under water in the framework of the phlogiston theory until Van Marum used it as an argument for the validity of Lavoisier's theory. Therefore, phlogistic explanations of the Dutch experiments did not predate the antiphlogistic ones, but instead, the phlogistic explanations of the electrical production of gas from water were made in reply to the claims that these experiments demonstrated the validity of Lavoisier's theory.

Although his results were less than totally compelling, Van
Marum was convinced that water had been decomposed. Perhaps he was
somewhat bolstered in this belief by his knowledge that in February of

^{106&}lt;u>Thid</u>. "the last experiment did not seem doubtful to us.
These experiments on the calcination of metal in water are
therefore not only very much in accord with the new system of calcination, but they furnish a new proof, that demonstrates, that water is
composed of the principles of pure air and of inflammable air."

1785 Lavoisier and Jean-Baptiste-Marie Charles Meusnier de 1a Place (1754-1793) had passed water through red hot iron tubes and had produced iron calx and inflammable air. 107 There was also a reference to the electrical decomposition of water published prior to Van Marum's. In a memoir, "Sur l'effet des étincelles électriques excitées dans l'air fixe," read to the Paris Academy on September 2, 1786, Monge used the possible electrical "décomposition de l'eau dissoute dans ce même fluid élastique [fixed air]" to explain what he believed to be an experimental anomaly. For he believed that an electric spark dilated fixed air because it decomposed impurities of water vapor contained in the fixed air. 108 Since Monge was instrumental in converting Van Marum to the antiphlogistic system and since the two were in correspondence, Monge may have been influenced by a knowledge of Van Marum's yet unpublished experiments in making the suggestion that water was electrically decomposed. Monge did refer to other experiments by Van Marum in the same memoir. 109

In addition to the account of Van Marum's experiments in the Verhandelingen of Teyler's Tweede Genootschap, an extract of Van Marum's "Premiere continuation" was published in Observations sur la physique in 1787. The editor's report of Van Marum's conversion was very terse:

"M. Van-Marum cherche ensuite à expliquer la calcination des métaux.

^{107 &}lt;u>Tbid.</u>, p. 138. <u>Supra</u>, p. 11.

¹⁰⁸ Tbid. Gaspard Monge, "Mémoire sur l'effet des étincelles électriques, excitées dans l'air fixe. Par M. Monge," Mémoires de l'Académie Royale de Sciences. Année M.DCCLXXXVI (published in 1788), p. 438.

^{109&}lt;u>Tbid.</u>, p. 430. An extract of Monge's article was published in <u>Observations sur la physique</u> 29(1786):275-280.

Il rejette la doctrine de Stahl pour embrasser celle qui lui est opposée."¹¹⁰ After reporting that Van Marum had calcined metals in atmospheric air and had been unable to calcine them in phlogisticated air, the editor related Van Marum's calcination of metals in water:

It étoit très-important de s'assurer si les métaux pouvoient se calciner dans l'eau. M. Van-Marum n'a pas oublié cette expérience. Elle a réussi toutes les fois qu'il n'employoit que la huitième partie de ce qu'il en calcinoit dans l'air. Il y avoit dégagement d'un fluide élastique dont il étoit intéressant de connoître la nature; après plusieurs essais instructueux, il parvint à établir un appareil pour le rassembler; la calcination de l'étain fournit de l'air inflammable, mais il n'en put obtenir celle du plomb notre Physicien se propose de répéter ces expériences avec de l'eau entièrement privée d'air par l'ébullition.

In summary, Van Marum considered his experiments to be a conclusive demonstration of the following parts:

- The electric discharge produced metals from calxes without any other agent acting on the calx.
- The electrical calcination of metals took place only in the presence of vital air.
- 3. The processes enumerated in 1. and 2. are not logically contradictory.

¹¹⁰ Martinus Van Marum, "Continuation des expériences électriques faites par le moyen de la machine teylerienne; par M. Van-Marum. Extrait,"

Observations sur la physique 31(1787):346. "M. Van Marum seeks then to explain the calcination of metals. He rejects the doctrine of Stahl to embrace that which is opposed to it."

^{111 &}lt;u>Tbid.</u>, 347. "It was very important to be assured that metals could be calcined in water. M. Van Marum did not forget this experiment. It had succeeded every time he employed only one eighth of what he had been able to calcine in air. An elastic fluid had been given off [during the calcination] whose nature it was interesting to know. After several instructive tries, he perfected an apparatus to collect the fluid; the calcination of tin furnished inflammable air, but he could not obtain it from the calcination of lead. . . . our physicist proposes to repeat his experiments with water entirely deprived of air by ebulition (boiling).

4. The electrical discharge produced the calcination of metals in water by decomposing the water and thus providing vital air.

Few other natural philosophers seemed to consider Van Marum's demonstration as conclusive. In fact, very little mention was made of his claim to have decomposed water. In addition to the Dutch and French accounts of his experiments, a German translation of his "Premiere continuation des expériences" was published in 1788. 112 Other than the summary in Observations sur la physique, few if any other journal articles on Van Marum's experiments mentioning his decomposition of water were published before 1790. 113 Cavendish did mention Van Marum's experiments in 1788, but only in reference to the results of the explosion of phlogisticated and dephlogisticated airs together. 114

¹¹² The Verh. TTG containing Van Marum's experiments were published simultaneously in French and Dutch, recto in Dutch and verso in French. The German translation appeared as Beschreibung einer ungemein groszen Elektrisier-Maschine und der damit im Teylerschen Museum zu Haarlem angestelten Versuche. Erste Fortsezung, Aus dem Höllandischen übersezt (Leipzig: Schwickert, 1788).

The most complete bibliography of Van Marum's writings and of writings alluding to his experiments is in Martinus Van Marum: Life and Work, vol. 1, pp. 287-360 by J. G. Bruijn. Other bibliographies of Van Marum's works include: D. Bierens de Haan's Bibliographie néerlandaise historique-scientifique des ouvrages importants dont les auteurs sont nés aux 16°, 17° et 18° siècles sur les sciences mathématiques et physiques avec leurs applications, extrait du Bullettino di bibliografia e di storia delle scienze matematiche e fisiche (Rome: Imprimerie des sciences mathématiques et physiques, 1883), pp. 183-184; and Catalogue of Scientific Papers 1800-1863 Compiled and Published by the Royal Society of London, 6 vols (London: George Edward Eyre and William Spottiswoode, 1867-1872), Vol. 4, pp. 270-272.

¹¹⁴ See Henry Cavendish, "On the Conversion of a Mixture of Dephlogisticated Air and Phlogisticated Air into Nitrous Acid, by the Electric Spark. By Henry Cavendish: Esq. F.R.S. and A.S.," Philosophical Transactions 78(1788): 261-276. Pp. 274-276 of this article contain a letter from Cavendish to Van Marum.

Conversely, there were numerous articles published between 1787 and 1789 that attempted to refute the decomposition of water by its passage over red hot iron, as claimed by Lavoisier and Meusnier. 115 For instance. Lamétherie published in the September 1787 issue of Observations sur la physique his own "Suite des expériences sur la prétendue décomposition de l'eau. 116 In the November issue of the same journal another such article appeared in the form of a letter to Lametherie. In it Le Couteulux de Puy (fl. 1787) explained the production of water by the electrical combustion of dephlogisticated and phlogisticated airs by saying that the water contained in the two gases was driven out by the electrical fire. That is, he believed the water produced in the exploding of the two gases together was a byproduct of the drying out necessary in order for inflammation to take place. 117 The 1788 and 1789 issues of Observations sur la physique contained articles arguing both pro and con the decomposition of water and for the new chemical system, but contained no mention of Van Marum's "demonstration" of the decomposition of water. 118

Other than Cavendish's reply to Van Marum's experiments concerning the combustion of phlogisticated and dephlogisticated air, the

¹¹⁵ See Dumas and Duveen, "Lavoisier's Decomposition and Synthesis of Water," pp. 113-129.

^{116.} Tean-Claude Lamétherie, "Suite des expériences sur la prétendue décomposition de l'eau; par M. De La Métherie," Observations sur la physique 31(1787):200-203.

^{117.} Lettre de M. Le Couteulx de Puy, à M. De La Métherie, "Observations sur la physique 31(1787):383-385.

 $[\]frac{118}{\text{Observations sur la physique}} \quad 33 (1788):103, 262, 384, 385, 457, \\ \text{and } 34 (1789):76, \overline{138}, 227, 229, 304, \\ \text{and } 360. \quad 32 (1788) \\ \text{ contains no articles} \\ \text{on the matter.}$

Philosophical Transactions contained no mention of Van Marum's decomposition of water. The 1788 and 1789 editions of the Philosophical Transactions did contain eight articles, including ones by Priestley and Cavendish, defending the phlogistic system and the elemental nature of water. If Van Marum's experiments of 1786 demonstrated the decomposition of water, it was little acknowledged. Deiman and Paets van Troostwijk, who had aided Van Marum in many experiments, published their article in 1789, arguing for the electrical decomposition of water, without mentioning Van Marum or his experiments. 120

Although Deiman and Paets van Troostwijk's article shows their commitment to the antiphlogistic system as of 1789, it is difficult to determine when they first rejected the phlogiston theory. According to Van Marum, he was for a time the first and only convert to Lavoisier's theory in Holland. In his account of the continuation of his experiments with the electrical machine at Teyler's Museum published in 1787, he identified Deiman and Paets van Troostwijk as still accepting the phlogiston theory as of 1786.

(c) Cette calcination de mercure fournit, selon moi, une preuve évidente pour le systeme, que la calcination d'un metal consiste seulement dans son union avec la principe d'air pur. . . Suivant le système de Stahl même les metaux ne se desaississent pas de ce prétendu phlogistique, à moins qu'ils ne subissent un certain degrè de chaleur, ou qu'ils soient dissolus par l'un ou l'autre acide: dans cette expérience pourtant le mercure n'acquiert pas un degrè de chaleur remarquable, et il ne se

¹¹⁹ Philosophical Transactions 78(1788):147, 261, 313, 379 and 79(1789):7, 139, 289, and 300.

¹²⁰ Deiman and Paets van Troostwijk mentioned the great electrical machine and John Cuthbertson in their article, they did not mention Van Marum at all. See "Sur une manière de décomposer l'eau," pp. 369-378 (Cuthbertson mentioned on p. 370).

trouve pas ici un acide. . . . Comment la calcination du mercure pourroit elle donc avoir lieu, s'il étoit necessaire pour cela, que le metal perdit auparavant de l'une ou de l'autre manière son prétendu phlogistique M. Paets van Troostwyk se tient pourtant à l'hypothêse du phlogistique, puisque il a nouvellement écrit avec M. Deiman l'apologie du phlogistique dans un memoire, qui a remporte l'année passée le prix de notre Société Hollandoise. 121

The essay Van Marum referred to was published in 1787 in the Verhandelingen uitgegeevan door de Hollandsche Maatachappye der Weetenschappen. Sometime between the time of Van Marum's writing in 1786 and the appearance of their article in 1789, Deiman and Paets van Troostwijk changed their views about the phlogiston theory. Perhaps

Martinus Van Marum, "Premiere continuation des expériences,"

Verh. TTG 4(1787), 200 note c. "This calcination of mercury furnishes,
in my opinion, a convincing proof of the system, that the calcination of
a metal consists only in its union with the principle of pure air...

Even according to Stahl's system the metals do not rid themselves of the
so-called phlogiston unless they experience a certain degree of heat, or
they are dissolved by one or another acid: However, in this experiment
the mercury does not acquire a remarkable degree of heat, nor is there
any acid present ... How could the calcination of mercury therefore
take place, if it was necessary for it that the metal lose beforehand
its so-called phlogiston in one way or the other[?] Mr. Paets van
Troostwijk, nevertheless, holds to the hypothesis of phlogiston since
he has recently written with Mr. Deiman the defense of phlogiston in a
memoir that won last year the prize of our Holland Society.

¹²² Adrian Paets van Troostwijk and Jan Rudolph Deiman,
"Antwoord op de Vraage, voorgesteld door de Hollandsche Maatschappye der Weetenschappen te Haarlem: I. Welken zyn de waarlyk onderscheidene soorten der Lucht-gelykende Vloeistoffen, aan welken men de naamen van vaste lucht, gedephlogisteerde lucht, ontvlambaare lucht, Saltpeter-lucht, zuure lucht, loog-lucht, en anderen gegeeven heeft; en waar in zyn dezelven van elkander, en van de lucht des Dampkrings onderscheiden?
2. Heeft elk deezer soorten van veerkrachtige Vloeistoffen zoo veel met de lucht van den Dampkring gemeen, dat zy voor eene soort van lucht verdiend gehouden te worden?
3. Hoe verre kan uit de Proeven en Waarneemingen omtrentde genoemde Luchten, de aart der Lucht van den Dampkring worden opegemaakt? Door de Heeren A. Paets van Troostwyk, en Joan Rudolph Deiman," Verhandelingen uitgegeeven door de Hollandsche Maatschappye der Weetenschappen te Haarlem 24(1787), 59-140

Van Marum's work played an important part in convincing them to accept Lavoisier's new theory. The evidence for this assumption is found in Deiman and Paets van Troostwijk's own account of their experiments. Although they did not mention Van Marum or his experiments in their article in Observations sur la physique in 1789, the article itself suggests a detailed knowledge of Van Marum's decomposition of water, for every difficulty that Van Marum experienced was avoided by an appropriate precaution in a manner suggesting either remarkable foresight or a forewarning of these difficulties. Van Marum had trouble with the electric discharge shattering his vessel; Deiman and Paets van Troostwijk used instead a tube and adjusted their equipment so that the discharge would not shatter the tube. Van Marum's results were obscured by the presence of atmospheric air in solution in the water, and Van Marum indicated that he would boil the water to rid it of atmospheric air when he repeated the experiment; Deiman and Paets van Troostwijk boiled their water and placed it under an air pump to further purge the water of atmospheric air. Van Marum had difficulty collecting the inflammable air; Deiman and Paets van Troostwijk's use of a glass tube made gas collection much easier. Van Marum used an iron wire and thus only produced inflammable air; Deiman and Paets van Troostwijk used gold or platina wires, which could not easily be calcined, in order to produce both hydrogen and oxygen. In short, Deiman and Paets van Troostwijk improved every part of Van Marum's experiment that had detracted from its conclusiveness. There can be little doubt that their experiment did not originate in the accidental manner they had claimed. Deiman and Paets van Troostwijk did not set out to test the electric commotion on various subjects and accidentally discover the

decomposition of water: they knew what to expect from the passage of an electric discharge through water from their knowledge of Van Marum's experiments, and they set out to demonstrate those expected results in an incontestable manner.

These experiments were witnessed by Friedrich Ludwig Schurer (fl. 1790). Schurer, professor of chemistry and physics at the Ecole d'Artillerie at Strasbourg, wrote Berthollet recounting Paets van Troostwijk's experiments. Schurer's letter was published in 1790 in the Annales de chimie. It is Schurer's account of details not mentioned by the Dutch chemists that makes most clear the careful preparation necessary to perform the experiments.

J'ai eu l'avantage de voir chez M. Paets Van-Troostwyk la belle expérience sur la résolution de l'eau en gaz oxigène & hydrogène par l'étincelle électrique, & la recomposition de l'eau par la combustion de ces gaz.

J'aurai l'honneur . . . de vous donner quelques détails qui pourront peut-être servir à faire repétér cette expérience avec plus de facilité. 124

Among the details Schurer related to Berthollet was: "Le succès de l'expérience dépend de la juste force de l'étincelle

^{123 &}lt;u>Poggendorff</u>, 2:869 identifies Schurer as being born in the sixties. Since Schurer was elected to the Hollandsche Maatischappij in 1790, one may assume that the <u>Annales de chimie</u> extract is not pothhumously published.

^{124&}quot;Extrait d'une lettre de M. Schurrer, professeur de chimie & de physique a l'Ecole d'Artillerie de Strasbourg, à M. Berthollet,"

Annales de chimie; ou recueil de mémoires concernant la chimie et les arts qui en dépendent 5(1790):276. (Hereinafter referred to as Annales de chimie.) "I have had the advantage of seeing at the place of M. Paets van Troostwijk the fine experiment on the resolution of water into oxygen and hydrogen gas by the electric spark and the recomposition of water by the combustion of these gases. I will be honored . . . to give you some details which perhaps would assist in repeating the experiment with greater of ease."

électrique."125 Too weak a spark gave no results and too strong a spark broke the tube. In order to get a strong enough spark Schurer advised:

Insuring that the spark was not too strong was not easy.

Pour parvenir donc à trouver la juste force de l'étincelle électrique sans risquer de casser le tube, on éloigne le fil d'or inférieur du supérieur d'environ $1\frac{1}{2}$ pouce, & on le fait communiquer avec la surface extérieure de la bouteille de Leide On appuie l'extrêmité du fil superieur qui sort du verre contre une grande boule de cuivre isolée, qu'on peut éloigner plus ou moins du conducteur de la machine électrique; on fait passer ensuite de petites étincelles par le tube (bien séché extérieurement), & on en augmente peu à peu la force, jusqu'à ce que l'on voye naître à chaque étincelle une quantité de très-petites bulles de fluide élastique qui se rassemblent au haut du tube. 127

Merely adjusting the force of the spark was not enough to insure good results; the spark also had to be a certain length for the best results. In order to find this length, Schurer advised that the

¹²⁵ Tbid., 277. "The success of the experiment depends on the exact force of the electric spark."

^{126&}lt;sub>Tbid</sub>. "The spark from a simple conductor, even from the great electric machine of the Cabinet of Teyler's, does not suffice, it is necessary to employ a Leyden jar; that of M. Van Troostwyk had around 120 square inches of armed surface."

¹²⁷ Ibid., 277-278. "In order to find the correct force of the electric spark without risking breaking the tube, the lower gold wire is removed to a distance of about 1½ inch from the upper one and connected with the exterior surface of the Leyden jar. The extremity of the upper wire that leads through the glass is supported against the large, isolated, copper ball, that can be removed more or less [of a distance] from the conductor of the electric machine; then one causes small sparks to pass through the tube (well dried on the interior) and the force is augmented little by little, until with each spark is released a quantity of very small bubbles of elastic fluid that collect in the top of the tube."

wires be moved closer and closer together until the spark measured one half an inch in the dark.

He also pointed out that it was very difficult to decompose water completely, although it could be done by releasing the residue after each inflammation and repeating the inflammations as Deiman and Paets van Troostwijk had done. Producing enough gas for one inflammation was a rather involved process since, according to Schurer, it took over 600 sparks to produce one and one-half inches of air in the small tube. 128

Schurer's explanation of the utility of the "S" curve in the glass tube also differed considerably from Deiman and Paets van Troostwijk's account of the adoption of the "S" shape: "Pour éviter d'autant plus sûrement que le tube ne se brise par la réaction de 1'eau sur ses parois, M. Van-Troostwyk y fait une double courbure . . ."129

Finally, Schurer pointed out that before passing the electric discharge through the tube, Paets van Troostwijk introduced a small air bubble in it to avoid breakage from the expansion of the water. This practice, not mentioned by Deiman and Paets van Troostwijk in their article in Observations sur la physique, allowed air to dissolve in the water and, in the words of Schurer, "empêche . . . que l'expérience ne se fasse avec toute l'exactitude possible." 130

^{128&}lt;sub>Ibid.,</sub> 279.

^{129 &}lt;u>Ibid.</u> "In order to avoid with all the more certainity that the tube did not break by the reaction of the water on its inner sides, M. van Troostwyk made a double curve in it. . . ."

 $¹³⁰_{\underline{\text{Ibid.}}}$, 280. "prevents . . . that the experiment be made with all the exactitude possible."

Thus Schurrer's letter indicates that Deiman and Paets van

Troostwijk's account of the decomposition and recomposition of water is
a polished synthesis that did not reflect the considerable experimental
difficulties which barred the achievement of convincing results. If

Deiman and Paets van Troostwijk had reported the details found in the
extract of Schurrer's letter, their inclusion of these details would
have belied the ease and accuracy of their experiments. More importantly,
it would have also denied the accidental nature of their discovery of
the decomposition of water. No one could believe in such an accident
if they were aware of the extent of experimental contrivance necessary.

In 1790 a letter from John Cuthbertson, dated Amsterdam

19 November 1789, describing his version of the Dutch experiments, was published in <u>Sammlungen zur Physik und Naturgeschichte von einigen</u>

<u>Liebhabern dieser Wissenschaften</u>. He described the experiments as having been made in conjunction with "meinen Freunden den Herren <u>D</u>. <u>Dieman</u> and <u>Paets van Troostwyk</u>." Thus Cuthbertson's account of the experiments differed from Deiman and Paet's van Troostwijk's in that he considered himself as a principal in the experiments. Cuthbertson was also much more cautious about what could be argued from the experiments. He wrote:

ist es mir vor kurzem gelungen, Wasser durch den elektrischen Schlag in Luft zu verwandeln, und zwar gerade in eine Mischung aus den beiden Luftarten, welche Herr <u>Lavoisier</u> und seine Freunde, ohne jedoch hinlängliche Gründe dazu zu haben, für die beiden Bestandtheile des Wassers halten, nämmlich in eine Mischung aus dephlogistisierter und brenbarer Luft. 131

¹³¹ Cuthbertson, Auszug eines Briefes von Herrn Cuthbertson zu Amsterdam vom 19 November 1789, Sammlungen zur Physik und Naturgeschichte von einigen Liebhabern dieser Wissenschaften 4, Bk.4(1790):453. "I

After describing the experiment and the apparatus used to produce air from water, Cuthbertson wrote:

Diese Wirkung des elektrischen Frunkens auf die entstandene Luft gibt deren Beschaffenheit hinlänglich zu erkennen. Uebrigens bin ich begierig zu hören, wie dieser Versuch von den beiden Parteien erkläret werden wird. 132

Thus the account of Schurrer, a witness to these experiments, and the account of Cuthbertson, a participant in them, both contradict Deiman and Paets van Troostwijk's presentation of them as a simple, objective, and conclusive demonstration of the compound nature of water. According to Schurrer, the experiments were complex and contrived. According to Cuthbertson, the experiments were not conclusive. However, Cuthbertson did indicate that he believed that such experiments could be made conclusive.

The conflicting accounts of Deiman and Paets van Troostwijk,
Schurrer, and Cuthbertson indicated differences of opinion with respect
to the conclusiveness or "crucial" nature of the Dutch experiments.
However, each of these accounts reveals an explicit acceptance of the
ability of an experiment to decide conclusively between two theories.
Even Cuthbertson, who did not endorse Deiman and Paets van Troostwijk's
conclusions and who argued that the antiphlogistic interpretation of
their experiments was made without sufficient basis, admitted that the

recently succeeded in changing water, through the electric shock into air and indeed directly into a mixture of the two air species, that Lavoisier and his friends, without having any sufficient basis, regard as both the component parts of water, namely in a mixture of dephlogisticated and inflammable air."

^{132 &}lt;u>Thid.</u>, p. 455. "This action of the electric spark on the resulting air gives the condition sufficient to identify [it]. Moreover I am eager to hear, how both parties will explain this experiment."

experiments would be conclusive once the products were positively identified.

Thus the association of electricity with phlogiston and the consideration of the action of electricity on metal calxes resulted in the identification of electricity as phlogiston. Although de Milly's usage of the electrical production of metal from calx as a crucial instance demonstrating that electricity and phlogiston are the same was not universally accepted, the discussion of electricity qua phlogiston resulted in an exploration and explanation within the context of the phlogiston theory of the chemical action of electricity.

By the time Van Marum turned to the electrical calcination of metals under water in order to demonstrate that calcination could not occur without oxygen and, conversely, that water could be decomposed to provide oxyge, the chemical properties ascribed to electricity in the terms of the phlogiston theory provided a potential rebuttal to Deiman and Paets van Troostwijk's assertion that water could be decomposed electrically.

Therefore, the reception of the Dutch experiments in the last decade of the eighteenth century followed the pattern exhibited in the writings of Deiman, Paets van Troostwijk, Schurer and Cuthbertson. It is characterized, first, by an acceptance of the crucial experiment in general or of the existence of experiments which would decide between two competing theories; and second, by a great division of opinion concerning the crucial nature of particular experiments. Usually those who accepted the Dutch experiments as a conclusive demonstration of Lavoisier's theory had already accepted that theory. Those who did not accept these experiments as a conclusive demonstration of Lavoisier's theory were either committed to the phlogiston theory already or to a view of nature in which electricity materially contributed to chemical changes.

CHAPTER IV

THE RECEPTION OF THE DUTCH EXPERIMENTS

Deiman and Paets van Troostwijk's experiments on the electrical decomposition of water were cited repeatedly for more than a decade in the debate between the advocates of the phlogistic and antiphlogistic theories. The antiphlogistic chemists supported the conclusion that water had been decomposed in the Dutch experiments and phlogistic chemists challenged this conclusion. In the same year that Schurer's article supporting the antiphlogistic interpretation of the Dutch experiments was published, Deiman and Paets van Troostwijk's experiments were summarized and their arguments criticized in the <u>Journal der Physik</u> by its editor, Friedrich Albrecht Carl Gren (1760-1798).

Gren differed with Deiman and Paets van Troostwijk over the role of electricity in the production of gases from water. He believed that there were questions about the role of electricity in the production of gases from water that needed to be answered. How was the shattering of the tubes to be explained if "das Wasser eine leitende Substanz ist?" What was "der Grund der leitenden und nicht leitenden

Friedrich Albrecht Carl Gren in "Schreiben des Herrn Paets van Trostwyk und Deimann an Herrn de la Metherie, über die Zerlegung des Wassers in brennbare und Lebensluft durch die Elektrischen Funken,"

Journal der Physik 2(1790):135. "water is a conducting substance?"

Eigenschaft?"² Gren argued that electricity, not water, is the source of the gases produced in the Dutch experiment. He believed the Dutch experiment "gerade gar nichts beweist, wenn sie nicht darthun, dass die beyden Luftarten <u>nicht</u> von der electrischen Materie herrühren können."³ Gren used Deiman and Paets von Troostwijk's own experiments on acids to dispute their conclusions.

Die Versuche mit Vitriolsäure und Salpetersäure beweisen vielmehr gegen sie; denn eben wegen der Anziehung dieser Säuern zum Brennstoff konnte dieser nicht zur brennbaren Luft gebildet und entwickelt, sondern es musste nur die dephlogistisirte Luft allein, oder der andere electrische Stoff frev gemacht werden.

Objecting that Deiman and Paets van Troostwijk had not examined the diminishing residue in their experiments, Gren identified it as being phlogisticated air and pointed out that its presence could not be adequately explained by antiphlogistic theory.

Die V. erhielten nämlich <u>allemal</u> einen Rückstand von Luft; den sie nicht untersuchten, und welcher <u>phlogistisirte</u> Luft ist. Sie folgern nur, dass er in der Folge nicht weiter würde statt gefunden haben; das ist aber noch nicht bewiesen. Diese phlogistisirte Luft ist eben der Stein des Anstoffes für die Antiphlogistiker, und sie sind immer genöthigt anzunehmen, sie präexistire schon in der Lebensluft.⁵

 $[\]frac{2_{\underline{\text{Ibid}}}}{\text{nonconductance}?"}$, p. 140. "the basis of the property of conductance and nonconductance?"

 $[\]frac{3}{\text{Lbid}}$, pp. 138-139. "proves exactly nothing at all, provided it does not demonstrate that both kinds of air cannot originate from the electric matter."

^{4&}lt;u>Ibid.</u>, p. 139. "The experiments with vitriolic acid and nitrous acid prove much more against them; for exactly on account of the attraction of these acids for inflammable matter the latter cannot form and develop inflammable air, but it must either set free dephlogisticated air alone or other electrical substances."

⁵<u>Ibid.</u> "The authors, of course, always obtained a residue of air; that they did not examine, and that is <u>phlogisticated</u> air. They only infer, that it would not have occurred further in the sequence;

Perhaps Gren did not understand or was not aware of the antiphlogistic explanation of the residue because he incorrectly identified the source of the residue according to antiphlogistic theory as being impurities pre-existing in the vital air, rather than impurities pre-existing in the water. Gren then pointed out that the continued appearance of a residue supported his identification of the electric fluid as being the source of the production of phlogisticated air. Moreover, he considered that Deiman and Paets van Troostwijk's experiment showing that gases electrically produced from water could be ignited to reform water "Beweist aber nichts dagegen, dass die Bestantheile der Luftarten von der electrischen Materie herrühren könnten." Gren also cited Priestley's claim that phlogisticated air has water as a component part and noted that Deiman and Paets van Troostwijk themselves had shown in their experiments on acids that the electric fluid did not produce inflammable air without water.

Gren's belief that electricity instead of water was decomposed in the Dutch experiments was based on assumptions about the nature of electricity itself.

Es ist ganz unläugbar, dass der von den Herrn Verfassern angestellte Versuch einer der wichtigsten in der Lehre der

that is, however, not yet proven. This phlogisticated air is a stumbling block for the antiphlogistic [chemist], and he always finds it necessary to assume that it already pre-exists in the vital air."

⁶<u>Ibid</u>., p. 141.

 $⁷_{\underline{\text{Ibid.}}}$, p. 139. "Proves but nothing on contrary, that the component parts of the kinds of air could have originated from the electric matter."

⁸<u>Ibid</u>., p. 141.

Electricität ist, der uns vielleicht zur Erklärung der so problematischen Natur des electrischen Fluidums einen Schritt weiter bringen kann.

Gren: believed that because the passage of electricity through water produced both phlogisticated and vital air "die Lehre von zweyen electrischen Materien dadurch auch noch mehr bestätigt."

Although Gren's commentary on the Dutch experiments was published in the form of footnotes to the summary of their article from Observations sur la physique, Gren intended to repeat their experiments on his own and also to repeat "die Versuche mit Oel, mit Weingeist, mit Lackmustinktur."

However, he did not.

In an article published in the same volume Gren described his elaborate preparations to produce gases by passing electricity through water, including his design of an improved apparatus consisting of a strong glass cylinder capped with metal and equipped with screw valves to make it air tight. However, in the course of his experiments he made "die Funker stärker" in order to increase "Luftenwickelung" and after the third discharge his apparatus "zersprang." Gren was at a

^{9 &}lt;u>Ibid.</u>, p. 138. "It is quite indisputable, that experiment employed by the author is one of the most important in the teaching of <u>electricity</u>, that perhaps can bring us a step closer to the explanation of the problematic nature of the electric fluid."

 $^{^{10}\}underline{\text{Tbid}}$, p. 140. "the teaching of two electric matters is therefore still better established."

 $^{^{11}\}underline{ ext{Ibid}}$, p. 139. "experiments with oil, with spirits of wine, with litmus tincture."

¹²Gren, "Beschreibung eines Apparats, durch den verstärken electrischen Funken brennbare und Lebensluft aus dem Wasser zu erhalten," Journal der Physik 2(1790):195-197.

loss to explain this explosion.¹³ He had undertaken to repeat the experiment in the first place believing that it would reveal more about the true nature of the electric fluid than it would support Lavoisier's theory.¹⁴ Therefore, he thought of the mishap in terms of electricity and wondered how and why electricity would cause a conductor, water, to explode.¹⁵

Gren wrote that he did not have time to repeat this experiment, but he believed that it would be instructive to use other fluids, oils, acids, etc., instead of water. Again, Gren's interest was not in what those proposed experiments would reveal about oils, acids, etc., but in what they would reveal about the nature of electricity.

Gren. was not alone in his rejection of the electrical decomposition of water. Jean-André Deluc (1727-1817) also objected to the conclusion that water was decomposed in the Dutch experiments. Deluc, a Genevan by birth, had emigrated to England in 1771 after his financial ventures in Geneva had failed. The Deluc soon became a fellow of the Royal Society and, in the so-called "water controversy," he championed Watt's priority for the discovery that water resulted from the ignition of phlogisticated and dephlogisticated airs. In a letter to Lamétherie, dated

^{13 &}lt;u>Ibid.</u>, p. 197. "the spark stronger," "air production," "shattered."

¹⁴Gren, "Beschreibung eines Apparats," p. 194.

^{15 &}lt;u>Ibid.</u>, p. 197. 16 <u>Ibid.</u>, pp. 197-198.

¹⁷Robert P. Beckinsale, "Jean-André Deluc," <u>DSB.</u>, 4:27-29. Deluc introduced Watt's claims before the Royal Society. See also Paul A. Tunbridge, "Jean-André Deluc, F.R.S. (1727-1817)," <u>Notes and Records of the Royal Society of London</u> 26(1971):15-33.

¹⁸ Supra, p. 85, footnote 56.

17 May 1790, Deluc remarked that he had read with interest the Observations sur la physique account of Deiman and Paets van Troostwijk's experiments and that he viewed their results as a "phénomène sans doute, trés-digne d'attention, mais qui ne me parôit point autoriser la consé-what was to become the basis of the standard objections to the argument that water had been decomposed in the Dutch experiments. He began by questioning Deiman and Paets van Troostwijk's logic, pointing out that he considered their entire case rested upon "cette hypothèse . . . 'qu'un mêlange des ces deux airs s'enflamme & produit de l'eau'."20 According to Deluc, it was necessary either to prove "a priori" that no other airs could be ignited to form or to demonstrate "d'une manière non-susceptible de méprise" that the "fluide aériforme" produced by the passage of an electric spark through water really was "un mêlange de deux airs e désignés."²¹ He concluded that Deiman and Paets van Troostwijk had done neither and that "cette partie du raisonnement sur la nature de l'eau, n'est jusqu'ici qu'une hypothèse."22

¹⁹ Jean-André Duluc, "Lettre de M. De Luc, à M. De La Métherie, sur la nature de l'eau, du phlogistique, des acides & des airs," Observations sur la physique 36(1790):144. "phenomenon without doubt, very deserving of attention, but which dees not appear to me to authorize the consequence which these Physicists have drawn from it." Deluc was probably referring to the original article of 1789, although Lamétherie had again mentioned the Dutch experiments in his "Discours préliminaire" of January 1790. See Observations sur la physique 36(1790):30.

²⁰ Deluc, "Sur la nature de l'eau," p. 145. "this hypothesis... that a mixture of these two airs ignites and produces water."

 $[\]frac{21}{\text{Tbid.}}$, p. 146. "In a manner not susceptible to mistake." "a mixture of the two air designated."

²²<u>Ibid.</u>, "this part of their reasoning on the <u>nature of water</u> is still only a <u>hypothesis</u>."

Deluc admitted that he would accept <u>hypothetically</u> that two airs were indeed produced in the Dutch experiments. However, in the arguments of Deiman and Paets von Troostwijk he found "une <u>pétition de principe</u>, savoir, 'que les <u>bases</u> respectives des ces <u>airs</u>, sont deux substances, qui ensemble, composent <u>l'eau</u>.'"²³ He considered this assumption a <u>pétition de principe</u> because some

physiciens qui n'admettent pas cette <u>composition</u> de <u>l'eau</u>, pensent que <u>l'air inflammable & l'air déphlogistiqué</u> contiennent séparément <u>l'eau</u> elle-même, associée à quelque autre substance, diffèrente dans chacun d'eux, & d'où procèdent leurs caractères distinctifs.

As far as Deluc was concerned, the substance that entered into combination with water to form inflammable air was phlogiston.

Indeed, Deluc believed that all <u>airs</u> were combinations of water, heat, and light. He based his chemical beliefs upon his knowledge of meteorology of "L'Atmosphère, les grands rapports de l'air à l'eau, & ceux du feu à la <u>lumière</u>, les influences de ces rapports dans les <u>météores</u> & celles des <u>météores</u> sur tous les corps terrestres."²⁵ He was dealing with one of the aspects of nature that he knew best. 26

²³ Ibid. "a petitio principii, to wit, 'that the respective bases of these airs are two substances which together compose water:'"

^{24&}lt;u>Thid</u>. "physicists that do not admit this composition of water, think that inflammable and dephlogisticated air separately contain water itself, associated with some other substance, different in each of them, and from which their distinctive characters proceed."

 $^{^{25}}$ <u>Ibid.</u>, p. 153. "The <u>Atmosphere</u>, the great relationships of air to water, and those of fire to light, the influence of these relationships upon atmospheric phenomena and those of atmospheric phenomena on earthly bodies."

Among Deluc's principal works were Ides sur la météorlogie, 2 vols. (Paris: Spilsbury, 1786 and Duchesne, 1787), and Recherches sur les modifications de l'atmosphere, 2 vols. (Geneve: 1772). He also wrote on geological subjects

Although he did not continue to discuss the Dutch experiments, he sent four more letters to Lamétherie in 1790 outlining his objections to the new nomenclature of Lavoisier and relating these objections to his knowledge of meteorology, chemistry, and electricity. The Deluc's objections to the new nomenclature and to the conclusion that water was decomposed in the passage of an electric spark through water were often repeated or echoed by those who sought to defend the phlogiston theory. In the same year, 1790, Gioachimo Carradori (1758-1818) published an article in the first issue of the new Italian Journal, Annali di chimica, rejecting the conclusion that water could be decomposed electrically. In a manner reminiscent of Deiman and Paets van Troostwijk's arguments in their article in Observations sur la physique, Carradori admitted that at first the Dutch experiments had almost won him over to Lavoisier's new system of chemistry.

L'Esperienze dei Sigg. PAETS VAN-TROOSTWYK e DEIMAN . . . non posso negarlo, mi fecero appena lette grand' impressione, e quasi mi credea sul punto d'essere obbligato dalla ragione ad abbandonare la dottrina di STAHAL, e gettarmi dal moderno partito degli Antiflogistici, pure dopo pochi momenti d'una seria, ed imparzial riflessione, che io mi proposi, di fare nell' istante,

using his knowledge of meteorology in his arguments. See W. E. Knowles Middleton, A History of Rain and Other Forms of Precipitation (London: Oldbourne, [1965]), pp. 115-129 and Robert P. Beckinsale, "Jean André Deluc," DSB, 4:27-29.

²⁷ Deluc, "Seconde lettre de M. De Luc, à M. De La Métherie, sur la chaleur, la liquéfaction et l'evaporation," Observations sur la physique 36(1790):193-207. Deluc, "Troisième lettre de M. De Luc, sur les vapeurs, les fluides aériformes et l'air atmosphérique," Observations sur la physique 36(1790):276-290. Deluc, "Quatrième lettre de M. De Luc, à M. De La Métherie; sur la pluie," Observations sur la physique 36(1790):363-379. Deluc, "Cinquième lettre de M. De Luc, à M. De La Métherie; sur le fluide électrique," Observations sur la physique 36 (1790):450-469.

prima di piegare la mia mente a prestare il suo consenso, mi s'affacciarono alcune ragioni, le quali togliendo di mezzo tutto quello, che aveano di seducente, mi scuoprirono le loro mancanze, e mi ritennero nella mia opinione. 28

Through this analysis of Deiman and Paets van Troostwijk's experiments, Carradori concluded that the Dutch experiments "non mi sembrano punto decisive, per mostrare, che l'acqua è un composto, secondo il sentimento di LAVOISIER, e degli altri suoi seguaci, d'ossigene, e d'idrogene."²⁹ In his search for shortcomings in the alluring arguments of the Dutch natural philosophers, Carradori arrived at no less than six objections to the conclusion that water had been decomposed electrically in their experiments. He believed the Dutch experiments were not conclusive because:

 Electricity might contain phlogiston. If it did, their results could easily be explained in terms of the phlogiston theory.³⁰

Giaochimo Carradori, "Riflessioni sull' esperienze dei Signori Paets Van-Troostwyk, e Deiman sulla decomposizione dell' acqua in aria infiammabile e deflogisticata, comunicate per lettera ad un suo Amico dal Sig. G. Carradori," Annali di chimica ovvero raccolta di memorie sulle scienze, arti, e manifatture ad essa relative di L. Brugnatelli 1(1790):1-4. (Hereinafter referred to as "Riflessioni," and the journal is hereinafter referred to as Annali di chimica.) "The experiment of Ms. Paets van Troostwijk and Deiman . . I cannot deny, no sooner than [they] made a great impression on me, and I almost believed myself on the point of being obligated by reason to abandon the doctrine of Stahl, and to cast myself to the modern alternative of the antiphlogistians, I proposed, yet after a short time of a serious and impartial contemplation, immediately to first turn my mind to see if I could raise any reason, with which to eliminate by all means, the ones [arguments] that had been so seductive, revealing to me their shortcomings; and withhold upon this my opinion."

^{29 &}lt;u>Thid.</u>, pp. 5-6. "do not seem to me at all decisive in showing, that water is a compound of <u>oxygen</u> and <u>hydrogen</u>, according to the sentiments of LAVOISIER and to those of his followers.

^{30&}lt;u>Ibid</u>., pp. 6-7.

- 2. Inflammable air might not be an element. Carradori supposed that electricity might contain the principle of inflammable air and that water could be its base. 31
- 3. Carradori, like Gren, did not believe that Deiman and Paets van Troostwijk's experiments on nitric and vitriolic acid were applicable to experiments on water since they did not demonstrate that electricity does not contain phlogiston. 32
- 4. Carradori knew that the Abbé Fontana had produced vital air from river water and that Karl Wilhelm Scheele (1742-1786) had demonstrated that water absorbs air. Therefore, Carradori asserted that despite their efforts to purify water of this absorbed air, the vital air that Deiman and Paets van Troostwijk reported in their experiments must have been generated from such absorbed air. 33
- 5. Contrary to Deiman and Paets van Troostwijk's assertions, Carradori knew that there were two types of inflammable air, heavy and light. The inflammable air produced from water in the Dutch experiments was yet to be identified with light inflammable air or air produced from metal. Therefore, Carradori assumed that the inflammable air produced from water might not be light inflammable air but heavy inflammable air instead.³⁴

³¹ Ibid., p. 7.

^{32&}lt;u>Ibid., pp. 9-11.</u>

³³ Ibid., pp. 13-14.

³⁴ Ibid., pp. 15-16. Priestley had noted that there were "heavier

6. Priestley had demonstrated that dephlogisticated air or oxygen was not the only air to support combustion by showing that dephlogisticated nitrous air also supported combustion. Therefore, the air produced from water in the Dutch experiments might well be dephlogisticated nitrous air rather than oxygen.

Carradori's arguments are a combination of the standard phlogistic objections to the decomposition of water and of his own objections to Deiman and Paets van Troostwijk's assumptions that the phenomena they reported could only be interpreted in terms of the decomposition of water into hydrogen and oxygen. The standard arguments against the decomposition of water included the identification of electricity with phlogiston, the identification of inflammable air as a compound, the identification of the vital air produced as originating from air already dissolved in the water through atmospheric absorbtion, and the identification of Deiman and Paets van Troostwijk's experiments on acids as not supportive of their conclusions. These arguments are all based on appeals to experience and can be reduced to one basic argument: Something external to the water contributes materially to the production of air from it. In the case of the Dutch experiments, the phlogiston of the

electric spark materially contributed to the production of inflammable air, and the air absorbed by water from the atmosphere to the production

kinds of inflammable air" in Experiments and Observations on Different Kinds of Air, and Other Branches of Natural Philosophy, Connected with the Subject, 3 vols. (Birmingham: Thomas Pearson, 1790), 1:311. See also Partington, History of Chemistry, 3:584.

³⁵ Carradori, "Riflessioni," p. 16.

of vital air. Therefore, water is an element and gases produced from it are either already present in solution in the water, or are compounds of water and electricity, or are compounds of water and of the phlogiston in electricity.

Carradori objected to Deiman and Paets van Troostwijk's assumption that the phenomena they had reported could be interpreted only in terms of the decomposition of water into hydrogen and oxygen and he based his objection upon an appeal to both experience and inexperience. Carradori appealed to experience by objecting that gases other than hydrogen and oxygen would support combustion. ³⁶ He did not claim to have thus disproved the electrical decomposition of water; he had only pointed to Deiman and Paets van Troostwijk's lack of experience to show that one could not assume that the products in their experiment were hydrogen and oxygen without further data and, more importantly, to show that their experiments did not disprove the existence of phlogiston. He wrote:

Vi dico dunque, che l'esperienze dei Sigg. PAETS VAN-TROOSTWYK, e DEIMAN sono eccellenti nel suo genere, e proveranno a maraviglia la decomposizione dell' acqua, ma che per ora portan seco alcuni dubbj, per i quali, finchè non rimangano appianti, non meritano il nome d'incontrastabili, e decisive. Però, giacchè finora non mi pare, che siano comparse esperienze tali, che decidano assolutamente la quistione dell' esistenza del flogisto, o d'un principo, communque lo vogliano chiamare, in cui risieda l'inflammabilità, io mi rimarrò nella mia opinione, prontissimo ad abbandonarla, qualora coi fatti, e con le ragioni me la dimonstrino soggetta ad errore. 37

^{36&}lt;sub>Ibid., p. 17.</sub>

^{37 &}lt;u>Ibid.</u>, pp. 17-18. "I say to you therefore, that the experiments of PAETS VAN-TROOSTWYK and DEIMAN are excellent for their kind, and prove marvelously the decomposition of water, but that for now I suffer doubts, which until settled, I am not going back on what I said: they do not merit the name of incontestable and decisive. In as

Unlike Carradori, the editor of the Annali di Chimica, Luigi
Vincenzo Brugnatelli (1761-1818), did not reject Deiman and Paets van
Troostwijk's conclusions. Brugnatelli, in a footnote to Carradori's
article, provided the antiphlogistic alternative to Carradori's position
by inserting an account of Schurrer's repetition of the Dutch experiments. 39 In 1790 Brugnatelli also published an Italian translation of
Deiman and Paets van Troostwijk's article on the electrical decomposition
of water from Observations sur la physique in another journal that he
edited, the Biblioteca fisica d'Europa. 40

Later, in his <u>Elementi di chimica</u>, published in 1795 and again in 1800, Brugnatelli accepted the new chemical theory of Lavoisier and the argument that water was decomposed in the Dutch experiments.⁴¹

Despite the objections of Gren and Carradori, the phlogistic interpretations of the Dutch experiments found support in Germany as well as in Italy. In 1791 Christoph Girtanner (1760-1800) outlined in the first edition of his Anfangsgründe der antiphlogistischen Chemie an

much as it does seem to me yet that such experiments appear to decide absolutely the existence of phlogiston or of a principle, whatever you wish to call it, in which inflammability resides, I will remain of my opinion, ready to promptly abandon it whenever it is demonstrated by means of facts and reason, that I am in error."

³⁹ Ibid., pp. 1-5, note 2.

⁴⁰ Paets van Troostwijk and Deiman, "Lettera de' Signori Paets van Troostwyk e Deiman sopra una maniera di decomporre l'acqua in aria infiammabile e in aria vitale," Biblioteca fisica d'Europa ossia raccolta di osservazioni sopra la fisica, matematica, chimica, storia naturale, medicina ed arti di L. Brugnatelli 13(1800):90-108.

⁴¹ Luigi Vincenzo Brugnatelli, Elementi di chimica appoggiati alle piu' recenti scoperte chimiche e farmaceutiche de L. Brugnatelli M.D., 3 vols. (Pavia: Baldassare Comino, 1795), vol. 1, p. 232 or (Venezia: 1800), vol. 1, p. 307.

analytic and synthetic demonstration of the composition of water. This demonstration consisted of an experiment, the results of which Girtanner explained by arguing that water was electrically decomposed and then the resulting gaseous products were ignited to reform water. 42 The apparatus he described for this experiment was a glass tube ten inches long and one-half a line in diameter, sealed on one end and stoppered on the other. Gold conducting wires one-twelfth an inch in diameter were inserted in each end. Like Deiman and Paets van Troostwijk, he specified that the water be both boiled and placed under an air pump to remove impurities of atmospheric air dissolved in the water. In addition. Girtanner prescribed the necessary conditions to avoid breakage in the experiment. 43 Although he did not mention the source of his experiment, both his description of the necessary apparatus and of the results suggest that Girtanner knew of the Dutch experiments. Moreover, in the preface to his Anfangsgründe Girtanner mentioned Deiman, Paets van Troostwijk, Van Marum, and others while discussing the role of electricity in chemical investigation:

Mit Recht hat man es der bisherigen Chemie zum Vorwurfe gemacht, dass sie sich um die Elektrizität so wenig bekümmert. Die antiphlogistische Chemie weicht diesem Vorwurfe aus. Sie untersucht die Wirkungen der Elektrizität auf die Körper. Und mit welchem glücklichen Erfolge dieses geschehe, davon zeugen die Entdeckungen eines Priestley, Cavendish, Troostwyk, Deiman, van Marum, Monge, und anderer grosser Männer. Aus eben dieser Ursache wird mann, in

⁴² Christoph Girtanner, Anfangsgründe der antiphlogistischen Chemie, 2nd ed. (Berlin: Johan Friedrich Unger, 1795), pp. 87-88.

^{43&}lt;sub>Ibid</sub>.

der gegenwärtigen Schrift, sehr viele elektrische Versuche finden, deren in den älteren chemischen Schriften keine Erwähnung geschehen ist 44

In 1792 a German translation of Lavoisier's <u>Traité élémentaire</u> de chimie was published. The editor of this translation, a medical administrator, Sigismund Friedrich Hermbstädt (1760-1883) also provided his own commentary, including a discussion of the importance of Deiman and Paets van Troostwijk's experiments to the establishment of the antiphlogistic system. He wrote:

Bei diesem . . . Versuche kemmt also keine Kohle, kein Eisen, mit dem Wasser in Verbindung, der Goldrath dient bloss dazu, um dem elektrischen Funken, einen Weg durch das Wasser zu bahnen, und seine Auflösng, in zwei gasförmige Flüssigkeitten, die in ihrer Vermischung eine Knalluft bilden . . . der durch die Entzündung, wieder Wasser erzeugt wird. Will man vielleicht einwenden, dass hier die inflammable Luft von Seiten der elektrischen Materie erzeugt worden sey, so muss ich gestehen, dass eine solche Einwendung, bloss Chimäre seyn würde, und dass ich nicht begreiffen könnte, wie mann absolut das Wahre von sich stossen kann, um nach Phantomen zu haschen.

Another natural philosopher who announced his acceptance of the antiphlogistic system and the electrical decomposition of water in

^{44&}lt;u>Tbid.</u>, pp. 11-12. "Previous chemistry has been rightly reproached that it uses electricity so little. Antiphlogistic chemistry responds to this criticism. This has produced fortunate results, hence evidenced by the experiments of Priestley, Cavendish, Troostwijk, Van Marum, Monge, and other great men. Just from this beginning one finds many electrical experiments in the forementioned writings of which there is no mention in the old chemical writings.

⁴⁵ Sigismund Friedrich Hermbstadt, in Antoine Laurent Lavoisier, Des Herrn Lavoisier's antiphlogistischer System der Chemie, 2 vols. in 1 (Berlin: bey Friedrich Nicolai, 1792), p. 120. "Thus with this experiment, no carbon, no iron comes in combination with the water, the gold wire serves merely to prepare a way for the electric spark through water, and [for] its dissolution, in two gaseous fluids, whose mixing forms on ignitable air . . . which through ignition will have produced water again. One may perhaps object that in this case inflammable air is produced from the electric matter, so I must argue, that such an objection is merely chimera and that I can not understand how one can discard the absolute truth to strain after phantoms."

1791 was Giovanni Antonio Giobert (1761-1834), professor of chemistry and mineralogy at the Royal Academy of Turin. 46 Giobert made his position clear by reviewing Carradori's objections to the Dutch experiments for the Annales de Chimie. Although Giobert listed each of Carradori's six objections to the conclusion that water was decomposed in the Dutch experiments, Giobert also included his own refutations of Carradori's objections. In reply to the assertion that electricity might be phlogiston and that hydrogen might not be an element, Giobert wrote:

On voit aisément ici que l'auteur ignoroit que le docteur Priestley a exclu ces difficultés en remarquant que c'est par la chaleur que l'électricité produit ces effets, qu'on obtient même au moyen du calorique. 47

Giobert also scoffed at Carradori's assertion that the vital air produced in the Dutch experiment resulted from impurities of atmospheric air absorbed by the water.

Puisque les expériences exactes que 1'on a faites sur la décomposition de 1'eau ont donné quinze mille huit cens trente-sept pouces cubes de gaz oxigène par livre, nous ignorons absolument si c'est ce volume si énorme que le physicien de Pistoia voudroit supposer en état simplement de mèlange avec une livre d'eau, par cela seul que l'abbé Félix Fontana en a tiré quelques pouces.⁴⁸

⁴⁶ Poggendorff, 1:900-901.

⁴⁷ Giovanni Antonio Giobert, "Extrait du premier volume des Annales de chimie du Docteur Brugnatelli, Pavie, 1790, par M. Jean-Antoine Giobert," Annales de chimie 12(1792):47-48. "One easily sees here that the author is unaware that Dr. Priestley had excluded these difficulties by remarking that it is by heat that electricity produces these effects, that one likewise obtains by means of caloric."

^{48 &}lt;u>Ibid.</u>, p. 48. "Since the exact experiments that have been made on the decomposition of water have given 15,837 cubic inches of oxygen per <u>livre</u> [one livre = 1.079 pounds], we do not know if the physicist of Pistoria would want to suppose that such an enormous volume [to be] in a simple state

Giobert defended Deiman and Paets van Troostwijk's induction from the electrical decomposition of acids to the electrical decomposition of water by saying that electricity was not necessary to decompose acids or water, and, therefore, the decomposition of either was general enough to allow an induction from one to the other. 49

Treating the question of what kind of inflammable air was produced, Giobert pointed out:

Les physiciens, dit-il, ont distingué deux espèces de gaz hydrogène, le pesant & le léger Nous croyons qu'il est inutile de rappeler ici que le gaz hydrogène pesant ne differe du gaz hydrogène métallique que par l'azote, le carbone, & souvent le gaz acide carbonique avec lesquels il se trouve mêlé, & que l'hydrogène du gaz hydrogène pesant ne forme pas moins de l'eau avec oxigène, à cette différence près qu'il reste un résidu après la combustion, & qu'il se forme de l'acide nitrique par la réaction de l'oxigène sur l'azote. Cette remarque est d'autant inutile, qu'il n'est pas question de résidu ni d'acide nitrique dans les expériences des physiciens hollandois. 50

Finally Giobert rejected Carradori's suggestion that the air produced in the passage of electricity through water might be dephlogisticated nitrous air rather than oxygen, for the air produced in the Dutch experiment left no residue upon combustion, furthermore, when combustion

of mixture with a <u>livre</u> or water, through that alone by which the Abbe Felix Fontana had drawn a few inches."

⁴⁹<u>Ibid.</u>, p. 48.

^{50 &}lt;u>Thid.</u>, p. 49. "physicists, he says, have distinguished two species of hydrogen, heavy and light. . . . We believe that it is useless to recall here that heavy hydrogen only differs from metallic hydrogen by the azote, carbon, and often carbonic acid gas with which it is found to be mixed, and that the hydrogen of heavy hydrogen gas does not form any water with oxygen, with this difference that there remains a residue after combustion, & that there forms some nitric acid by the reaction of oxygen with azote. This remark is altogether unnecessary as there is no question of residue or nitric acid in the experiments of the Dutch physicists."

was supported by dephlogisticated nitrous air, there was always a residue. 51

The French defense of the electrical decomposition of water was by no means universal even after 1789. In 1793 the volume of the Mémoires de l'Academie des Sciences for 1789 was finally published. In it was an article by Antoine Baumé (1728-1804) entitled "Observations sur les expériences faites pour prouver la décomposition et la recomposition de l'eau," arguing against the decomposition of water. Baumé began his arguments by stating that water was "un liquide élémentaire, indestructible et inaltérable dans toutes les opérations de chimie."52 Any apparent decomposition of water or production of water from gases could be explained by Baumé's assumption that since water "a une si grande disposition à s'unir avec les substances qu'elle rencontre, qu'il est impossible de l'avoir parfaitement pure et privée de toutes matières étrangères."⁵³ If two substances combined to produce water, it meant to Baumé that they had water in them beforehand and conversely if water produced two substances, it meant to Baumé that the substances were present in the water as impurities beforehand.

⁵¹Ibid., p. 50.

⁵²Antoine Baumé, "Observations sur les expériences faites pour prouver la décomposition et la recomposition de l'eau," Mémoires de l'Académie des Sciences Année MDCC.LXXXIX. (Paris: De l'Imprimerie de DuPont, 1793), p. 88. "an elemental liquid, indestructible, and inalterable in all operations of chemistry."

^{53 &}lt;u>Tbid.</u> "has so great a disposition to unite with substances it encounters, that it is impossible to have it perfectly pure and devoid of foreign materials."

Baumé based his arguments partially on an appeal to authority, including "Aristote et . . . beaucoup d'autres philosophes de la Grèce aussi anciens," and "les physiciens de tous les siècles et de toutes les nations." More specifically, Baumé included "les Boile, les Boërrhave, les Staahl, les Muschenbroëch, les Sgravesande, les Desagulliers, etc. etc., et beaucoup de physiciens de nos jours." 55

As experimental evidence Baumé offered experiments conducted in 1786 by Louis Lefevre de Gineau (1751-1829) at the Collège Royale. In these experiments Lefevre had ignited inflammable and vital air together to produce water and then weighed the water produced. Although Lefevre reported that the weight of the water produced was only a few grains less than that of the combined airs, Baumé reported that "Ce résultat . . . ne m'a point fait illusion." He knew that the water produced in the experiments originated in water which had evaporated into the airs prior to the experiment. He noted that after the ignition "il restoit

 $^{^{54}\}underline{\text{Ibid}}$., pp. 88-89. "Aristotle and . . . many other philosophers from the most ancient Greeks" and "physicists of all centuries and nations."

 $^{$^{55}\}underline{\text{Ibid}}$, p. 89. "the Boyles, Boerhaaves, Stahls, the Musschenbroeks, 'sGravesandes, Desagulierses, etc. and many physicists of our own day."

. . . un volume d'air qui n'a pu brûler" and therefore "la plus grande partie de l'air contenu dans ce ballon est de l'air élementaire inaltérable et indestructible comme l'eau." Moreover, Baumé believed that if the experiment was repeated on a more exact and greater scale, "on obtiendroit infiniment plus d'eau que le poids des airs qu'on employeroit."

He then turned his attention to the experiments "qu'on a presentées comme décomposant l'eau."⁵⁹ Since Baumé knew that water had no parts, he argued that the gases produced from water resulted from air contained in the water or from the metal used to "decompose" it.⁶⁰ Thus he could explain the production of vital air from water by saying that the vital air was in solution in the water and the production of inflammable air from water by saying that the "matière inflammable" ⁶¹ was furnished by metal as it was calcined.

Although Baumé directed the arguments in his article against the claimed decomposition of water by its passage over red-hot iron, the article is indicative of the resistance in France after 1789 to the idea that water could be decomposed electrically.

 $⁵⁷_{\underline{\text{Ibid.}}}$, p. 91. "there remains . . . a volume of air that had not been ignited," and therefore "the greater part of the air contained in the balloon is elemental, inalterable and indestructible as water."

⁵⁸<u>Tbid.</u>, p. 93. "one would obtain infinitely more water than the weight of the airs that one would use."

⁵⁹<u>Ibid</u>. "that have been presented as decomposing water."

^{60&}lt;sub>Ibid</sub>.

⁶¹ Ibid. "inflammable matter."

In 1795 the Institut National was formed and filled the place of the disbanded Académie Royale des Sciences. Arguments were soon aired there in favor of the decomposition of water and the new system. In June of 1796, the letter of Jean-Baptiste Van Mons (1765-1842) was read, reporting "plusieurs expériences chimiques faites par lui ou par la Société des chimistes d'Amsterdam."

Van Mons . . . fait parvenir à la Classe un compte plus détaillé que celui qu'il avait déjà envoyé des expériences des chimistes d'Amsterdam, sur la décomposition de l'eau par l'etincelle électrique. 64

Baumé still remained a devotee of the phlogiston theory, and according to the <u>Process-verbaux de l'Institut National</u> "le Cn Baumé, Associé, lit un Mémoire initulé <u>Observations sur la décomposition et al recomposition de l'eau."⁶⁵ Although the memoir was not published in the <u>Mémoires de l'Institut National</u>, perhaps because by the 1800 publishing date the issue was a dead letter in France, one might imagine that it resembled Baumé's earlier memoir of the same title.</u>

⁶²For a detailed account of the dissolving of the Académie
Royale and the formation of the Institut National see Roger Hahn, The
Anatomy of a Scientific Institution: the Paris Academy of Sciences,
1666-1803 (Berkeley: University of California Press, 1971).

⁶³ Institut de France, Académie de Sciences, Procès-verbaux des séances de l'Académie tenues depuis la fondation de l'Institut jusqu'au mois d'août 1835, 10 vols. (Hendaye, 1910-1918), 1 (an IV-an VII):62. (Hercinafter referred to as Procès-verbaux de l'Institut National.) "several chemical experiments made by him or by the Society of chemists of Amsterdam." (Revolutionary date 1 messidore an 4.)

^{64&}lt;u>lbid.</u>, p. 65. "Van Mons . . . sent to the class a more detailed account than that he had already sent of the experiments of the Amsterdam chemists on the decomposition of water by the electric spark."

^{65&}lt;u>Thid.</u>, p. 170. "Citizen Baumé, <u>Associé</u>, read a memoir entitled <u>Observations sur la decomposition et recomposition de l'eau</u>.

Further arguments for the electrical decomposition of water appeared in 1796 in Crell's <u>Chemische Annalen</u>. In conjunction with Nicolas Bondt (1765-1796) and an Amsterdam apothecary named Antoni Lauwenberg (<u>fl</u>. 1796), ⁶⁶ Deiman and Paets van Troostwijk had performed a new and different set of experiments that they believed further demonstrated the electrical decomposition of water. Pointing out that their original experiments had not been regarded as decisive by partisans of the phlogiston theory, Deiman and Paets van Troostwijk described their initial search for a means to produce larger and more convincing quantities of air from the electrical decomposition of water as fruitless. ⁶⁷ Just as in their earlier experiments, an "accident" led to discovery:

doch endlich zeigte uns der Zufall (der in chemischen und physischen Untersuchungen oft mehr leistet, als die durchdachtesten Versuche) einen Weg, um auf eine sehr leichte Art eine grössere Menge dieser Luftarten, vermittelst der Elektricität, zu erhalten.68

While examining the passage of the electric fluid through carbonic acid gas, the Dutch natural philosophers obtained a residue which could be completely dissipated by electrical ignition. Therefore,

⁶⁶ Gerrits, Grote Nederlanders, p. 198 and Poggendorff, 1:1390.

⁶⁷ Jan Rudolph Deiman, Adrian Paets van Troostwijk, Nicolas Bondt, and Antoni Lauwrenberg, "Nachricht wegen einiger Versuche, welche die Zersetzung des Wassers durch den elektrischen Funken näher bestätigen. Von Hrn. J. R. Deiman, A.P. v. Troostwyk, N. Bondt and Louwerenburgh," Chemische Annalen für die Freunde der Naturlehre, Arzneygelahrtheit, Hanshaltungskunst und Manufacturen von D. Lorenz von Crell 2(1796): 291-292.

^{68 &}lt;u>Ibid.</u>, p. 292. "However, chance (which often achieves much more in physical and chemical research than the most thought-through attempts) showed us a method, to obtain in a very easy manner a greater amount of these species of air using electricity."

they assumed that the residue was hydrogen and oxygen resulting from the electrical decomposition of water vapour contained as an impurity in the carbonic acid gas. ⁶⁹ Using the same type of apparatus as they had used in their 1789 experiments on the electrical decomposition of water, Deiman, Paets van Troostwijk and their associates undertook a series of experiments to prove that the water vapour in carbonic acid gas and other gases as well could be decomposed electrically. After describing experiments on marine acid and the acid gas of spar, ⁷⁰ the authors argued

Wenn mann diese Versuche mit den schon längst bekannten Versuchen von der Zerlegung des Wassers, vermittelst der Elektricität, vergleicht, so wird jeder unpartheyische Chemiker eingestehen, dass wir dadurch einen grossen Schritt weiter zur Wahrheit gekommen, und dass sehr viele Zweifel, welche man gegen die Zerlegung des Wassers in Wasserstoff und Sauerstoffgas vorgebracht hat, auf diese Weise gehoben sind.71

However, Deiman and Paets van Troostwijk's new arguments that water could be decomposed were still not accepted by partisans of phlogistic theory.

One of those who continued to reject vehemently the antiphlogistic system and the electrical decomposition of water was Johann Samuel Traugott Gehler (1751-1795), editor of the Sammlugen zur

^{69&}lt;sub>Ibid</sub>.

 $⁷⁰_{\underline{\text{Ibid}}}$, pp. 293-298. The acid gas of spath or spar etches glass.

^{71 &}lt;u>Ibid.</u>, p. 299. "When one considers this experiment with already long known experiments of the decomposition of water by means of electricity, every impartial chemist will admit that we have made a great step toward the truth, and that very many doubts which have been advanced against the decomposition of water into hydrogen and oxygen, have in this way been dispelled."

Physik. Through his editorship, Gehler had been associated with the 1790 publication of a letter from Cuthbertson describing the Dutch experiments. At that time, Gehler did not object to Cuthbertson's account of the production of air from water by the passage of an electric spark, perhaps because Cuthbertson did not claim in his letter that the experiment demonstrated the truth of the antiphlogistic system. However, Gehler missed few opportunities after that to dispute the claims of Deiman and Paets van Troostwijk. In his Physikalisches Wörterbuch Gehler twice attacked the assumption that water could be decomposed. In the article "Wasser" published in 1791, Gehler related the experiments of Deiman, Paets van Troostwijk and Cuthbertson along with Deluc's objections to their conclusions. He concluded:

Bis jetz ist man wenigstens noch nicht genöthigt, von der Meinung der Alten, dass das Wasser ein einfacher elementarischer Stof. sey, abzugehen. Vielmehr läst es sich sehr wohl vertheidigen, dass dasselbe einen Bestandtheil, wie der meisten Körper, so auch der Luftgattungen, ausmache, und vorzüglich, wie Herr Achard, Westrumb und viele andere Naturforscher glauben, die Basis der reinen dephlogistirten Luft sey.⁷⁴

^{72&}lt;sub>Supra</sub>, p. 112.

⁷³ Johann Samuel Traugott Gehler, "Wasser," Physikalisches
Wörterbuch oder Versuch einer Erklärung der vornehemsten Begriffe und
Kunstwörter der Naturlehre mit kurzen Nachrichten von der Geschichte
der Erfindungen und Beschreiben der Werkzeuge begleitet in alphabetischer
Ordnung 5 vols., 1st ed. (Leipzig: in Schwickertschen Verlage, 17871795), 4:653-654.

⁷⁴ Tbid., p. 654. "Up to now one is not yet obliged in the least, to depart from the opinion of old, that water is a simple elementary material. There remains much more [evidence] to defend very well, that it is a component part of most substances, thus also constitutes air spaces and particularly, as Herr Achard, Westrumb and many other natural philosophers believe, is the basis of pure dephlogisticated air."

In a supplement to the <u>Wörterbuch</u> published in 1795 Gehler continued his attack against Deiman and Paets van Troostwijk's conclusions. After first mentioning the Dutch experiments, Schurrer's confirmation of them, and Hermbstädt's opinion that the Dutch experiments demonstrated the truth of the antiphlogistic system, ⁷⁵ Gehler marshalled arguments to the contrary taken from the writings of Deluc and Lichtenberg. ⁷⁶ He then concluded, in the name of logic and simplicity, "dass also die Zusammensetzung und Zerlegung des Wassers noch keinesweges als unwidersprechliche Thatsache anzusehen sey." ⁷⁷ In a revised edition of Gehler's Wörterbuch published after his death, the arguments against the decomposition of water remained the same. ⁷⁸

Thus Deiman and Paets van Troostwijk's claims for the electrical decomposition of water caught the attention of French, Italian, and German natural philosophers. The Dutch claim of the electrical decomposition of water could have reached England through Van Marum who visited London in 1790. Although his travel diary is not complete, in it Van Marum did mention that he associated with Jan Ingen-Housz (1730-1799) and Charles Blagden (1748-1820) and that he visited with William Nicholson

^{75&}lt;sub>Gehler, "Wasser," Wörterbuch, 5(supplement):990-992.</sub>

^{76 &}lt;u>Ibid., pp. 992-994. Infra, p. 171.</u>

⁷⁷ Ibid., p. 994. "that the combination and decomposition of water is yet in no way to be seen as an undeniable fact."

⁷⁸ Johann Samuel Traugott Gehler, "Wasser," Physikalisches Wörterbuch oder Versuch einer Erklärung der vornehmsten Begriffe und Kunstwörter der Naturlehre mit kurzen Nachrichten von der Geschichte der Erfindungen und Beschrieben der Werkzeuge begleitet in alphabetischer Ordnung. 6 vols., new ed. (Leipzig: in Schwickertschen Verlage, 1798-1801), 3:653-654.

(1753-1815) and John Smeaton (1724-1792). Van Marum also visited numerous instrument shops in London and met George Adams, Cavallo, Peter Dolland (1730-1830) and Edward Nairne (1726-1806). Moreover, Van Marum's electrical decomposition of water was discussed in the 1797 Encyclopedia Britannica. 80

Despite Van Marum's visit, few, if any, English publications prior to 1794 mentioned Deiman and Paets van Troostwijk's experiments. George Adams, whom Van Marum had met in 1790, is an example of the British reaction to developments in electro-chemical knowledge from 1786 until 1795. Adams, mathematical instrument maker to King George III, 81 wrote numerous popularizations of scientific subjects, including An Essay on Electricity, first published in 1784. Adams' Essay appeared in a second edition in 1785, 83 a third edition in 1787, 84 and a fourth edition in 1792. In it Adams included accounts of the experiments of Beccaria,

⁷⁹ Marum, "Notes on a Voyage to London in 1790," Martinus Van Marum: Life and Work, 2:266-272.

^{80&}quot;Electricity," <u>Encyclopaedia Britannica</u>, 3rd ed. (1797), 6:489. The same article made no mention of Deiman and Paets van Troostwijk.

⁸¹ Arthur Henry Grant, "George Adams," DNB, 1:97. Supra, p. 75.

⁸²George Adams, An Essay on Electricity; in which the Theory and Practice of that Useful Science, Are Illustrated by a Variety of Experiments, Arranged in a Methodical Manner. To which is Added, an Essay on Magnetism (London: by the author, 1784).

Adams, An Essay on Electricity, Explaining the Theory and Practice of that Useful Science; and the Mode of Applying It to Medical Purposes. With an Essay on Magnetism, 2nd ed. (London: for the author, 1785).

⁸⁴ Adams, 3rd ed. (London: R. Hindmarsh for the author, 1787).

Nollet, Priestley, Franklin, and Cavallo, ⁸⁵ among others, but did not mention the experiments of Deiman and Paets van Troostwijk, of or Van Marum.

In the same vein as Adams's Essay was George Cadogan Morgan's (1754-1798) Lectures on Electricity published in 1794. Morgan, a phlogiston adherent and lecturer at Hackney College, ⁸⁶ mentioned in his Lectures neither the experiments of Deiman and Paets van Troostwijk nor those of Van Marum. Morgan did include, however, an extensive examination of the conductivity of fluids very similar in approach to Cavendish's then unpublished researches on the same subject. ⁸⁷ In this examination of the conductivity of fluids, Morgan explained the breakage of vessels containing fluids by the passage of an electric discharge in terms of mathematics and mechanical law. ⁸⁸

Although Morgan's <u>Lectures</u> included no electro-chemical experiments, he was aware of the possibilities of the use of electricity in chemical investigation. In the introductory lecture, he extolled the value of electrical knowledge, writing:

In chemistry, much has been done by its union with electricity; but much more may be rationally expected. The properties of all

⁸⁵Adams, An Essay on Electricity, Explaining the Principles of that Useful Science; and Describing the Instruments Contrived either to Illustrate the Theory, or Render the Practice Entertaining. To which is now Added, a Letter to the Author from John Birch, Surgeon, on the Subject of Medical Electricity, 4th ed. (London: for the author by R. Hindmarsh, 1792), pp. 283, 288, 471, 483, respectively.

⁸⁶ Charlotte Fall Smith, "George Cadogan Morgan," DNB, 13:912-913.

⁸⁷ George Cadagon Morgan, <u>Lectures on Electricity</u>, 2 vols. (Norwich: F. March, 1794), 2:61-131.

^{88&}lt;u>Ibid.</u>, pp. 195-196.

fluids and solids are found to have been changed, when previously exposed to the action of the electric fluid. It separates the component parts of those substances on which the strongest fire of a reverberatory has no effect, and it is capable of being applied with accuracy and ease, where no other cause of change is applicable. In this connexion, however, our greatest desiderata are certain improvements in our apparatus.⁸⁹

Morgan admitted that he had once meant to describe a series of experiments that would "shew the connexion between electricity and chemistry," but instead settled on describing the apparatus involved. 90 Apparatus was Morgan's forte and he devoted the latter part of his Lectures to descriptions of various "Chemico Electrical Apparatus,"91 noting:

It should be here observed, that as the power of heat, when applied in chemistry, requires the action of three several bodies, so in applying the electric fluid, we are always obliged to consider the change it produces, not only in the body upon which it is designed to act, but in the body that conveys it, and in the medium surrounding that part of the circuit in which the explosion is most powerful. Thus if I convey the charge of a battery through sulphur, the conducting metal is affected, the sulphur is burned, and the air which surrounds the sulphur is at the same time rendered impure. 92

British natural philosophers were turning their attention to the chemical implications of electrical phenomena. In 1794 published accounts of the electrical decomposition of water began to appear in England. One of the first, if not the first, such accounts was in a footnote to the English translation of Méthode de nomenclature chimique of Louis-Bernard Guyton de Morveau (1737-1816), Lavoisier, Berthollet, and Antoine-François de Fourcroy (1755-1809). In the footnote the translator, George Pearson

⁸⁹ Ibid., 1:xx-xxi.

^{90&}lt;sub>Ibid</sub>., 2:468.

^{91&}lt;sub>Ibid</sub>., 2:469.

⁹²Ibid., 2:470.

(1751-1828), wrote:

The experiment of Messrs. <u>Paets van Troostyk</u> and <u>Deiman</u>, published above three years ago, is singularly curious and interesting, because it seems to at once prove, both by analysis and synthesis, that water is a compound of Hydrogen and Oxygen. It affords, perhaps, the strongest proof hitherto obtained of the decomposition or analysis of water. Notwithstanding the importance of this experiment, I believe it has not received confirmation: I have only heard that an experienced Chemist did not succeed in his attempt to repeat it. But I have now the satisfaction of informing philosophical men that Mr. <u>Cuthbertson</u>, late of Amsterdam, (so advantageously known for his improvements in the construction of the Air Pump, Electrical Machines, and other instruments) obligingly desired me to see him make this experiment a few days ago: of which a short account may be acceptable.93

Pearson described the apparatus used as a bent glass tube 1/15 of an inch in diameter and eleven inches in length. According to Pearson, Cuthbertson produced so much air in his repetition of the Dutch experiment that "it occupied nearly the space of half an inch of the length of the tube." After Cuthbertson ignited the air "it instantly disappeared, excepting a residue of about 1/40 of the air which had been produced." Pearson also noted that the water used in the experiment "did not render lime water turbid, nor turn paper stained with litmus to a reddish colour." That is, it contained no traces of acid.

In 1795 Tiberius Cavallo provided a more complete account of the Dutch experiments. Just as he mentioned Van Marum's experiments in the third edition of his <u>Complete Treatise</u> on <u>Electricity</u> in 1786, Cavallo

⁹³George Pearson, in a note to A Translation of the Table of Chemical Nomenclature, Proposed by De Guyton, Formerly De Morveau, Lavoisier, Bertholet, and De Fourcroy: With Additions and Alterations: to which Are Prefixed an Explanation of the Terms, and Some Observations on the New System of Chemistry (London: for J. Johnson, 1794), p. 56.

^{94&}lt;u>lbid</u>. According to phlogiston theory, water and nitric acid should be produced, if inflammable and vital air are ignited together.

also mentioned the experiments of Deiman and Paets van Troostwijk in the fourth edition, published in 1795. In fact, Cavallo included an English translation of Deiman and Paets van Troostwijk's entire account of their experiments. His only comment on the matter was:

It is necessary to add, for the satisfaction of my readers, that most of the valuable experiments which are mentioned in the preceding letter, having been repeated in London, have been found to answer in the manner above stated with all the accuracy which can be expected in such cases. Some of the observations might require farther elucidation and investigation; but this examination would lead us too far into the doctrine of permanently 96 elastic fluids, which is foreign to the subject of this work.

A reference to the electrical decomposition of water by William Nicholson (1753-1815) also was published in 1795. Nicholson, an official of the East India Company, friend of Priestley, commercial agent for Wedgwood, and a natural philosopher, 97 had admitted prior to 1795 that either the phlogistic system or the new system might be right. 98 In 1790 he had related in his Introduction to Natural Philosophy both the phlogistic and the new chemical theory and pointed out that the new theory was "maintained by facts and deductions, which, if they should fail in over-throwing the doctrine of Stahl, will, however, be of great advantage to science in many respects." 99 Nicholson adhered to phlogistic explanations in this work "because it is the most generally received." 100 However, in The First Principles of Chemistry, also published in the same year, Nicholson discussed phlogiston as a principle "not yet

⁹⁵ Cavallo, <u>A Complete Treatise</u>, 4th ed. (1795), pp. 168-191.

⁹⁶Ibid., p. 191.

⁹⁷ Arnold Thackray, "William Nicholson," DSB, 10:107-109.

⁹⁸William Nicholson, An Introduction to Natural Philosophy, 3rd ed., 2 vols. (London: for J. Johnson, 1790), 2:151.

^{99 &}lt;u>Tbid</u>. 100<u>Tbid</u>.

incontrovertibly established," saying "it still remains a problem to be decided, whether water . . . be a simple or compound substance." 102

By 1795 and the publication of his <u>Dictionary of Chemistry</u>
Nicholson had decided in favor of the "new theory." In the article on
"Water" he described both the decomposition of water by its passage over
red-hot iron and by the electric discharge. After briefly recounting
the experiments of Deiman and Paets van Troostwijk, Nicholson mentioned
that the Dutch experiment had been repeated by Cuthbertson in the
presence of Dr. Pearson. 103

Thus according to Pearson, Cavallo, and Nicholson, the Dutch electrical decomposition of water had been repeated in England in or prior to 1794. Although Cavallo did not mention who repeated these experiments, like Nicholson, he was probably referring to Cuthbertson, who built the great electrical machine at Teyler's. If Cuthbertson was not the first to repeat the Dutch experiment in England, he certainly was one of the first.

Born in Derham, Cumberland, Cuthbertson, then in his early twenties, left England for Holland in 1768 and did not return until 1793. While in

 $^{$101}_{\hbox{William Nicholson,}}$$ The First Principles of Chemistry (London: for G. G. M and J. Robinson, 1790), p. 91.

^{102&}lt;u>Ibid</u>., p. 96.

¹⁰³ Nicholson, A Dictionary of Chemistry, Exhibiting the Present State of the Theory and Practice of that Science, Its Application to Natural Philosophy, the Processes of Manufactures, Metallurgy, and Numerous other Arts Dependent on the Properties and Habitudes of Bodies, in the Mineral, Vegetable, and Animal Kingdoms (London: for G. G. and J. Robinson, 1795), pp. 1018, 1023-1024. Nicholson referred here to George Pearson. Supra, p. 143.

¹⁰⁴ Maurice Daumas, Scientific Instruments of the Seventeenth

Holland he wrote three volumes published in Dutch in 1769, 1782, and 1793 describing both his electrical instruments and the experiments that he had performed with them. 105 However, Cuthbertson did not include a description of the experiments he had performed with Deiman and Paets van Troostwijk in 1789, such as the one that had been published in the 1790 Sammlungen zur Physik. While the German translation of these three volumes, entitled Abhandlung von der Elektricität, contains no reference to the electrical decomposition of water, there is a radical difference between the character of the second and third parts. The second part, originally published in 1782, contains experiments in the same popular genre as those found in the Encyclopaedia Britannica, Priestley's History, Cavallo's Complete Treatise, and Adams's Essays. However, the third part published in 1793 details precise experiments on the calcination of metals in dephlogisticated and common air that are very similar in nature to those found in the publications of Van Marum. 106

and Eighteenth Centuries, ed. and trans. Mary Holbrook (New York: Praeger Publishers, 1972), p. 251. Daumas says that Cuthbertson did not return until 1801, but Nicholson and others indicate that Cuthbertson was in London in 1795 or before. Cuthbertson himself, in his Practical Electricity, and Galvanism, Containing a Series of Experiments Calculated for the Use of Those Who Are Desirous of Becoming Acquainted with that Branch of Science (London: for J. Callow, 1807), v, says that he returned in 1793.

 $^{^{105}}$ Cuthbertson, Practical Electricity and Galvanism, v.

¹⁰⁶ Cuthbertson, Abhandlung von der Elektricität nebst einer genauen Beschreibung der dahingehörigen Werkzeuge und Versuche, 2 vols. (Leipzig: im Schwikertschen verlage, 1786 and 1796). Compare experiments in 1:129-133 to those in 2:138-140 (Note:volume 1 contains parts 1 and 2, volume 2, part 3). See also "Electricity," Encyclopaedia Britannica, 2nd ed. (1779):4:2678-2682, Priestley, History, 3rd ed. (1775), 2:150-164, Cavallo, Complete Treatise, 1st ed. (1772), pp. 213, 282, 316-322, and Adams, Essays, pp. 46-50, 139, 140.

Cuthbertson made no reference to either the phlogiston theory or oxidation theories in his experiments, but in his <u>Practical Electricity and Galvanism</u> published in 1807, he indicated that he had performed calcination experiments in Amsterdam in 1792 and 1793 to demonstrate that the electric discharge converted metals to oxides. According to Cuthbertson, he had been repeating the calcination experiments of Van Marum because he did not believe them to demonstrate conclusively that electricity oxidized metals.

The discovery that metals could be ignited by electric discharges, gave rise to a supposition that they might also be converted into oxides by the same means. Many attempts have been made to ascertain this, but the fact remained without proof till, in the year 1787, Dr. Van Marum and myself, produced flocculi from different metals, by subjecting them to strong electric discharges . . . We imagined that the flocculi . . were the oxides of the metals we used, aad [sic] in order to prove this we entered upon a course of experiments; but having perhaps, from improper management, the misfortune to break several glasses in the process, Dr. Van Marum declared himself so much discouraged by these accidents, as to decline prosecuting the subject. When we consider, however, the opulence of that society, of which he was director, it is not easy to conceive that so trifling an accident . . . should be a sufficient reason for his relinquishing this investigation, more especially as he had command of an electrical apparatus which I had made for that society, not only the most proper for that purpose, but unequaled in the whole world, and from which I now fear that we have little to expect. 107

Although the incident Cuthbertson described fits Van Marum's description of the electrical decomposition of water, Cuthbertson did not

¹⁰⁷ Cuthbertson, Practical Electricity and Galvanism, pp. 197198. Cuthbertson's attitude toward Van Marum reflects the fact that he and Van Marum had engaged in several disputes over the relative merits of each other's designs for electrical machines and over whose experiments were the most exact. See Martinus van Marum: Life and Work, 3: 128. Cuthbertson's estimate of Van Marum's experiments may have been adopted by Maurice Daumas in his Scientific Instruments, p. 220, for Daumas asserts that Cuthbertson after his dispute with Van Marum became very successful and Van Marum amounted to very little.

specifically allude to the decomposition of water. In order to calcine metal wires electrically, Cuthbertson evacuated the air from a cylinder half-filled with water and then filled it with dephlogisticated air. If the water had risen in the cylinder after the electric discharge was passed through the wire, 108 then "so hat man Grund, zu denken, dass eine Verkalkung statt gefunden habe."

Cuthbertson reported that he successfully calcined wires of iron, copper, lead, and tin in this manner, but that no calcination took place with wires of silver, gold, or platina. Cuthbertson also noted that wires of lead and tin could be calcined even in common air. 110 However, Cuthbertson later wrote that he had performed calcination experiments in 1792-1793, trying to improve on Van Marum's results without any great success, and that only after his return to London did he achieve success through the design of a more sophisticated apparatus than that described in the Abhandlung. 111

Cuthbertson also referred in the third part of the Abhandlung to the "Beschreibung einer Elektrisirmaschine" of Deiman and Paets van Troostwijk, a publication detailing the machine that Cuthbertson had built for Deiman and Paets van Troostwijk from the prototype of the

¹⁰⁸ Cuthbertson, Abhandlung, vol. 2, pp. 139-140.

 $¹⁰⁹_{\mbox{\sc Tbid}}$, p. 140. "Thus one has a basis to think that calcination has taken place."

^{110&}lt;sub>Ibid</sub>.

¹¹¹ Cuthbertson, <u>Practical Electricity</u>, p. 198. A comparison of Cuthbertson's cylinder design in 1793 and in 1807 as found in the <u>Abhandlung</u>, 2:140 and in the <u>Practical Electricity</u>, p. 199, reveals the difference in instrumentation that Cuthbertson identified as necessary for "success."

machine at Teyler's. 112 The same machine was described by Deiman and Paets van Troostwijk in Observations sur la physique in 1789 in their account of the electrical decomposition of water. 113

Thus Cuthbertson wrote on calcination and the experiments of Van Marum, Deiman and Paets van Troostwijk before he returned to London in 1793. After his return Cuthbertson gave a course of lectures and demonstrated to his own satisfaction the oxidation involved in calcination. In addition, Pearson, the first Englishman to perform and publish an account of the electrical decomposition of water, also had indicated that Cuthbertson principally was responsible for the introduction of the repetition of the Dutch experiments into England. 115

Pearson, a physician and pupil of Joseph Black, was one of the first to champion Lavoisier's new system of chemistry in England. ¹¹⁶ In 1798 Pearson was one of those sponsoring Van Marum's membership in the Royal Society of London. ¹¹⁷ In February of the previous year Pearson had read his own experiments on the electrical decomposition of water to the Royal Society. His account of these experiments was published in both the Philosophical Transactions ¹¹⁸ and in the first volume of a new

¹¹² Cuthbertson, Abhandlung, 2:42-43, 136.

^{113&}lt;sub>J. G. de Bruijn, "Van Marum Bibliography," Chapter V of Martinus Van Marum, Life and Work, 1:323, 332. Also Supra, p. 12.</sub>

¹¹⁴ Cuthbertson, Practical Electricity, p. 198.

¹¹⁵ Supra, pp. 143, 145.

¹¹⁶ E. L. Scott, "George Pearson," <u>DSB</u>., 10:445-447.

¹¹⁷ Martinus Van Marum: Life and Work, 1:32.

 $^{^{118}\}mathrm{George}$ Pearson, "Experiments and Observations Made with the

scientific journal edited by William Nicholson, A Journal of Natural

Philosophy, Chemistry, and the Arts, more commonly known as Nicholson's

Journal.

In his discussion of the experiments of Deiman and Paets van

Troostwijk, Pearson mentioned Cuthbertson as one of the few able to repeat
those experiments successfully:

Hence, during the six years which have elapsed since its publication, [Deiman and Paets van Troostwijk's article in Observations sur la physique] no confirmation has been published except the experiment repeated by Mr. Cuthbertson, for my satisfaction, as related in my work on the chemical nomenclature; but I have heard of many persons, and some of whom were experienced electricians and chemists, who have made the attempt.

Pearson also mentioned Cuthbertson's decomposition of water in the second edition of his translation of Guyton de Morveau's <u>Table of Chemical Nomenclature</u>, published in 1799. 120

View of Ascertaining the Nature of the Gaz Produced by Passing Electric Discharges Through Water. By George Pearson, M.D. F.R.S.," Philosophical Transactions 87, Pt. 1 (1797):142-158.

¹¹⁹ George Pearson, "Experiments and Observations Made with the View of Ascertaining the Nature of the Gaz Produced by Passing Electric Discharges through Water; with a Description of the Apparatus for These Experiments," A Journal of Natural Philosophy, Chemistry and the Arts 1(1797):243. (Hereinafter referred to as Nicholson's Journal.)

¹²⁰ Pearson, "Explanation," A Translation of the Table of Chemical Nomenclature, Proposed by De Guyton, Formerly De Morveau, Lavoisier, Bertholet, and De Fourcroy; with Explanations, Additions, and Alterations: to which Are Subjoined, Tables of Single Elective Attraction, Tables of Chemical Symbols, Tables of the Precise Forces of Chemical Attractions; and Schemes and Explanations of Cases of Single and Double Elective Attractions, 2nd ed. (London: for J. Johnson, 1799), p. 86.

Because he supported Lavoisier's oxidation theory, Pearson might be expected to praise Deiman and Paets van Troostwijk's account of the electrical decomposition of water. Pearson did use his own experiments to argue that water was decomposed, but he was also highly critical of Deiman and Paets van Troostwijk's experiments on the matter. Pearson agreed with the criticisms of Carradori and others in that he did not believe the Dutch experiments conclusively proved the electrical decomposition of water. His first criticism of Deiman and Paets van Troostwijk's article was that "from much experience I can safely affirm, that it is scarcely possible for the student, or even the proficient, to institute the . . . experiment with success from the explanation published."

Pearson also disbelieved the Dutch accounts of the continued diminishment of residue bubbles after successive inflammations:

In at least fifty experiments I have never seen the residue of gaz less than 1/40th of the gaz produced, although the water had been freed from air by the most effectual means. But Mr. Schurer (Annales de Chimie, tom. v. p. 276) testified that he saw Mr. Van Troostwyk make the experiment; and that after it was repeated many times, on the same parcel of water, there was no residue at all. I have very good grounds for believing, that this is one of the number of inaccuracies in the account published of this subject. 122

After his criticism and summary of Deiman and Paets van

Troostwijk's articles as well as Schurer's repetition of their experiments, Pearson outlined his experimental procedure for obtaining

 $^{$^{121}}_{\rm Pearson},$ "Experiments and Observations," $\underline{\rm Nicholson's}$ Journal 1(1797):243.

^{122&}lt;u>Ibid., p. 242.</u>

the decomposition of water, explaining the importance of establishing a reliable demonstration of the electrical decomposition of water.

I am very sensible that it would be unnecessary for me to explain the importance of a process which may at last afford the demonstration of the composition of water, by the fullest and unequivocal evidence of its analysis and synthesis; a demonstration which no other single process but the present promises to afford.

I propose therefore in this paper:

1. To give such a description of the experiment of rendering water into gaz by electric discharges, as shall enable any person who is versed in pneumatic chemistry, and acquainted with the theory and practice of electricity, to repeat it with success. By this description, also, I apprehend I shall make known more generally the very elegant, and frequently most satisfactory, mode of decompounding and compounding bodies, by means of the fire of the electric discharge. 123

Pearson not only proposed to describe the experiment in such a manner that it could be easily repeated; he also sought to eliminate all the objections mentioned by the phlogistic critics of the Dutch experiment:

For although it seems most probable that water is really decompounded in Mr. van Troostwjk's experiment, it must be confessed that it does not make appear a single unequivocal and decisive property of hydrogen and oxygen in the gaz produced. The disappearance of this gaz by combustion, or in some other way, instantly on passing through it an electric spark, it is true, is a property known only to belong to the mixture of oxygen and hydrogen gaz; but it is well ascertained, that things of totally different species may agree in one or more properties. And there is at least a possibility, that electric discharges may produce various other kinds of gases in water, beside hydrogen and oxygen from decompounded water; and which may have the property of instantly disappearing on the passing through them of an electric spark. 124

In his attempt to avoid uncertainties that had been criticized in the Dutch experiments, Pearson related two different techniques that might be used to decompose water electrically. The first of these was

^{123&}lt;u>Ibid</u>., p. 243.

¹²⁴ Ibid.

the same method used by Deiman and Paets van Troostwijk. Pearson called this method the interrupted or incomplete discharge because:

Pearson believed the disadvantage of the interrupted method was that

if the discharge be not seemingly as strong as the tube can bear without breaking, the gaz is not produced from it; and on this point hinges this extremely delicate process. 126

He listed six prerequisites for success with this method and they incicate, Pearson's assertions to the contrary, there was little difference between Pearson's precautions and Schurer's.

- "(1) The electrical machine must possess sufficient power."

 Pearson preferred a plate machine rather than a cylindrical one because he did not think that a cylindrical one could "be made to act with due regularity, constancy, and force," and therefore could not "be made to answer in this process if a large quantity of gaz be required. . . ."

 Schurer had also specified that the correct force of the spark was necessary to decompose water. 127
- "(2) The Leyden jar must have a sufficient quantity of coated surface; without which the discharge will not be sufficiently powerful

^{125&}lt;sub>Ibid</sub>., p. 247.

¹²⁶ Ibid.

 $[\]frac{127}{\text{1bid}}$, p. 244. This and the remaining five items appear on pp. 244-246.

to produce the gaz required." Pearson reported that "the proper quantity as found by experience, was about 150 or 160 square inches"

Schurer had also specified that the Leyden jar have a large enough surface area, but specified only 120 square inches.

- "(3) The distance between the insulated ball, and the prime conductor, must always be less than the distance between the extremities of the wires." Pearson asserted that "not the least notice of this circumstance has been taken" and then described the same process of trial and error adjustment of the spark length that Schurer had described.
- "(4) The extremities of the upper and under wire within the tube must be at a certain distance from one another." Both Schurer and Pearson specified a distance that would prevent breakage and insure gas production, Schurer one-half of an inch and Pearson five-eighths or seven-eighths of an inch.
- "(5) The upper wire fixed into the closed extremity of the tube must be of a proper length and thickness." Pearson thought that the correct wire length prevented breakage and insured sufficient production of gas. Schurer had also specified the length of the upper wire for the same reasons, but Schurer did not mention any relationship between diameter and gas production. Schurer had preferred a wire one-twelfth of a line in diameter and one and one-fourth inches long.
- "(6) The tubes must be of a proper length and diameter."

 Pearson "found the most convenient length to be from nine to ten inches," and the most convenient diameter to be between one-eighth and one-twelfth of an inch. Schurer had used a tube ten inches long and one and one-half a line in diameter.

In Pearson's second method, that of the complete or uninterrupted discharge, he preferred a tube only five inches long and one-fifth or one-sixth of an inch wide. He used only one conducting wire in this tube, the second conductor being either a brass cap fitted over the open end of the tube or a brass dish in which the tube rested on its open end. The space between the wire and the brass conductor (either cap or dish) was only one-twentieth of an inch, a very short distance compared to the five-eighths of an inch used in the interrupted discharge method. Using a Leyden jar of only fifty square inches of surface, he produced much more gas with much less breakage than occurred with the interrupted discharge method. Pearson had to use a Leyden jar of 150 square inches of surface when he used the dish, but still he produced much more gas with much less breakage than in the interrupted discharge method. Because the repeated passage of the electric discharge made a small hole in the cap, Pearson found the brass dish preferable to the cap. 128 He also noted that in order to pass the electric discharge through water or other fluids for long periods of time

it may be an object to employ the wind, or perhaps the power of a horse, to turn the electrical machines, the expense of labourers being considerable. 129

From his numerous experiments Pearson selected those that he believed would

serve to explain the nature of the process, and shew the power of the plate electrical machines . . . particularly . . . those

^{128 &}lt;u>Tbid.</u>, pp. 246-247.

¹²⁹ Ibid., p. 248.

. . . which afforded the most useful results concerning the nature of the gaz obtained. $^{130}\,$

In other words, Pearson described only what he considered to be the best of his experiments and thus most supportive of his conclusions. He first related his results using the Dutch method of interrupted discharges.

Although Pearson did not use tabular form and instead related each experiment, one by one, the arrangement of his results in a table allows easy comparison and comprehension of the details and results of his experiments (see table 2). Pearson found in these experiments that if he did not boil the water or use an air pump to remove the air in solution from the water, a residue always remained after the bases produced from the water had been ignited. He reported that the residue was nearly the same in each experiment, one-half an inch in length and one-ninth of an inch in diameter, and he summarized:

Hence it seems that water is decompounded by the electric discharge, before the whole of the common or atmospherical air is detached from the water by merely the impulse of each discharge. Yet I think it probable that, after the discharges have been passed through the same water for a certain time, the whole of the air contained in the water will be expelled, and no gaz be produced, but that compounded by means of the electric fire from water; in which case, supposing the gaz so produced to be at least merely hydrogen and oxygen gaz, it will totally disappear on passing through it an electric spark. But I have never been able to determine this point, because the tubes were always broken after obtaining a few products, or long before it could reasonably 31 be supposed the whole of the air of water was expelled from it.

Pearson also tested a large quantity of air generated by the passage of electricity through water by adding nitrous gas to it, and noted that

¹³⁰ Ibid., p. 299.

¹³¹ Ibid., p. 300.

TABLE II

TABLE SUMMARIZING PEARSON'S EXPERIMENTS ON PAGES 299 AND 300
(No Such Table Exists in Pearson's Article)

Experiment	Number of Discharges	Time in Hours	Electrical Machine Inches of Plate	Type of Water	Boiled	Treated by Air Pump	Volume of l l (incl	W	Dimunition
A	1,600	3	34	New River	No	No	2/3	1/9	2/3 to 1/2
A	1,600	3	34	Distilled	No	No	2/3	1/9	2/3 to 1/2
В		4		New River	Either		2/3	1/9	15/16 to 19/20
В		4		Distilled	Either		2/3	1/9	15/16 to 19/20
C	1,600	3	, 32	New River	No	Yes	3/4	1/9	19/20
С	1,600	3	32	Distilled	Yes	Yes	3/4	1/9	19/20
D	600	3/4	32	River	No	No	1/2	1/10	19/20
E	?	4 days	32	. ?	?	Yes	**56,5488	1/10	*
F	6,000	?	?	. ?	?	?	3	3/20	. *

^{*}No ignition of products attempted.

Note: New River water is probably water drawn from the aquaduct known as the "New River." See A History of Technology, ed. Charles Singer, et al., 5 vols. (Oxford: Clarendon Press, 1958), 4:492.

[?]No mention made by Pearson.

^{**}Pearson gave volume produced as 56,5488 cubes, 1/10 of an inch each.

nitrous acid was formed as a result. He dried the remaining air over lime, then added an amount of oxygen to this air in an amount equal to one-half its bulk. Although he expected water to be produced, he could detect none. Pearson believed that the production of nitrous air indicated the presence of oxygen in the unknown air. Once all the oxygen had reacted with nitrous air, he then expected a remainder of uncompounded hydrogen that with the addition of further oxygen would form water upon ignition.

Since there was a discrepancy between his results and his expectations, Pearson offered an explanation:

The failure of the appearance of moisture was imputed to a bit of lime accidentally left in the tube which was burst by the explosion, and dispersed through the tube; or else the quantity of water produced was so small, comparatively with the residuary gaz, that the water was dissolved by it in the moment of its composition. . . .

That a quantity of water can be compounded under the same circumstances as in this experiment, and be apparently dissolved in air, so as to escape observation, even with a lens, was proved by passing an electric spark through a mixture of hydrogen and oxygen gaz, well dried by standing over lime. 132

Although he believed that the interrupted discharge method led to inconclusive results, Pearson affirmed from his experiments utilizing this method that water was decomposed. He then described the results obtained with his improved method of complete or uninterrupted discharge. Using his improved method, Pearson was still not able to avoid a residue of gas after the ignition of the products. The advantages of his improved method were a reduction in the time of the experiment and a reduction in breakage. Although he did not relate them in this form, a tabular

^{132&}lt;sub>Ibid.</sub>, pp. 300-301.

treatment allows an easy comparison of his results (see table III).

Pearson's judgment that his complete discharge method was superior to the incomplete discharge method of Deiman and Paets van Troostwijk may be questioned. Although the method did produce more gas with less breakage. Pearson's experiments were less conclusive concerning the nature of those gases than were Deiman and Paets van Troostwijk's. In fact, he had difficulty demonstrating that the gases produced in his experiments were hydrogen and oxygen. In the third experiment Pearson noted that the volume of gas did not increase after 8,000 discharges, and he postulated that the gas must be recombining as quickly as it was being produced. He had observed a flashing and the disappearance of the bubbles as they rose in the water, a phenomenon that he believed to be supportative of the assertion that the gases were being reignited and transformed into water. Assuming that much of the hydrogen and oxygen had been used up in this re-ignition process, Pearson did not attempt to ignite the one-fifth of a cubic inch of gas that remained. Instead he "added an equal bulk of nitrous gas." As a result the mixture was diminished by one-fifth. After adding more oxygen and then igniting the mixture, Pearson observed no diminution. Because this result did not confirm the presence of hydrogen, as he believed it should have, if the experiment had been performed correctly, Pearson explained:

Hence all the hydrogen gaz and oxygen gaz, produced by the decomposition of water, had been burnt during the process; the oxygen gaz thus detected being considered to be only that expelled from the water. 133

^{133&}lt;sub>Ibid</sub>., p. 303.

TABLE III TABLE SUMMARIZING PEARSON'S EXPERIMENT ON PAGES 301-303 (Using the complete or uninterrupted discharge)

Experiment	Number of Discharges	Electrical Machine Inches of Plate	Water	Time	Volume Produced in Cubic Inches	Fraction of Tube	Dimunition after Ignition
I	10,200	24	Cistern	11:34	1/4		
I ** ·	16,836	24	Cistern	17:09	1/2	5/8	5/8
rı	14,600	24	***	***	1/3	***	2/3
III	8,000	24	***	***	1/5	***	*
III **	12,000	24	***	***	1/5	***	*
IV	***	24	New River	***	1/8	***	*

^{*} Not ignited.

^{**} Generation of gas continued.

^{***} Not specified.

Although he did not say so, Pearson's fourth experiment was intended to illustrate that the results of his third experiment are not typical of the production of hydrogen and oxygen from water. In the fourth experiment he decomposed water, added nitrous air, and recorded that the mixture was diminished by one-half. He then added oxygen and ignited this second mixture and a further dimunition occurred. Noting that the residues of the third and fourth experiments gave different results to the same chemical tests, he argued that the residues must be different. 134

Pearson felt no qualms in concluding that water was decomposed by the passage of an electric discharge through water. He listed five reasons that when

considered singly and conjunctively... must be admitted by the most rigorous reasoner, or severest logician, to be demonstrative that hydrogen, and oxygen gaz were produced . . . 135

Pearson's five arguments can be summarized as:

- The gas produced by the passage of electricity through water was considerably diminished by electrical ignition.
- 2. Some of the gas produced by the passage of the electric discharge through water was apparently transformed into nitrous acid by the addition of nitrous gas.
- 3. The remaining residue could be ignited with oxygen to reform water.
- 4. The bubbles of gas generated by the passage of an electric discharge through water occasionally burned in their ascent in water.

^{134&}lt;sub>Ibid.</sub>, p. 304.

5. Items 1. through 3. could be duplicated using hydrogen and oxygen obtained from means other than the passage of an electric discharge through water. Item 4. was also suggestive of the ignition of hydrogen and oxygen. 136

If compared with that of Deiman and Paets van Troostwijk,

Pearson's "demonstration" of the nature of the gases produced by the

passage of an electric discharge through water relies on less extensive

tests of the nature of the gases produced. That is, Deiman and Paets van

Troostwijk made more tests to determine the presence of oxygen and also

made tests on acids to demonstrate by analogy the production of hydrogen.

Moreover, if compared with his account of Cuthbertson's experiments,

Pearson's own experiments are less demonstrative in one respect. According to Pearson, Cuthbertson succeeded in recombining the gases produced

to the extent that only a residue of one-fortieth of the gas produced

remained. The best diminution Pearson reported was one-twentieth

remaining.

As others before him, Pearson had questioned the role of electricity in the production of gases from water. Admitting that he was not so certain of the mode and origin in the production of gas in his experiments as he was of the nature of the gas, Pearson attributed the electrical decomposition of water to the caloric contained in the fire of the electrical discharge.

With regard to the origin and mode of production of these two gazes, our present observations and experiments do $\underline{\text{not}}$ afford complete demonstrative evidence; but although some hypotheses must be

^{136&}lt;sub>Ibid</sub>.

admitted, I conceive that the body of evidence we possess can afford a satisfactory interpretation of the phenomena, 137

It is demonstrable that the electric discharge and spark contain fire; and very probably they are merely a state of fire. Fire may be considered as consisting of caloric and light It is demonstrable also, that the ponderable parts of oxygen and hydrogen gaz constitute water. There is strong evidence that these gazes consist of a peculiar species of matter, which is ponderable; and of imponderable matter, which is separable from them in the state of fire, or flame. 138

Pearson assumed that the fire of the electric discharge was "so condensed" and acted "with so much rapidity" in its passage through water that

In the moment of its diffusion, a small part of this condensed fire interposes betwixt the constituent elements of the ultimate and invisible particles of water, that is, betwixt the hydrogen and the oxygen, of which water is compounded, so as to place them beyond the sphere of their chemical attraction for one another; and each ultimate particle of hydrogen and of oxygen uniting with a determinate quantity of fire, new compound ultimate particles, consisting of hydrogen and caloric, and of oxygen and caloric, that is, hydrogen gaz and oxygen gaz are compounded. 139

Using the intensity and rapidity of the electric discharge, he could also explain other phenomena involved with the decomposition of water such as the lack of oxidation of the conducting wires and the appearance of bubbles from both the upper wire and the lower wire or brass cup. According to Pearson, the wires were not oxidized because the electric discharge acted with too much rapidity. On the other hand, when red-hot iron was used to decompose water, the iron did oxidize because it

¹³⁷ The account of Pearson's experiments published in the Philosophical Transactions 87(1797):142-158 ends here. The account published in Nicholson's Journal 1(1797):304 continues to discuss the role of electricity in the decomposition of water.

^{138&}lt;sub>Pearson</sub>, "Experiments and Observations," <u>Nicholson's Journal</u> 1(1797):304-305.

^{139 &}lt;u>Ibid</u>., p. 349.

decompounded water with a slower heat. He also believed that the bubbles sometimes appeared in two places, the upper wire and the lower wire or brass cup, because the intensity of the electric discharge was the greatest at these two points. 140

Comparing the explanations of the phenomena resulting from the passage of the electric discharge through water given by the competing phlogiston and oxidation theories, Pearson explained the limits of chemical demonstration.

With regard to the evidence afforded by the foregoing experiments concerning the composition of water and of hydrogen and oxygen gaz. These substances are now accounted for in two ways only; namely, 1. By saying that these two gazes consist of water and imponderable matter; and that during combustion the water is precipitated. 2. By saying that the two gazes consist of a peculiar basis, one of which is named oxygen and the other is hydrogen, each of which is rendered into the gaz state by uniting to caloric, and perhaps also to light; . . . If complete demonstration could be given, there would not be two opinions; for its proofs, if understood, command universal assent: but the case being otherwise, that opinion must be adopted on the side of which the evidence preponderates 141

Pearson believed that the oxidation theory had a preponderance of evidence in its favor. Despite his admitted inability to prove by an appeal to sense experience that the gases produced were hydrogen and oxygen, Pearson assumed that he had sufficiently demonstrated the composition and decomposition of water.

The body of evidence is indeed so numerous, and of such a nature, that, in the minds of those who understand its import, and who rely on the accuracy of the weights and measures employed, it produces as much conviction concerning the composition of water as can be obtained by the evidence of almost any other case of

^{140&}lt;sub>Ib<u>id</u>., p. 350.</sub>

¹⁴¹ Ibid., p. 352.

composition. I must, however, beg leave to protest against those able philosophers, who have maintained, that the composition of water . . . has received full and complete demonstration . . . For in the chain of causes and effects there are some links which cannot be explained by the direct evidence of sense . . For instance. . . I cannot give the full and complete demonstration of the composition of water and these gazes: for, as I proceed in the interpretation, I at length come to demonstrate the mode of agency of the particles of the hydrogen and oxygen gaz on one another when they produce water caloric and light. . . . accordingly I imagine that the gazes consist of hydrogen and oxygen, which are ponderable—united to caloric, and perhaps light, which are imponderable . . . Now here I have not any evidence of sense; for I cannot perceive, by the senses, the existence of the composition of the gazes . . . nor of their decomposition, and the union of their ponderable parts. 142

Pearson accepted the demonstration of the composition of water, despite the lack of sensual demonstration, because he thought that "chemistry, in its present state, ought not to pretend to vie with mathematical philosophy in its demonstrations." He also believed that he had opened the path for natural philosophers with more time to demonstrate the composition of water, a demonstration that might someday attain the same certainty as mathematical demonstrations.

Although Pearson's experiments marked the beginning of an increase in the acceptance of the electric decomposition of water, phlogistic chemists continued to reject the Dutch experiments as a demonstration of the phlogistic theory. Indeed, some considered the Dutch experiments as a demonstration of the phlogistic theory. For instance, Carradori in a letter to Francesco Dupre (f1. 1797), published in the 1797

Annali di chimica, again rejected both the electrical decomposition of water and the new system. Carradori held to the phlogistic view that water could

^{142&}lt;sub>Ibid.</sub>, pp. 354-355.

^{143&}lt;sub>Ibid</sub>., p. 355.

not be decomposed and that any inflammable air produced from water must have been provided by the bodies used to attempt "decomposition." Believing that the whole antiphlogistic system rested on the unproved assumption that water was a compound, he argued that one could not prove the decomposition of water using electricity because by assuming that electricity did not contribute materially to the production of gases in its passage through water, antiphlogistic chemists had assumed what they sought to prove.

Tutta la fabbrica di Lavoisier in fondo si sostient sopra questa proposizione, cioè, che l'acqua è un composto, e risulta dalla combinazione dell' aria infiammabile con l'aria vitale. . . . Ma questa proposizione è elle provata? Per analisi non certamente; perchè l'encaustazione dei metalli, e l'e ettricismo non son mezzi sicuri per risuscirvi. Gli Italiani diranno sempre, voi supponete quel che dovete provare, l'aria infiammabile non viene dall' acqua, ma dai corpi che adoprate. 144

To support his argument, Carradori asserted that if electricity decomposed water, then fire should also, and it did not. 145 He also pointed out that the residue that often resulted from the ignition of the gases produced from water by the passage of electricity proved that the water produced at the same time must have come from the decomposition of the gases upon their ignition. Thus according to Carradori, the gases

¹⁴⁴ Gioachimo Carradori, "Lettera sopra il nuovo sistema di chimica scritta al Sig. Francesco Duprè dal Dott. G. Carradori," Annali di chimica 13(1797):80-81. "The whole structure of Lavoisier is itself founded upon this proposition, that is, that water is a compound, and results from the combination of inflammable air with vital air. . . . But is this proposition proved? Certainly not by analysis, because of the calcination of metal, and [because] electricity is not the reliable means to prove it. Italians would always say, that you have supposed what you ought to prove, inflammable air does not come from the water, but from the materials employed."

^{145&}lt;sub>Ibid., p. 81.</sub>

produced in the Dutch experiment were compounds, and water was one of their elemental constituents.

perchè dopo la combustione dell' aria infiammabile vi è sempre un residuo, e questo darà sempre luogo ad opporre, che l'acqua vien tutta dall' arie decomposte; e che essa con quel che rimane e qualch' altro incoercibile elemento, dava loro, e forma, e consistenza. In somma ni provino prima rigorosamente, che dall' acqua si ottiene anch' una bolla d'aria infiammabile, ed io ammetterò la nuova Chimica. 146

Although Carradori included an offer to adopt the new chemistry if anyone would demonstrate to him that one bubble of inflammable air originated from the water, one might easily believe that Carradori could have never accepted such a proof because he too had supposed "quel che dovete provare," that is, that electricity materially contributed to the fluids through which it passed.

An antiphlogistic reply to Carradori's arguments was published in the next year. Van Mons attacked Carradori on behalf of the new system in a review of the 1797 Annali di chimica published in the 1798 edition of Annales di chimie. After summarizing Carradori's arguments against the electrical decomposition of water, Van Mons replied:

"Les Italiens diront toujours, dit Carradori, vous supposez ce que vous devez prouver." (Mais les plus sensés parmi les chimistes et les physiciens italiens, qui ont repété nos expériences, et en ont adopté les conséquences, se contentent de nos preuves). 147

¹⁴⁶ Ibid., p. 82. "Because after the combustion of inflammable air there is always a residue, and that would always give rise to the objection that the water came completely from the decomposition of the air; and what remains are [the] incoercible elements which give it form and consistency. In summary, first prove to me rigorously that one bubble of inflammable air can be extracted from water and I will admit the new chemistry [is right]."

¹⁴⁷ Jean-Baptiste Van Mons, "Annaly di chimica, etc. Annales de chimie et histoire naturelle; par le citoyen Brugnatelli. Pavie,

In 1797, the fourth edition of Cavallo's <u>Complete Treatise</u> was published in German translation. The earlier German editions of the <u>Complete Treatise</u>, or <u>Vollständige Abhandlung der Elektricität</u>, had been translated with a commentary by Gerhler. 148 However, Gehler died before he could begin the fourth edition and his friend Joachim Moriss Wilhelm Baumann (fl. 1797) provided the translation and commentary necessary for the fourth edition. 149 That Baumann accepted and perhaps shared Gehler's disdain for the antiphlogistic interpretation of the Dutch experiments is evidenced in his treatment of the account of Deiman and Paets van Troostwijk's experiments contained in the fourth edition of the <u>Complete Treatise</u>. Rather than translate and comment on these experiments himself, Baumann used Gren's translation and commentary from the 1790 <u>Journal der physik</u>. 150 In the few comments that Baumann added, he only referred the reader to the articles on the matter in Gehler's <u>Wörter-buch</u> and to Lichtenberg's foreword to the sixth edition of "Erxleben's

^{1797,} tom. XIII; Extrait par le cit. Van Mons," Annales de chimie 26(An 6 or 1798):102. "'The Italians will always say, Carradori says, that you are supposing what you should prove' (but of the most sensible Italians chemists and physicists, who have repeated our experiments and who have adopted the consequences, are contented with our proofs.)"

^{148&}lt;sub>Tiberus</sub> Cavallo, <u>Vollständige Abhandlung der theoretischen und praktischen Lehre von der Elektricität nebst eignen Versuchen von Tiberius Cavallo</u>, trans. with commentary and notes by Johann Samuel Traugott Gehler and Joachim Moriss Wilhelm Baumann, from 4th English ed., 2 vols. (Leipzig: in der Weidmannische Buchhandlung, 1797), iii-ix.

¹⁴⁹ Ibid., xi-xii.

¹⁵⁰ Ibid., p. 328.

¹⁵¹ Ibid., pp. 334, 346.

Naturlehre." Baumann failed to include Cavallo's note explaining that the experiments of Deiman and Paets van Troostwijk had been successfully repeated in England.

In 1799, an article critical of some of Pearson's conclusions and written by an unnamed correspondent was published in <u>Nicholson's</u>

<u>Journal</u>. The anonymous author thought Pearson's experiments "well devised and conducted, and his conclusions fair and satisfactory," but he could not accept Pearson's explanation of how the passage of electricity could both decompose water into gases and recompose the gases into water. 153

The author believed that "the electric fluid, common fire, and light, those universal and general agents of nature . . . appear . . . to be not only confounded, but also to be so imperfectly considered, as to be the cause of endless confusion in every department of philosophy." He particularly questioned the role of electricity with respect to caloric.

The electric fluid, then, imparts caloric to oxygen, and so does light.—What ideas then are we to form of the electric fluid and of light?—Are they merely modifications of simple caloric, or are they compounds in which caloric forms a part? 155

¹⁵² Ibid., p. 346.

^{153&}quot;Observations on Electricity, Light, and Caloric, Chiefly Directed to the Results of Dr. Pearson's Experiments on Electric Discharges through Water. By a Correspondent," Nicholson's Journal 2 (1798, published 1799):396.

^{154&}lt;sub>Ibid</sub>.

^{155&}lt;sub>Ibid., pp. 396-397.</sub>

The anonymous correspondent's primary "animadversion" was that caloric played a contradictory role in the formation of gases from water and in the formation of water from gases. How could caloric both separate and combine these two gases? His answer was that it could not.

According to the present system of chemistry, caloric, homogeneous, simple caloric, destroys combinations which itself had formed; it attaches itself to particles of matter, and forms itself into repulsive spheres around them: and yet certain spheres of caloric in this state of repulsion will rapidly attract other spheres of the same caloric in similar states of repulsion! In short, caloric is hot or cold, attractive or repulsive, visible or invisible, just as the occasion may serve; and Proteus-like, it takes all shapes and forms:--we dread to meet it in Jove's thunderbolt, and court its influence in the cooling breeze! 156

Although Nicholson made comments in footnote form to some of this author's statements, he neither endorsed nor rejected the conclusions of the article.

In addition to the publication of the abstract of Pearson's experiments in the 1797 <u>Philosophical Transactions</u>, the more complete account in the 1797 edition of <u>Nicholson's Journal</u>, and the criticism of his experiments in the 1798 <u>Nicholson's Journal</u>, summaries of his experiments were published in the 1798 <u>Annales de chimie</u> and the 1799 <u>Annalen der Physik</u>. The article in the 1798 <u>Annales de chimie</u> by Pierre-Auguste Adet (1763-1834)¹⁵⁷ summarized Pearson's experiments, as

^{156&}lt;sub>Ibid</sub>., p. 397.

¹⁵⁷ Pearson, "Expériences et observations, de M. G. Pearson, sur la nature du gaz qui est produît par les décharges électriques à travers l'eau; extraites du Journal physique de Nicholson, par le cit. P. A. Adet," <u>Annales de chimie</u> 27(an 6 or 1798):161-180. Pages 166 through 178 are mostly quotations from Pearson's article.

published in <u>Nicholson's Journal</u>, and quoted Pearson at length on the role of electricity as caloric in the decomposition of water and on the nature of demonstration in chemistry. Adet, <u>docteur régent</u> of the faculty of medicine at Paris and one of the founders of the <u>Annales de chimie</u>, added little if any editorial commentary to his summary of Pearson's experiments. 158

The 1799 notice of Pearson's experiments in the Annalen der

Physik is significant in that it can be contrasted with the preceding
article of the same volume by Georg Christoph Lichtenberg (1742-1799)
defending the phlogistic interpretation of the passage of electricity
through water. Lichtenberg, professor of experimental philosophy at
Göttingen, was one of the last defenders of the phlogiston theory.

Although he is reported to have changed his mind prior to his death,
in this article published in the year of his death, he attacked the
conclusions that Deiman and Paets van Troostwijk had announced in 1789.

Lichtenberg's discussion of the Dutch experiments began with his questioning Deiman and Paets van Troostwijk's assertion that the experiments
that they had related would change the opinions of anyone believing in
the phlogistic theory.

Dieser Versuch soll, wie ich höre, sogar einige der eifrigsten Phlogistiker bekehrt haben*) Ich weiss nicht, wer diese Menschen gewesen sind; aber so viel weiss ich, sehr leicht müssen sie zu bekehren gewesen seyn. 160

^{158&}lt;u>DSB</u>., 1:64-65.

 $^{$159^{\}rm H}$Georg Christoph Lichtenberg," Olexa Myron Bilaniuk, <math display="inline">\underline{\rm DSB}_{\bullet}$, 8:320-323.

^{160&}lt;sub>Georg</sub> Christoph Lichtenberg, "Bermerkungen über einen Aufsatz des Herrn Hofr. Mayer zu erlangen: über den Regen, und Herrn de Luc's Einwürse gegen die französiche Chemie," <u>Annalen der Physik</u>

He pointed out that before the discovery of the so-called "decomposition" of water:

- 1. Natural philosophers such as Deluc, John Reinhold Forster (1729-1798), and Johann Karl Wilcke (1732-1796) either believed electricity to be a compound or discussed it as if it were a compound.
- 2. Electricity had been thought to contain either fire, acid, phlogiston, or some combination of these.
 - 3. Electricity was known to decompose nitrous air.
 - 4. Electricity smelled like phosphorous or sulfur.
 - 5. Electricity tasted acidic.

Therefore, he concluded "dass in dieser Materie so etwas steckeu könne, wie Basis der dephlogistisirten und Basis der inflammabeln Luft, man nenne es nun wie mann will." 161

In an attempt to counter objections that there was no change in weight when the combination of dephlogisticated air and inflammable air formed water, he argued that since it was capable of penetrating all substances and present in all bodies, the electric matter was too subtle to be weighed. Lichtenberg could also explain the non-electrical decomposition of water claimed by Lavoisier and Meusnier in terms of the

^{2(1799):142-143. &}quot;This experiment, so I hear, is supposed to have even converted some of the most zealous phlogisticiens. I do not know who these converted people were, but I do know they must have been easy to convert." *) is an editor's footnote to Pearson article in the same volume.

 $¹⁶¹_{\underline{\text{Tbid}}}$., p. 144. "That something could be thus contained in this matter, call it what you will, as the basis of dephlogisticated and inflammable air."

phlogiston theory by appealing to the action of an all-pervasive electric fluid.

Wäre es da nicht möglich, dass, wenn ich Wasserdampf durch einen glühenden Flintenlauf gehen lasse, durch die Glühhitze die anliegende electrische Materie in Flintenlause, die sich immer wieder aus der ganzen Erde ersetzte, zerlegt würde, ein Theil sich mit dem Dampfe verbände und inflammable Luft machte, und der andere mit eben demselben die dephlogistisirte, die sich nun mit dem Eisen vereinigte und es verkalkte?¹⁶²

Thus, using phlogiston theory he could explain facts "da nach der französischen Chemie der Amsterdammische unerklärt bleibt." 163

Lichtenberg believed the phlogistic explanation to be consistent with the facts which he accepted. Indeed, "was die französischen Chemisten Facta nennen wollen, keine Facta sind." His refutation of the Dutch experiments and of the "French chemistry" was based on an appeal to past experience and theory rather than on an appeal to experiments. That is, he did not seek to demonstrate further the "truth" of the phlogistic system by relating the performance of new and more conclusive experiments or by relating a more precise repetition of old experiments, because he believed that the experiments already performed and related by others provided all the data necessary for a correct conclusion. Lichtenberg considered it a sufficient refutation

^{162 &}lt;u>Thid.</u>, p. 145. "Is it not likely that, when I pass steam through a glowing gun barrel, the electric matter of the gun barrel, which is always replaced by the earth, is driven off by the red hot heat, one part unites with the steam and forms inflammable air and another parts likewise unites with the steam and forms de-phlogisticated air that then unites with the iron and calcines it?"

^{163 &}lt;a href="Ibid">Ibid. "Since the Amsterdam [experiments] remained unexplained by French chemistry."

^{164 &}quot;Ibid., p. 146. "what the French chemists want to call facts are not facts."

of Lavoisier's theory to show that the phlogistic system explained what he believed the French chemistry only purported to explain. Moreover, he questioned what he considered to be a tendency of antiphlogistic partisans to explain everything in terms of the new theory: "Man hat dieses freilich nach der neuen Chemie zu erklären gesucht; denn was erklärt die nicht?"

When confronted with two rival theories that both explained the phenomena, Lichtenberg believed that one should adhere to the established theory:

Furthermore, he disapproved of the new chemistry because it forsook the simplicity of universal elements.

was für Sicherheit läst sich von einem Systeme der Chemie erwarten, worin eine Materie, ein Stoff, der sich allen offenbart, noch nicht in Rechnung gebracht ist? 167

However, Lichtenberg found one indisputable point in both theories; that electricity played a key role in each.

^{165 &}lt;u>Ibid.</u>, p. 148. "One has freely sought to explain this according to the new chemistry, since what does it not explain?"

 $[\]frac{166}{1\mathrm{bid}}$, pp. 152-153. "Only the physicist is concerned about the truth of all, about the structure of Nature in general. What help is it, to trace and finish an addition to this plan, if they do not join it to the remainder, which is already solidly established . . .?"

¹⁶⁷ Ibid., p. 153. "For what guarantee can we expect from a system of chemistry wherein a material, a substance, that manifests itself in all things is not taken into account?"

Wenn man doch dieses recht ernstlich beherzigte! Das electrische Fluidum ist der <u>Spiritus sylvestris</u> aller neuen Chemie, der phlogistischen so wohl als der antiphlogistischen. Was für Revolutionen werden dann nicht entstehen, wenn man lernen wird, ihn einzusperren und zu handhaben. 168

A summary of Pearson's experiments immediately followed

Lichtenberg's article with a note by the editor that "erhält dieser

Auszug durch den vorstehenden Aufsatz Lichtenberg's ein neues Inter-:
esse."

169

The editor, perhaps Gilbert, may have believed that Pearson's
experiments held the answers to the phlogistic objections to the electrical decomposition of water, because he wrote in a note to Lichtenberg's
article "Einen Versuch einer Erklärung desselben nach der antiphlogistischen Chemie findet mann in Aufs. II dieses Stücks."

Moreover, he
pointed out in a note to Pearson's experiments that they might serve to
answer Gren's question of how the explosion of his glass tube filled with
water could be explained, since water was a conductor.

171

In the extract
of Pearson's experiments the editor of Annalen der physik also included
the anonymous criticisms of Pearson's conclusions that had been published

¹⁶⁸ Ibid., p. 153. "If one but earnestly takes this to heart! The electric fluid is the Spiritus sylvestris of all new chemistry, phlogistic as well as antiphlogistic, what sort of revolutions will not arise then, when man shall learn to imprison it and manipulate it."

Pearson, "Untersuchen über die Luft, welche aus dem Wasser durch electrische Funken entwickelt wird, von George Pearson Med. D. F.R.S.," Annalen der Physik 2(1799):154. "this article attains a new interest through Lichtenberg's foregoing essay."

^{170&}quot;George Christoph Lichtenberg's Bemerkungen über einen Aufsatz," p. 145, note. "One finds an attempt of explanation of the same [experiment] according to antiphlogistic chemistry in article 2 of this book.

^{171 &}quot;Untersuchen über die Luft," p. 157, note.

in $\underline{\text{Nicholson's}}$ $\underline{\text{Journal}}$, as well as Nicholson's editorial comments on these criticisms. 172

By the 1799 publication of Pearson's experiments in Annalen der Physik there was a growing agreement that the passage of electricity through water produced hydrogen and oxygen. Many German natural philosophers, even if they rejected the existence of phlogiston, believed that electricity was a compound and materially entered into the process. 173 For example, in 1799 Johann Anton Heidmann (1755-1855) referred to the experiments of Deiman and Paets van Troostwijk in his Vollständige auf Versuche und Vernustchlüsse gegründete Theorie der Elektricität. Heidmann, a doctor of medicine and member of the medical faculty at Wien, provided a compendium of electrical experiments conducted after 1775 in his Vollständige Versuche.

In addition to relating the experiments of electrical calcination and revivification of metals and the passage of electricity through fluids, gases, acids, bases, and indicators by Van Marum, Cuthbertson, Deiman, Paets van Troostwijk, and others, Heidmann also related his own experiments on these various subjects. 174 Although Heidmann cited both the phlogistic 175 and antiphlogistic 176 explanations of many

¹⁷² Ibid., pp. 176-184.

¹⁷³ For a discussion of the reception of Lavoisier's theory in Germany, see Georg W. A. Kalhbaum and August Hoffman, <u>Die Einführung der Lavoisier'schen Theorie im Besonderen in Deutschland. Uber den Anteil Lavoisier's an der Festellung der das Wasser Zusammensetzenden Gase. Monographieen aus der Geschichte der Chemie, Heft 1. Reprinted from Leipzig: Johann Ambrisius Barth, 1897 (Leipzig: Zentral-antiquariat, 1970).</u>

¹⁷⁴ Johann Anton Heidmann, Vollständige auf Versuche und Vernustschlüsse gegründete Theorie der Elektricität für Aerzte, Chymiker und Freunde der Naturkunde, 2 vols. (Wein: J. C. Schuender'schen, 1799), vol. 2, pp. 116-119, 123-124, 161, 259.

¹⁷⁵<u>Ibid.</u>, pp. 156-159. ¹⁷⁶<u>Ibid.</u>, pp. 160-162.

experiments, he offered the compromise that other German chemists including Gren had adopted. Without using the word phlogiston, Heidmann identified electricity as a compound of oxygen and "Feurematerie." Heidmann also treated water as if it were a compound of hydrogen and oxygen. 178

Although he discussed the nature of both water and electricity, Heidmann never explained the passage of electricity through water in terms of his own theory. Heidmann supported his view that electricity contained oxygen with his own calcination experiments in which he reported that he could calcine metals electrically in the absence of vital air.

Alle diese Erfahrungen haben also alle Überzeugung an sich, dass die Verkalkung der Metalle, wo sie immer durch den elektrischen Funken hervorgebracht wird, bloss seinen dabey entbundenen Bestandtheilen, nämlich dem Sauer- und Wärmstoffe ohne aller fremder Einwirkung zuzuschreiben sey. 179

He realized that his calcination experiments could be interpreted differently; "dass vielleicht der elektrische Funken das in diesen Gasarten aufgelöste Wasser zersetzet, dadurch Lebensluft freygemacht, und die Verkalkung der Metalle bewirket habe." However, he advanced

<sup>177
&</sup>lt;u>Ibid.</u>, p. 163. "Fire matter." For more information on this compromise, see Gren, <u>Principles of Modern Chemistry, Systematically Arranged by Dr. Frederic Charles Gren</u>, 2 vols. (London: for T. Cadell, et al., 1800), 1:15 and J. H. White, <u>The History of the Phlogiston Theory</u> (London: Arnold, 1932), pp. 165-183.

^{178&}lt;sub>Ibid.</sub>, pp. 142-143.

^{179 &}lt;u>Ibid.</u>, pp. 256-257. "Thus all these experiments have demonstrated that the calcination of metals, always where it is obtained through the electric fire, is merely to be ascribed to the presence of its component parts, namely heat and oxygen, without any foreign influence."

^{180 &}lt;u>Ibid.</u>, p. 257. "That perhaps the electric fluid decomposed water dissolved in these gas species, thereby having freed oxygen and having caused the calcination of metal."

what he considered to be three good reasons for dismissing this alternative explanation:

- 1. Dass auch in der Lebensluft sich Wasser aufgelöset befinde, wobey man sich nicht vorstellen kann, dass der elektrische Funken erst die Zersetzung des Wassers bewirken müsste, um Lebensluft frey zu machen, da ohnehin schon freye Lebensluft Verhanden ist.
- 2. Müsste nach so häufig durchgeleiteten elektrischen Funken in Gasarten, wo gar keine freye Lebensluft vorhanden ist, diese geringe Menge der Lebensluft, die durch die Zersetzung des Wassers entbunden würde, nach und nach verzehret werden, und es könnte keine fernere Verkalkung Statt haben; welches aber gegen die Erfahrung ist.
- 3. Wäre die Zersetzung des Wassers die Ursache der Verkalkung, so müsste man in jeder Gasart eine Vermehrung der Luftsäule und Wasser stoffgas als den zweyten Bestandtheil des Wassers wahrnehmen. Auch dieses streitet gegen die Erfahrung. $^{181}\,$

Girtanner, one of the first in Germany to accept the antiphlogistic system, also compromised between the phlogistic and antiphlogistic systems. In an article on the nature of azote, published in Annales de chimie and in the Philosophical Magazine in 1800, Girtanner turned his attention to the conflict of the two systems concerning the production of azote from the decomposition of water and the production of nitrous acid from the ignition of hydrogen and oxygen. He shrewdly

^{181&}lt;sub>Ibid.</sub>, pp. 257-258.

[&]quot;I. That dissolved water is also found in vital air, whereby we cannot imagine that the electric fire must first effect the decomposition of water to free vital air, since free vital air is already present.

^{2.} After frequent electric sparks conducted in gas species where no free air is present, this small amount of vital air, which would be released through the decomposition of water, must be again and again consumed, and no further calcination could occur; this, however, is contrary to the experiment.

^{3.} Were the decomposition of water the cause of the calcination, then one should observe in each gas species a mixture of hydrogen and oxygen, the two components of water. This also ran contrary to the experiment.

assumed that the experimental results of both sides were correct:

C'est ainsi que je raisonnois; j'avois appris, par l'histoire de la chimie, que dans toutes les disputes dans lesquelles les deux partis obtiennent des résultats opposés des mêmes expériences, il y a une erreur dans la manière de s'exprimer, et que, dans le fond, les deux partis ont raison. 182

Whereas adherents to the new chemistry had assumed that the production of azote during the decomposition of water and the formation of nitrous acid during the combustion of hydrogen and oxygen had both resulted from impurities of nitrogen in the gases and in the water, Girtanner in his consideration of the experiments of the two systems, assumed that azote was actually produced in both cases, that 1'azote est une eau privée d'une partie de son oxigène," and thus a compound of hydrogen and oxygen. 183

Although he had accepted the experimental results described by partisans of the phlogistic system, in no way did Girtanner consider his article to be a compromise of <u>theories</u>. "Je suis intimement persuadé que le systême de Lavoisier est conforme à la nature." 184 Moreover, his

¹⁸² Christoph Girtanner, "Mémoire dans lequel on examine si l'azote est un corps simple ou composé; par Christophe Girtanner,"

Annales de chimie 34(an 8 or 1800):8 and "Memoir on Azot, and the Question, Whether It Be a Simple or Compound Body. By Christopher Girtanner," The Philosophical Magazine Comprehending the Various Branches of Science, The Liberal and Fine Arts, Agriculture, Manufactures, and Commerce (Hereinafter referred to as Philosophical Magazine) 6(1800):337. The Philosophical Magaine translation follows: "Such as the manner in which I reasoned. I had learned from the history of chemistry, that in all disputes in which two parties obtained contrary results from similar experiments there was a mistake in the mode of expression, and that both at Bottom were in the right."

¹⁸³ Girtanner, "Mémoire dans lequel on examine azote," p. 16. "Azote is water deprived of a part of its oxygen."

 $[\]frac{184}{\text{1Did}}$, p. 7. "I am thoroughly persuaded that the system of Lavoisier is true to nature."

total acceptance of the antiphlogistic system is evident in the conclusion of his article.

Je soumets ces ideés aux lumières et à la critique des illustres chimistes français, éditeurs des Annales de chimie, pères de la science: ce sont eux qui l'ont créee. Avant eux, la chimie n'étoit qu'un amas informe de faits mal arrangés, et plus mal expliqués encore. 185

While a diminishing number of natural philosophers continued to defend the phlogistic system, the modified German acceptance of the new system reflected the decline of the phlogiston theory. However, the most famous phlogistician, Priestley, held out until his death in various publications that air could be produced from water without the decomposition of water by several processes, including mere boiling and the reduction of the air pressure over water by the means of a vacuum pump, without any "perceivable limit." However, as early as 1796, Priestley himself admitted the ascendancy of Lavoisier's chemical theory. He wrote:

There have been few, if any, revolutions in science so great, so sudden, and so general, as the prevalence of what is now usually termed the new system of chemistry, or that of the Antiphlogistians, over the doctrine of Stahl

¹⁸⁵ Ibid., p. 40. "I submit these ideas to the inspiration and criticism of the illustrious French chemists, editors of the Annales de chimie, fathers of the science: It is they who created it. Before them chemistry was only a shapeless mass of facts badly arranged and still more poorly explained."

¹⁸⁶ Joseph Priestley, "Further Experiments Relating to the Generation of Air from Water," <u>Transactions of the American Philosophical Society</u>, Held at Philadelphia for Promoting Useful Knowledge 4(1799):11-12. These experiments were read to the Society on 19 February 1796. By 1799 Priestley's arguments had been published in the United States, France, and England. For a bibliography, see Priestley: <u>A Scientific Autobiography</u>, pp. 388-391.

The English reviewers of books, I perceive, universally favor the new doctrine. In America also, I hear of nothing else. It is taught, I believe, in all the schools on this continent [North America] and the old system is entirely exploded. . . I hardly know of any persons, except my friends of the Lunar Society 187 Birmingham, who adhere to the doctrine of phlogiston. . .

Yet Priestley continued to advocate the phlogiston theory. In 1800, in his The Doctrine of Phlogiston Established and that of the Decomposition of Water Refuted, he discussed the experiments of Deiman, Paets van Troostwijk, and Dr. Pearson: "It is alleged in favor of the decomposition of water, that both dephlogisticated and inflammable air have been procured by taking electric explosions in water" He did not question the accuracy of these experiments, but he did question their interpretation. He reasoned that because "several agents are concerned" in the electrical production of air from water, what, and how much to ascribe to each of them is not easy to say." Priestley identified the metals used to conduct electricity to the water as the agents contributing the phlogiston necessary to produce inflammable air by the union of water and phlogiston. 188

Priestley's arguments were publicly rejected even by chemists in his new American homeland. In 1797 John MacLean (1781-1814) published
Two Lectures on Combustion: Containing an Examination of Dr. Priestley's
Considerations on the Doctrine of Phlogiston, and the Decomposition of

¹⁸⁷ Joseph Priestley, The Doctrine of Phlogiston Established and that of the Composition of Water Refuted (Northumberland: for the author by A. Kennedy, 1800), pp. 4-5.

^{188&}lt;sub>Ibid</sub>., p. 54.

Water. 189 In 1799 James Woodhouse (1770-1809) issued "An Answer to Dr. Joseph Priestley's Considerations on the Doctrine of Phlogiston, and the Decomposition of Water. 190 Perhaps Pierre-August Adet's "Reflexions" on Priestley's Considerations on the Doctrine of Phlogiston might best represent the ascendant state of antiphlogistic chemistry in 1799.

At the seance of 16 ventose an 6, Fourcroy and Berthollet read Adet's "Reflexions" to the Institut National and signed them into the minutes noting

Il ne nous convient pas de prendre un ton affirmatif sur le judgement qu'on doit porter sur cette discussion, mais le Cn Adet a fait un excellent usage des moyens que lui fournissoit la chimie antiphlogisticienne et il a bien mis le public en état de juger. 191.

Berthollet and Fourcroy, partisans of the new chemistry, were safe in letting the public judge from Adet's article because he ended it with an enumeration of the diminishing number of those who continued to espouse the phlogistic theory:

¹⁸⁹ Considerations on the Doctrine of Phlogiston, and the Decomposition of Water by Joseph Priestley, IL.D. F.R.S. and Two Lectures on Combustion and an Examination of Doctor Priestley's Considerations on the Doctrine of Phlogiston by John MacLean M.D., ed. with a sketch of the life and letters of Doctor MacLean by William Forster (Princeton, New Jersey: Princeton University Press, 1919).

¹⁹⁰ James Woodhouse, "An Answer to Dr. Joseph Priestley's Considerations on the Doctrine of Phlogiston, and the Decomposition of Water; Founded upon Demonstrative Experiments. By James Woodhouse, M.D. Professor of Chemistry in the University of Pennsylvania, &c.," American Philosophical Transactions 4(1799):452-475. See also Denis Duveen and Herbert S. Klickstein, "The Introduction of Lavoisier's Chemical Nomenclature into America," ISIS 45(1959):278-292 and Sidney S. Edelstein, "The Chemical Revolution in America from the Pages of the 'Medical Repository,'" Chymia 5(1959):155-179.

¹⁹¹ Proces-verbaux de l'Institut National 1(16 ventose an 6):359. "It is not proper for us to take a position in this discussion, but Citizen Adet has made excellent usage of the means furnished him by

Ceux qui s'occupent de chimie peuvent être divisés en deux classes; celle des partisans du phlogistique, et celles des antiphlogisticiens. Le docteur Priestley fait l'énumération des premiers, et il n'est pas sans intérêt de les connoître: ce. sont, en Allemagne MM. Crell, Westrumb, Gmelin, et Mayer: à Birmingham, M. Keir et quelques autres amis du docteur Priestley; il apprendroit sans doute avec plaisir qu'il peut compter en France les citoyens lametherie, Sage, et Baumé. Les autres forment la seconde classe.

According to the <u>Procès-verbaux de l'Institut National</u> "la Classe [of Sciences physiques et mathématiques] approuve le Rapport et en adopte les conclusions." Adet's "Réflexions" was also published in 1799 in the <u>Annales de chimie</u>. 194

"Les autres forment la seconde class" said Adet, and indeed they did. By 1799, the electrical decomposition of water and the new chemical system had been widely published, well discussed, and increasingly accepted. The second edition of Pearson's translation of Guyton de Morveau's Chemical Nomenclature published in 1799 illustrates that none of Pearson's previous caution concerning the limits of demonstration

antiphlogistic chemistry and he has well put the public in a state to judge [for themselves]. 16 ventose, an 6 is March 6, 1799. For information about the French Republican calendar see "The French Revolution," Encyclopedia Britannica, 11th ed., vol. 11, p. 170.

¹⁹² Pierre-Auguste Adet, "Réflexions sur la doctrine du phlogistique et la décomposition de l'eau par Joseph Priestley, docteur ès lois, membre de la Société Philosophique de Philadelphie, etc. Ouvrage traduite del'anglais, et suivi d'une réponse, par P. Adet," Annales de chimie 26(1798 or an 6):308-309, or <u>Procès-verbaux de l'Institut National</u>, 1:359. (Punctuation differs slightly in the two.) "Those who are occupied with chemistry can be divided into two classes; that of partisans of phlogiston and that of antiphlogistic partisans; Doctor Priestley enumerated the first and it is of interest to know them: They are Crell, Westrumb, Gmelin, and Meyer in Germany: M. Keir and a few other of Priestley's friends in Birmingham; he would be pleased to learn, no doubt, that he can count in France citizens Lametherie, Sage, and Baumé. The others form the second class." One might also add Carradori in Italy.

¹⁹³ Proces-verbaux de l'Institut National 1(16 ventose an 6):359. "The class approves the report and adopts its conclusions."

¹⁹⁴ Supra, p. 183, fn. 192.

in chemistry remained. Referring to the electrical decomposition of water, Pearson said:

In the Philosophical Transactions, <u>Part I. for 1797</u>, p. 142, will be found my experiments of producing Gas by passing electric discharges through water. I used a different apparatus from that of the original contrivers of the experiment; with which I collected, with infinite labour and extreme difficulty, a sufficient quantity of Air to add to it, 1st, Nitrous Gas, by which I found it contained Oxygen Gas; and, 2d, To the residue I added Hydrogen Gas; and on passing an electric spark through this mixture of residue and Hydrogen, it took fire and became water. Is not this an <u>Experimentum Crucis</u>, and perfectly demonstrative of the composition of water? 195

Thus Deiman and Paets van Troostwijk's argument that they had demonstrated the decomposition of water met with a varied reception from European natural philosophers. Partisans of the phlogiston theory rejected the antiphlogistic interpretation of the Dutch experiments for methodological reasons, but these reasons were based upon two preconceptions that originated in the phlogiston theory. Convinced that gases are compounds and water is an element and that electricity is or contains phlogiston, the phlogisticians rejected the following four assumptions that were implicit in the antiphlogistic interpretation of the Dutch experiments:

1. Electricity does not contribute materially to chemical action.

In the tradition of Milly, Carradori, Deluc, Gren, Lichtenberg (and even Deiman, Van Marum, and Paets van Troostwijk, before they adopted Lavoisier's theory), partisans of the phlogiston theory believed that electricity qua phlogiston contributed to chemical reactions. For this reason, phlogisticians could not accept Deiman and Paets van Troostwijk's arguments that the action of electricity on acids was pertinent to the consideration of the action of electricity on water. In the context of the phlogiston theory,

¹⁹⁵ Pearson in Guyton, A Chemical Nomenclature, p. 86.

the action of electricity on acids or water was a phlogistication (adding or phlogiston), not a decomposition. Whereas decompositions might be analogous, reactions involving combinations varied according to the substances being combined.

- 2. Because inflammable air is produced electricially from water, it is a constituent of water. Lamétherie, Cavendish, Priestley, Kirwan, Watt, and others had identified inflammable air as phlogiston. Therefore according to the phlogiston theory, the electrical production of inflammable air from water indicated that the inflammable air was provided by the electric fluid.
- 3. Because vital air is produced electrically from water, it is a constituent of water. Experiments made by Priestley, Fontana, and others illustrated that water absorbs a certain amount of air from the atmosphere which could be expelled from the water by an electric discharge. Moreover, some phlogisiticians, such as Priestley, Gren, and Lichtenberg, believed that the vital air produced electrically from water was a compound of electricity (phlogiston) and water.
- 4. Because the air expelled from water by the passage of an electric discharge can be ignited to reform water, the air is a mixture of inflammable and vital air. Other airs, such as nitrous air, were known to support ignition. Moreover, more than one kind of inflammable air was known to exist, so there was no reason to assume that the inflammable air produced from water was what the antiphlogisticians called hydrogen.

The followers of Lavoisier's new system of chemistry were not daunted by these phlogistic objections to their assumptions. They in turn replied:

- 1. Electricity enters into chemical action only to provide heat.

 Even chemists such as Morgan, who did not discuss the electrical decomposition of water, accepted the ability of electricity to provide the heat necessary for chemical decomposition or combination. Thus antiphlogistic chemists believed the chemical action of electricity on water to be analogous to the action of electricity on other compounds such as acids.
- 2. Because electrical experiments on acids to not produce hydrogen, hydrogen does not originate from the electric fluid.
- 3. The vital air absorbed by water can only account for a very small part of the vital air produced electrically from water. Since the vital air could not have been produced from air absorbed by the water or the electric fluid, it must originate with the decomposition of water.
- 4. Only hydrogen and oxygen can be ignited to form water as a sole product. Although there are more than one kind of inflammable air and although other kinds of air will ignite, the union of heavy inflammable air and other airs does not form water as a sole product. Moreover, chemical tests such as Pearson's procedure of adding first nitrous air and then inflammable air, indicated that the airs produced electrically from water were oxygen and hydrogen.

Thus partisans of the phlogistic and antiphlogistic theories continued to differ in their interpretation of the Dutch experiments, and as both sides pointed out, they assumed what they sought to prove, in that each position depended upon presuppositions about the nature of water and of electricity, that originated in the theory they sought to demonstrate. As Pearson aptly noted, although he later argued that the electrical decomposition of water was an Experimentum Crucis, the

phlogistic and antiphlogistic system both explained the phenomena produced in the Dutch experiments once their initial assumptions were granted.

Although the conflict between Lavoisier's new chemical theory and the phlogiston theory resulted in general, but not universal, acceptance of the former by 1800, Deiman and Paets van Troostwijk's experiments on the passage of the electric commotion through water did not provide European natural philosophers with the decisive experiment capable of serving as the Baconian signpost at this crossroads of two theories. The numerous repetitions and varying interpretations of the Dutch experiments, as detailed in the previous chapter, illustrate that the Dutch experiments were used to argue both sides of the question and that even chemists who embraced the antiphlogistic theory differed in . their reception of the Dutch experiments. Not only did natural philosophers differ over the elemental nature of water, but also over the elemental nature of electricity and over the role of heat and light in chemical phenomena. If Deiman and Paets van Troostwijk's experiments ever served as an experimentum crucis, they only did so retrospectively. When the issue was decided and the antiphlogistic theory generally accepted, the Dutch experiments could be used to demonstrate what was already accepted: the compound nature of water.

Once there was a general acceptance of the antiphlogistic theory and of the electrical decomposition of water, the electrical decomposition of water was used as a crucial instance in another debate of the era concerning the question whether animal or galvanic electricity was electricity or another fluid <u>sui generis</u>. It was in this debate, the

the Galvani-Volta controversy, that the new chemical system failed to explain electrochemical phenomena, and, accordingly, conceptions of the nature of electricity and its role in chemical change again were brought to the fore.

CHAPTER V

THE DECOMPOSITION OF WATER AS A CRUCIAL INSTANCE IN THE IDENTIFICATION OF GALVANISM WITH ELECTRICITY

The Galvani-Volta controversy is a subject worthy of a separate and lengthy treatment. To summarize it briefly, in 1791 Luigi Galvani (1737-1798) announced in his <u>De viribus electricitatis in motu musculari commentarius</u> that the severed muscles of truncated frog legs could be induced to twitch by the establishment of a bi-metallic circuit connecting the muscle to the nerve endings. Galvani viewed his discovery as a demonstration of the existence of animal electricity, a fluid similar to electricity, but peculiar to organic tissue. 1

By 1793 Volta was publicly rejecting Galvani's interpretation of the phenomena, and in two letters transmitted to the Royal Society via Cavallo, Volta argued that galvanic phenomena were simply electricity generated by the contact of two dis-similar conductors. 2 Galvani

Luigi Galvani, A Translation of Luigi Galvani's De Viribus Electricitatis In Motu Musculari Commentarius: Commentary on the Effect of Electricity on Muscular Motion, trans. Robert Montraville Green (Cambridge, Massachusetts: Elizabeth Licht, 1953). See also Theodore M. Brown, "Luigi Galvani," DSB, 5:267-269.

Alessandro Volta, "Account of Some Discoveries Made by Mr. Galvani, of Bologna; with Experiments and Observations on Them, In Two Letters from Mr. Alexander Volta, F.R.S. Professor of Natural Philosophy in the University of Pavia to Mr. Tiberius Cavallo, F.R.S.," Philosophical Transactions 83(1793):10-44.

was vehemently defended by his nephew, Giovanni Aldini (1762-1834), ³ and the concept of animal electricity was later upheld by Friedrich Wilhelm Heinrich Alexander Von Humboldt (1769-1859). Between 1793 and 1795 Humboldt performed numerous experiments comparing galvanic and electrical phenomena from which he argued that electric and galvanic phenomena were caused by two separate and distinct fluids. His experiments were widely circulated, especially on the continent; they were read to the Institut National in 1796, ⁵ and between 1797 and 1799 they were published in German, French, and Spanish. ⁶

Bern Dibner, "Giovanni Aldini," <u>DSB</u>, 1:107-108. See also Giovanni Aldini, <u>Joannis Aldini de animali electricitate dissertationes duae</u> (Bononiae: Instituti Scientiarium, 1794).

Kurt R. Bierman, "Friedrich Wilhelm Heinrich Alexander Von Humboldt," DSB, 6:549-555.

⁵Procés-verbaux de l'Institut National 1(21 brumaire an.5):126. Humboldt's collected works were presented to the Institut National 26 prairial an 7. <u>Ibid.</u>, 1:587.

[&]quot;See Julius Löwenburg, Alexander Von Humboldt: Bibliographische
Ubersicht seiner Werke, Schriften und zerstreuten Abhandlungen.
Unveränderter Neudruck dieses Tiels aus dem 1872 erschienenen Werk
Alexander von Humboldt. Eine wissenschaftliche Biographie, herausgegeben von Karl Bruhns (Stuttgart: F. A. Brockhaus, 1960), p. 6,
no. 25, 29, 30 and p. 7, no. 42, 43, 44, 45, 46, 47. As Kurt R. Biermann
has pointed out in the DSB, v. 6, p. 554, this bibliography is not complete. A summary of Humboldt's experiments also appeared in Journal de
physique. See Alexander Von Humboldt, "De l'irritabilité de la fibre
nerveuse et musculaire; par Van Humboldt," Journal de physique 46(an 61798):465-474 and "Suite des expériences sur l'irritation de la fibre
nerveuse et musculaire; par Frédéric Alexandre Van-Humboldt," Journal
de physique 47(an 6-1798):65-75, 189-197, 310-313 (this third part has
"Von" instead of "Van" in title).

Humboldt, with what might be considered disarming frankness, if it had not been such a prevalent tactic of his time, wrote in his discussion of Volta's theory, "Il sera bien agréable pour moi d'exposer ici cette théorie dans toute sa simplicité. . . . je l'ai regardée moimême, assez long-temps comme satisfaisante." However, according to Humboldt, his "nouvelles expériences" had forced him to change his mind. One of the essential differences that he found between electricity and galvanism was in the substances that would conduct them. Although many substances would conduct both,

les conducteurs électriques les plus parfaits, comme les os, la flamme, l'air raréfié, sont isolants pour le fluide galvanique. On peut donc regarder comme certain que l'électricité et le galvanisme ne sont point identiques.

Moreover, Humboldt noted the galvanic fluid could not pass across severed muscles, while electricity could pass through all substances (including severed muscles) except glass, which stopped the electric current but not the electric action. 10

Although he rejected the contact theory of Volta and in general adopted Galvani and Aldini's concept of animal electricity,

Frederich Wilhelm Heinrich Alexander von Humboldt," <u>Expériences</u> sur le galvanisme, et en général sur l'irritation des fibres musculaires et nerveuses, trans. J. Fr. N. Jadelot (Paris: Chez J. F. Fuchs, An 7-1799), p. 368. "It would be very easy for me to advocate this theory in all its simplicity . . . For a rather long time I myself have regarded it as satisfying."

^{8&}lt;sub>Ibid</sub>.

^{9 &}lt;u>Ibid.</u>, p. 443. "the most perfect conductors of electricity, such as ice, flame, rarified air, are isolators of the galvanic fluid. One can therefore regard as certain that electricity and galvanism are not identical."

^{10 &}lt;u>Ibid</u>., pp. 478-479. Humboldt refers to induction here.

Humboldt did propose major modifications in Galvani's theory. He explained similarities in galvanic and electrical phenomena by appealing to the "liaison" of galvanic phenomena with those originating from other causes.

That is, he conceived of "les fluides galvanique, électrique, et magnétique" as having "beaucoup de rapports entr'eux, et ne diffèrent-ils que comme le sang, le lait, et le suc des plantes, par exemple, diffèrent les uns des autres.

"12

One of the most important of these relationships, according to Humboldt, was between galvanic and chemical phenomena. Citing the experiments of Edward Ash (1764-1829) and of Giovanni Valentino Mattia Fabbroni (1752-1822), Humboldt discussed at length the chemical phenomena associated with galvanism, the most important being the decomposition of water by a galvanic chain. Repeating the experiments of Ash, or "Asch" as Humboldt called him, he noted that whenever one placed wet zinc on silver for four or five hours, the water gave sensible indications of decomposition, including the occasional evolution of bubbles and the oxidation of the metal. 13 Like Ash, Humboldt interpreted these phenomena

¹¹ Ibid., p. 456.

^{12 &}lt;u>Ibid.</u>, p. 454. "Many relationships between them, and perhaps they differ as blood, milk, and the sap of plants, for example, differ among themselves."

^{13 &}lt;u>Ibid.</u>, pp. 463, 470. Humboldt only referred to Ash as a doctor who had written him from Oxford. Mottelay, A <u>Bibliographical</u> <u>History of Electricity</u>, p. 337 note, dated the letter as 10 April 1796. Ash's experiments were little known until Humboldt published discussions of them. See <u>Poggendorff</u>, 1:70. Although George Sarton, "The Discovery of the Electric Cell (1800), with Fascimile reproduction (no. XI) of Alexander Volta's Memoir, 'On the Electricity Excited by the Contact of Conducting Substances of Different Kinds,' (Philosophical Transactions of the Royal Society, London, 1800, pp. 403-431, 1 pl.) "<u>Isis</u> 15 (1931): 125 identified Ash as Dr. John Ash (1723-1798), Edward's uncle, a letter written by Ash in 1800 (or after John Ash's death) indicates that the Ash in question was probably Edward. <u>Infra</u>, p. 261.

in terms of the decomposition of water. He wrote: "On peut croire, par analogie avec d'autres phénomènes, que ces bulles sont du gaz hydrogène qui se dégage de 1'eau décomposée."

Humboldt collected the gas produced by the galvanic decomposition of water, but he could not obtain a positive chemical test for hydrogen. He explained this failure by suggesting that too small an amount of hydrogen had been produced to obtain a positive test for hydrogen and by assuming that the small amount of hydrogen produced was inseparably mixed with azote. Despite his inability to demonstrate conclusively that hydrogen was produced in his experiment, Humboldt still believed in the relationship of chemical and galvanic phenomena. He considered chemical phenomena to play a key role in the maintenance of the equilibrium of the galvanic fluid in living bodies. Humboldt wrote of this relationship:

Je regarde comme prouvé, que les organes contiennent un fluide particulier tant qu'ils sont excitables, que dans l'état naturel des muscles et des nerfs, il s'y trouve constamment, accumulé, et qu'on peut considérer ces organes comme inégalement charge's de ce fluide . . . Il se fait continuellement, dans les nerfs et dans les muscles, des décompositions et des combinaisons nouvelles; et comme le procédé chimique de vîtalité est modifié dans chacun de ces organes . . , on conçoit qu'il doit se faire à chaque instant, une répartition plus ou moins inégale du fluide galvanique. . . .15

^{14 &}lt;u>Ibid.</u>, pp. 472-473. "One can believe, by analogy with other phenomena, that these bubbles are hydrogen gas which is given off by the decomposition of water."

^{15&}lt;u>Ibid</u>., pp. 395-396. "I regard as proven, that the organs contain a particular fluid while they are excitable, that in the natural state of muscles and nerves, it is found constantly accumulated, and that one can consider these organs as inequally charged with this fluid . . . Decompositions and new combinations continually occur in the nerves and muscles; and as the chemical process of vitality is modified

Even though he did not conceive of galvanism as originating in chemical causes, Humboldt accepted the importance of the ability of chemical, physical (for example, temperature), and electrical changes to modify the transmission of the galvanic fluid. 16

Humboldt was aware that the chemical phenomena associated with galvanism were extremely similar to those associated with electricity. Indeed, he based his argument of the <u>liaison</u> of electricity, galvanism, and magnetism on their similar effects. After discussing the chemical effects of electricity, including the decomposition of water or the production of hydrogen from water by the passage of an electric discharge through it (which he attributed to Van Marum), ¹⁷ the acid-like effect of electricity on tournesol, its acid taste, its ability to form nitric acid by igniting mixtures of azote and oxygen, its odor of "phosphore," he summarized:

Dans les réflexions précédentes on a rassemblé tout ce que nous pouvons nous flatter de savoir sur les propriétés chimiques et sur les parties constituantes du fluide électrique, et nous voyons que l'on a cru apercevoir dans ce fluide bien des substances qui appartiennent aux milieux environnants, et qui en sont seulement séparées par l'électricité. Il en résulte qu'on peut la considérer comme étant une substance gazeuse, et comme celle de toutes ces substances qui contient le plus de calorique. 18

in each of these organs . . . , one imagines that there should be in each instant, a more or less inequal distribution of the galvanic fluid."

^{16&}lt;sub>Ibid</sub>., pp. 456, 466.

¹⁷ Ibid., p. 528, note 123.

¹⁸ Tbid., p. 450. "All that we can flatter ourselves as knowing on the chemical properties and constituent parts of the electric fluid has been gathered together in the preceding reflections, and we see that many substances that belong to surrounding mediums and which are separated solely by electricity have been thought to be perceived in this fluid. As

It was from the chemical effects of electricity that Humboldt drew another demonstration of the separate identities of galvanism and electricity. Appealing to the experiments and views of Deluc, Gren, Lichtenberg, and Wilhelm August Lampadius (1772-1842), Humboldt described electricity as a compound of which only one constituent was known. The galvanic fluid, on the other hand, was a simple fluid seeming "avoir plus de rapport avec le calorique, que le fluide électrique." Thus Humboldt not only upheld Galvani's theory of animal electricity and rejected Volta's contact theory, but, in addition, he appealed to the chemical effects of both electricity and galvanism to make his point. He was not the first to examine and discuss chemical phenomena in the study of galvanism, but he was one of the first well-known figures to do so.

Those who adopted Volta's ideas or ideas similar to Volta's but who were less influential and less vocal on the matter included Cavallo, Erasmus Darwin (1731-1802), and William Charles Wells (1757-1817). Just as Humboldt added to and modified Galvani's theory of animal electricity, those agreeing with Volta espoused their own version of Volta's theories. Darwin in his Zoonomia discussed galvanic phenomena as if they were electrical and denied that "the experiments . . . lately published by Galvani, Volta, and others, to shew a similitude between the spirit of animation, which contracts the muscular fibres, and the electric fluid"

a result one can consider it as being a gaseous substance, and as the one of all these substances (gases) that contains the most caloric."

 $^{^{19}\}underline{\text{Lbid}}.,~\text{p. 451.}$ "to have more relation with caloric than [with] the electric fluid."

In 1795, in the fourth edition of his <u>Complete Treatise</u>,

Cavallo reported that he could not confirm, even with a doubler (a
device constructed by Abraham Bennet (1750-1799) for the augmentation
of weak electrical charges) that the galvanic fluid was electrical in
nature. ²² In a most objective manner, he reported the experiments and
theories of both Galvani and Volta, noting the many similarities between
the galvanic and electric fluids and the exceptions to these similarities. ²³ Finally, Cavallo admitted that electricity could be produced by
the contact of two metals, but that even this fact did not conclusively
demonstrate that galvanism was electricity produced by the contact of
conductors. ²⁴

²⁰ Erasmus Darwin, Zoonomia; or, the Laws of Organic Life, 2 vols. (Dublin, for P. Byrne and W. Jones, 1794-1796), 1:68.

²¹Ibid., 1:128.

²² Cavallo, Complete Treatise on Electricity, 4th ed. (1795), 3:29. A doubler consists of three brass plates; the first is charged by the source in need of augmentation, the second is charged by induction from the first, and the third by induction from the second. Then plates one and three which contain an equal and like charge, are placed together near plate two. When plate two is grounded and plate three is removed, the charge on plate one has been doubled. After the process has been repeated several times weak charges are strong enough to be detected by an electroscope or even to produce visible sparks. Nicholson invented an improved doubler. For further information see Mottelay, Bibliographical History of Electricity, pp. 290, 336 and George B. Prescott, Electricity and the Electric Telegraph (New York: D. Appleton & Co., 1877), pp. 20-22.

²³Cavallo, <u>Complete Treatise on Electricity</u>, 4th ed. (1795), 3:65.

²⁴<u>Tbid</u>., pp. 111, 134, 137-138.

William Charles Wells, perhaps best known for his writings on dew, was one of the many British loyalists forced to leave America by the American Revolution. He first had been forced to leave Charleston because he had refused to sign an "Association." or a pledge to resist the crown. Later Wells returned, only to flee with the withdrawal of the British Army. He again returned and was arrested. After being released from jail, he left Charleston for the last time in 1783 and emigrated to London where he became a less than successful surgeon. 25 In March of 1795 he read a paper to the Royal Society agreeing with Volta on the electrical origin of galvanic phenomena. However, Wells rejected Volta's contact theory and suggested instead the only explanation that he believed could be right, that the electricity in galvanic phenomena was not produced by the contact of two conductors, but by the friction of the conductors upon their contact. 26 Thus, those who favored or shared Volta's views also added modifications or qualifications that did little to enhance his case.

In 1796, the Institut National heard a memoir on galvanism written by Humboldt and then voted to form a commission to study and

²⁵ William Charles Wells, Two Essays: One Upon Single Vision with Two Eyes; the Other on Dew. A Letter to the Right Hon. Lloyd, Lord Kenyon and an Account of a Female of the White Race of Mankind, Part of Whose Skin Resembles that of a Negro; with Some Observations on the Causes of the Differences in Colour and Form Between the White and Negro Races of Men. By the Late William Charles Wells, with a Memoir of his Life Written by Himself (London: Archibald Constable and Co. et al., 1818), pp. vii-xiv. Wells wrote the "memoir of his life" on his death-bed.

²⁶Wells, "Observations on the Influence, which Incites the Muscles of Animals to Contract in Mr. Galvani's Experiments. By William Charles Wells. M.D. F.R.S.," Philosophical Transactions of the Royal Society of London 85(1795):246-262.

report on galvanic phenomena. The commission initially consisted of Raphael-Bienvenu Sabatier (1773-1811), Charles-Augustin Coulomb (1736-1806), Jacques-Alexandre-César Charles (1746-1823), Nicolas-Louis Vauquelin (1763-1829), Antoine-François Fourcroy (1755-1809), Jean-Noel Hallé (1754-1822), and Philippe-Jean Pelletan (1747-1829). 27 Guyton de Morveau became an adjoint to the commission nine days after its formation. 28 The report of the commission, 29 as well as the accounts read to the Institut National of the galvanic experiments conducted by Galvani, 30 Berthollet, 31 Humboldt, 32 and Aldini, 33 either supported or verified Galvani's explanation of galvanic phenomena.

At a time when the idea of animal electricity was widely preferred over Volta's interpretation of galvanic phenomena, Volta announced what he considered to be a decisive proof that galvanic phenomena were electrical in nature. In a letter to Sir Joseph Banks (1743-1820), president of the Royal Society, Volta described his "pile" of alternating metal discs, each set separated from the other by moistened cloth. Volta believed that he had demonstrated with the pile that animal

407.

^{27 &}lt;u>Procès-Verbaux de l'Institut National</u> 1(Seance du 21 brumaire, an 5):126.

²⁸<u>Ibid</u>., 1(1 frimaire, an 5):13 **6**

²⁹<u>Ibid</u>., 1(6, 11, 21, 26 prairial, an 6):399, 400, 403, 406,

^{30&}lt;sub>Ibid.</sub>, 1(21 brumaire, an 6):295.

^{31 &}lt;u>Ibid</u>., 1(6 pluviose, an 5):163.

^{32 &}lt;u>Ibid.</u>, 1(1 prairial, an 6):397.

³³<u>Ibid</u>., 1(16 vendemiare, an 7):476 and 1(21 pluviose, an 7): 522.

tissue was not a necessary ingredient for the production of galvanic electricity and that it was indeed a phenomenon dependent upon the contact of two different conductors. ³⁴ In the words of Nicholson, one of the first Englishmen to repeat Volta's experiment, Volta had "added a discovery which must for ever remove the doubt whether galvanism be an electrical phenomenon. ³⁵ Nicholson and Sir Anthony Carlisle (1768-1840) had been the first in England to repeat Volta's experiments. In fact, Banks had shown Volta's letter to Carlisle in April 1800. Carlisle in turn had shown it to Nicholson, and together, Nicholson and Carlisle had repeated Volta's experiments prior to their being read at the Royal Society on June 26. ³⁶ Although Nicholson believed Volta's experiments impressive, he expressed surprise that Volta omitted any reference to the "chemical phenomena of galvanism." That is, after the contacts to Volta's pile were

made sure by placing a drop of water upon the upper plate, Mr. Carlisle observed a disengagement of gas round the touching

³⁴Alessandro Volta, "On the Electricity Excited By the Mere
Contact of Conducting Substances of Different Kinds. In a Letter From
Mr. Alexander Volta, F.R.S. Professor of Natural Philosophy in the University of Pavia, to the Rt. Hon. Sir Joseph Banks, Bart. K.B.P.R.S.,"
Philosophical Transactions 90(1800):403-431. See also George Sarton,
"The Discovery of the Electric Cell," Isis 15(1931):124-157.

³⁵ William Nicholson, "Account of the New Electrical or Galvanic Apparatus of Sig. Alex. Volta, and Experiments Performed With the Same.--W. N.," <u>Nicholson's Journal</u> 4(1800):181.

 $[\]frac{36}{\text{Ibid.}}$ See also "Royal Institution," The Morning Chronicle, Friday, 30 May 1800.

³⁷Nicholson, "An Account of the New Apparatus of Volta," p. 181.

wire. This gas, though very minute in quantity, evidently seemed to me to have the smell afforded by hydrogen This with some other facts, led me to propose to break the circuit by the substitution of a tube of water between the two wires. 38

So began a series of experiments with which Nicholson would announce to the world that the galvanic fluid, like electricity, could generate hydrogen and oxygen from water. 39 Since this event served to further Volta's argument that galvanic phenomena were electrical in nature, one might be tempted to share Nicholson's surprise that Volta had not mentioned it. One might even suspect that Volta had not noticed it. Why did Nicholson and Carlisle see and mention this phenomenon when Volta had not? There is little in Carlisle's background that would provide an answer, but in the case of Nicholson one can see that the "discovery" of the galvanic decomposition of water was based on a prior belief that electricity decomposed water and that galvanism was electricity. Nicholson knew of the electrical decomposition of water through his editorship of A Journal of Natural Philosophy, Chemistry, and the Arts, and, according to his own Chemical Dictionary, he accepted it as a fact. 40 Through his editorship Nicholson was also aware that Volta had identified galvanic phenomena as being electrical in nature. In an article on the torpedo, a popular example of animal electricity, Nicholson had chosen to explain the shock of the torpedo in terms of one of Volta's inventions, the electrophore.

³⁸ Ibid., p. 182. Italics are mine.

 $^{^{39}\}mathrm{Humboldt}$ had only discussed the production of hydrogen from water.

⁴⁰Supra, pp. 145, 149-150, 170.

⁴¹Nicholson, "Observations on the Electrophore, Tending to

Finally, Nicholson had been influenced by his knowledge of the works of Fabbroni, who, beginning in 1792, had argued that galvanic phenomena were chemical phenomena independent of either animal electricity or electricity. Fabbroni had initially presented this view in a memoir read to the Accademia dei Georgofili of Florence in 1792, 42 but the idea was little known until 1799 when a second memoir by Fabbroni was published in Journal de physique. 43 In it, Fabbroni attributed the action of two metals upon animal tissue to the "phénomène de Sulzer." As Fabbroni pointed out, Johann Georg Sulzer (1720-1799) had discussed the action of two metals applied to the tongue in his Theorie des plaisirs, published in 1767. 44 Fabbroni was convinced that it was the chemical action, the "oxidation progressive," evoked by the contact of two metals that accounted for galvanic phenomena. He wrote:

Galvani, Aldini, Volta, et d'autres physiciens également habiles . . . n'ayant pas présent que l'action chimique s'exerce avec la promptitude de l'éclair; surpris de celle avec laquelle ces deux métaux différens font sentir leurs effets sur la fibre animale, crurent qu'on ne pouvoit les attribuer qu'au fluide électrique. La transmission du galvinisme [sic] à distance et par chaîne, favorisoit leur idée, qui fut ensuite généralement

Explain the Means by Which the Torpedo and Other Fish Communicate the Electric Shock," Nicholson's Journal 1(1797):355-358.

⁴² Mario Gliozzi, "Giovanni Valentino Mattia Fabbroni", DSB, 4:503.

⁴³ Giovanni Valentino Mattia Fabbroni, "Sur 1'action chimique des différens métaux entr'eux, à la température commune de 1'atmosphère, et sur 1'explication de quelques phénomènes galvaniques," Journal de physique, de chimie, d'histoire naturelle et des arts, 49 (1799 or an 8): 348. (Title page reads an 7, article an 8.) This journal is a continuation of Observations sur la physique. After 1794, Observations sur la physique was published under this title. Volumes beginning in 1794 will hereinafter be referred to as Journal de physique.

^{44&}lt;sub>Ibid</sub>.

reçue, malgré les objections très-fortes qu'on pouvoit opposer dans quelques cas, au moins, à leur système. On a observé, à la vérité, quelques signes d'électricité lorsqu'on sépare deux métaux qu'on avoit mis auparavant en contact: mais on sait trèsbien que même plusieurs opérations chimiques sont constamment accompagnées par un <u>disequilibre</u> de feu électrique, et par conséquent par des marques sensibles d'électricité. . Je ne prétends pas exclure toute influence electrique dans les faits prodigieux du galvanisme; je veux prouver seulement que ce principe n'a point de part au phénomène de Sultzer, et que plusieurs autres faits analogues dérivent de la même source.45

Thus Fabbroni attributed the ultimate cause of galvanic phenomena to chemical action. His views on the matter were not the same as Volta's; in fact, Fabbroni had denied that electricity was the stimulus in galvanic phenomena. To some extent, his explanation supported Volta over Galvani in that Fabbroni associated galvanic phenomena with electricity by admitting that the chemical action of the two metals produced electrical side effects. Among the other examples of chemical phenomena generating electricity that he mentioned was electrification resulting from the cooling of molten chocolate. Fabbroni's explanation of the chemical origin of galvanic phenomena could easily appeal to those

⁴⁵Fabbroni, "Sur l'action chimique," p. 350. "Galvani, Aldini, Volta, and other equally skillful physicists not being aware that chemical action is exerted with the speed of lightning; [being] surprised at the speed which these two different metals make their effects felt on animal fiber, believed that one could only attribute them to the electric fluid. The transmission of galvanism at a distance and by chain, favored their idea, which was generally admitted, despite very strong objections which one could oppose in at least a few cases to their system. In truth, a few signs of electricity have been observed when one separates two metals that one had previously put in contact; but, one knows very well that likewise several chemical operations are constantly accompanied by a dis-equilibrium of the electric fire, and consequently by sensible signs of electricity. . . . I do not pretend to exclude all electric influence in the prodigeous facts of galvanism; I want only to prove that this principle is no more than part of the phenomena of Sulzer, and that several other analogous facts derive from the same source."

who accepted the new chemistry because his explanations were based on oxidation theory.

Il me parut donc qu'une action chimique avoit eu lieu d'une manière évidente, et qu'il ne falloit pas chercher ailleurs la nature du nouveau stimulus que dans l'expérience de Sultzer, on appelloit galvanisme. C'étoit manifestement une combustion, une oxidation du métal. Le principe stimulant pouvoit donc être, ou le calorique qui se dégage; ou l'oxigène qui passe à des combinaisions nouvelles. . . . 46

Nicholson's <u>Journal</u> carried accounts of Fabbroni's theories in October of 1799, translated from the <u>Bulletin des sciences sur la</u>

<u>Société Philomatique de Paris</u>, ⁴⁷ and again in June of 1800, translated from the <u>Journal de physique</u> article of 1799. ⁴⁸ Although Nicholson did not make editorial comment on these articles, he did mention Fabbroni in his announcement of the decomposition of water by the galvanic pile of July 1800.

Thus far I have followed this able philosopher [Volta]; . . . But I cannot here look back without some surprize, and observe that the chemical phenomena of galvanism, which has been much so insisted on by Fabbroni, more especially the rapid oxidation of the zinc should constitute no part of his numerous observations.

⁴⁶ Ibid., p. 351. "It appeared to me therefore that a chemical action had taken place in an evident manner, and that it was not necessary to seek farther into the nature of the new stimulus, that is called galvanism, than in the experiment of Sultzer. It was manifestly a combusion, an oxidation of metal. The stimulating principle therefore could have been either the caloric that is given off; or the oxygen that passes to new combinations. . . ."

⁴⁷ Fabbroni, "On the Chemical Action of Different Metals on Each Other at the Common Temperature of the Atmosphere by Cit. Fabroni,"

Nicholson's Journal 3(1799):308-310.

⁴⁸ Fabbroni, "On the Chemical Action of the Different Metals upon Each Other at the Common Temperature of the Atmosphere, and upon the Explanation of Certain Galavanic Phenomena. By M. Fabbroni," Nicholson's Journal 4(1800):120-127.

⁴⁹ Nicholson, "Account of the new Electrical or Galvanic Apparatus of Sig. Alex. Volta," <u>Nicholson's Journal</u> 4(1800):181.

In summary, Nicholson saw and reported the galvanic decomposition of water because he was knowledgeable about and because he believed in the following concepts:

- The electrical decomposition of water into hydrogen and oxygen.
- Volta's theory that galvanic phenomena are electrical in in nature.
- Fabbroni's theory that galvanic phenomena were chemical in origin.

Therefore, the galvanic decomposition of water fit perfectly into Nicholson's theoretical outlook. In the debate between the partisans of the phlogiston theory and the proponents of Lavoisier's new chemical theory, natural philosophers had assumed that either electricity materially entered into chemical combinations, or that it did not. If they assumed the latter, they usually accepted the electrical decomposition of water as a crucial instance indicating the truth of Lavoisier's theory. If they assumed the former, they usually viewed hydrogen and oxygen as compounds of water and a material substance provided by electricity. Nicholson and Carlisle shifted this debate by assuming that electricity did decompose water and using the Voltaic or galvanic production of hydrogen and oxygen from water as a crucial instance that demonstrated the electrical nature of galvanism.

However, something occurred in the galvanic decomposition of water that did not concide with Nicholson's theoretical expectations. Nicholson and Carlisle produced a phenomenon that, unexplained, might weaken their assumption that water was decomposed by the Voltaic cell.

Using Nicholson's improved doubler to check a pile of silver crowns alternated with zinc discs, Nicholson and Carlisle determined the charge of each end of the pile," the silver end . . . in the minus, and the zinc end in the plus state." They passed the discharge from this pile through a glass tube, half an inch in diameter, filled with water and corked on each end with a brass wire inserted through each cork. When the two wires were one and three quarter inches apart, Nicholson and Carlisle obtained a stream of bubbles from the lower wire while the upper wire "became tarnished, first deep orange, and then black." When they turned the tube over, the bubbles still came from the lower wire! The new upper wire which had before been the site of the evolution of bubbles became tarnished. Nicholson and Carlisle then reversed the pile. The evolution of gas always came from the silver, or minus side.

We had been led by our reasoning on the first appearance of hydrogen to expect a decomposition of the water; but it was with no little surprize that we found the hydrogen extricated at the contact with one wire, while the oxigen fixed itself in combination with the other wire at the distance of almost two inches. This new fact still remains to be explained, and seems to point at some general law of the agency of electricity in chemical operations. As the distance between the wires formed a striking feature in this result, it became desirable to ascertain whether it would take place to greater distances from the general tenor or experiments, it appears to be established, that this decomposition is more effectual the less the distance between the wires 52

⁵⁰Ibid., p. 182.

⁵¹<u>Ibid</u>., p. 183.

^{52&}lt;sub>Ibid</sub>.

In the course of their continued experiments, Nicholson and Carlisle tried the same experiment with non-oxidizable wires of platina and obtained bubbles from both wires. "It was natural to conjecture that the larger stream from the silver side was hydrogen, and the smaller oxigen." Working on this assumption, they attempted to obtain each gas separately. After thirteen hours of the generation of gas, Nicholson reported "72 grains by the gas from the zinc side, and 142 grains from the gas from the silver side." The total of 1.17 cubic inches was "nearly the proportions in bulk, of what are stated to be the component parts of water." However, Nicholson admitted imperfections in the apparatus and suggested that the experiment could better be repeated in closed vessels. 54

Carlisle had also repeated the experiment using tincture of litmus instead of water. He found that

The oxidating wire, namely, from the zinc side, . . . lowest in the tube; . . . changed the tincture red in about ten minutes as high as the extremity of the wire. The other portion remained blue 55

He assumed that "either an acid was formed, or that a portion of the oxigen combined with the litmus, so as produce the effect of an acid." 56

Although the galvanic decomposition of water and the effect of the galvanic fluid on litmus tincture were analogous to the effects of the electric discharge on water and, according to some investigators;

⁵³Ibi<u>d</u>., p. 185.

⁵⁴Ibid., p. 186.

⁵⁵<u>Ibid., p. 183.</u>

⁵⁶Ibid.

analogous to its effects on litmus solution; the appearance of hydrogen at only one wire and of oxygen at only the other wire could not be explained or predicted by the new chemical system of Lavoisier. Moreover, the separate production of gases had not been reported in accounts of the electrical decomposition of water. Perhaps the difficulty of decomposing water electrically without mishap either obscured these phenomena or made them difficult to perceive prior to the introduction of the voltaic pile, but it is just as likely that they were unobserved or ignored because nothing in the new chemical theory suggested the possibility of such pherodical pherodical theory suggested the possibility of such pherodical pherodical theory suggested the possibility of such pherodical pherodic

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⁵⁷Supra, p. 164.

collection and testing of each gas produced, a development the new era in chemical investigation.

Nicholson and Carlisle's experiments were repeated as publicized even before they were read to the Royal Society on 1800. According to an account published in the Morning Chron May 30, 1800, Dr. Thomas Garnett (1766-1802) of the Royal Ins

in his Lecture on the composition and decomposition of wa a curious experiment, . . An account of the experiment lately received by the President of the Royal Society fro Volta; it was repeated by Mr. Nicholson and Mr. Carlisle days ago, and on Wednesday [the 28th] exhibited by Dr. Ga

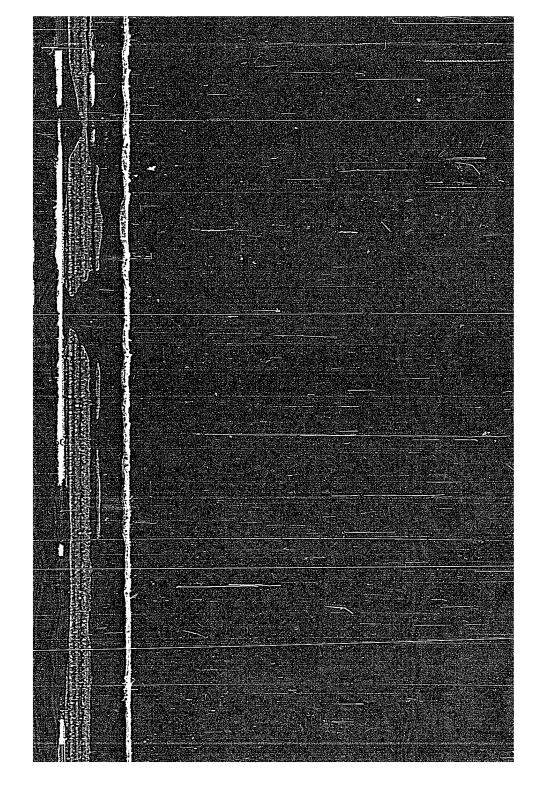
The account of Garnett's experimental demonstration went on the galvanic decomposition of water. The report suggested the discovery "may throw light on several phenomena of the Animal as well as Chemistry and Electricity." 59

Garnett's lecture and repetition of the galvanic dec of water were given in his public lectures for the scientific the Royal Institution which met at 8 P.M. Monday, Wednesday, According to some accounts of the history of the Royal Instit Garnett initially credited the discovery of the Voltaic pile French, and as a result, Joseph Banks, one of the trustees of

^{58&}quot;Royal Institution," The Morning Chronicle, Friday 1800.

⁵⁹Ibid.

or British Register 9(1 July 1800):573. 1,307 members and gut the right to attend Garnett's lectures, but the lecture room See "An Account of the Origin and Progress of the Royal Inst: Great Britain," Monthly Magazine 9(1 June 1800):478.



analogous to its effects on litmus solution; the appearance of hydrogen at only one wire and of oxygen at only the other wire could not be explained or predicted by the new chemical system of Lavoisier. Moreover, the separate production of gases had not been reported in accounts of the electrical decomposition of water. Perhaps the difficulty of decomposing water electrically without mishap either obscured these phenomena or made them difficult to perceive prior to the introduction of the voltaic pile, but it is just as likely that they were unobserved or ignored because nothing in the new chemical theory suggested the possibility of such phenomena.

Pearson did report the appearance of two streams of bubbles, but he did not speculate that they might be different gases. Instead, he assumed that the electric discharge was the most intense at the points where the bubbles appeared. 57

The passage of the galvanic influence through water, unlike the passage of an electric discharge, did not present the experimental difficulties that obscured the phenomena connected with the decomposition of water. Moreover, the decomposition of water was more widely accepted as a fact in 1800 than in 1789. A primary objection made by phlogiston theory adherents against the electrical decomposition of water had centered around the difficulty of testing singly the gases produced by the passage of the electric discharge through water. As Nicholson pointed out, the phenomena of galvanic decomposition of water allowed the separate

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collection and testing of each gas produced, a development that opened a new era in chemical investigation.

Nicholson and Carlisle's experiments were repeated and publicized even before they were read to the Royal Society on 26 June 1800. According to an account published in the Morning Chronicle of May 30, 1800, Dr. Thomas Garnett (1766-1802) of the Royal Institution

in his Lecture on the composition and decomposition of Water, made a curious experiment, . . An account of the experiment had been lately received by the President of the Royal Society from Signor Volta; it was repeated by Mr. Nicholson and Mr. Carlisle a few 58 days ago, and on Wednesday [the 28th] exhibited by Dr. Garnett.

The account of Garnett's experimental demonstration went on to describe the galvanic decomposition of water. The report suggested that the discovery "may throw light on several phenomena of the Animal Economy, as well as Chemistry and Electricity." ⁵⁹

Garnett's lecture and repetition of the galvanic decomposition of water were given in his public lectures for the scientific course of the Royal Institution which met at 8 P.M. Monday, Wednesday, and Friday. 60 According to some accounts of the history of the Royal Institution, Garnett initially credited the discovery of the Voltaic pile to the French, and as a result, Joseph Banks, one of the trustees of the Royal

⁵⁸"Royal Institution," <u>The Morning Chronicle</u>, Friday, 30 May 1800.

^{59&}lt;sub>Ibid</sub>.

^{60&}quot;Royal Institution of Great Britain," The Monthly Magazine; or British Register 9(1 July 1800):573. 1,307 members and guests had the right to attend Garnett's lectures, but the lecture room held only 300 See "An Account of the Origin and Progress of the Royal Institution of Great Britain," Monthly Magazine 9(1 June 1800):478.

Institution, asked its director, Benjamin Thompson, Count Rumford, (1753-1814), to instruct Garnett to correct his error. 61

In England, many of the early articles on the Voltaic pile continued to be published in <u>Nicholson's Journal</u>. An article on the subject by William Cruickshank of Woolwich (d.ca. 1811) was published in the same issue of the journal as Nicholson's article. Although his article was published simultaneously with Nicholson's, Cruickshank describes experiments performed after Nicholson and Carlisle's. He briefly referred to the similarities of the galvanic and electric fluids, saying:

I shall not give any particular account of the apparatus employed, being a pile, and not differing materially from that in use . . . When the machine was in full action, sparks, which were perfectly visible in the day time, could be taken at pleasure, by making a communication in the usual way . . .; the shock given at that time was very strong, and a gold leaf electrometer . . . was very sensibly affected: these circumstances, some of which I believe have been already ascertained by Messrs. Nicholson and Carlisle, shew the strong resemblance of this influence to electricity. 62

^{61&}lt;sub>K</sub>. D. C. Vernon, The Foundation and Early Years of the Royal Institution, reprinted from the Proceedings of the Royal Institution vol. 39, no. 179, 1963, p. 18, and Thomas Martin, "Presidental Address: Early Years at the Royal Institution," British Journal for the History of Science 2(1964):110. Martin quotes a letter from Rumford to Banks dated 29 May 1880 "I am very sorry to find, on making enquiry of Dr. Garnett, that your information was accurate respecting his having described the late discoveries of our friend Volta to the French." Martin also adds that Rumford wrote Banks on the 30th saying that Garnett would correct his mistake and that the wording of the correction would be submitted to Banks for approval. Because the Chronicle account of Garnett's experiments printed the same day mentions Volta and not the French, one might assume that Garnett had corrected his error prior to the 30th. Moreover, if the article was correct, Nicholson and Carlisle had performed their experiments only a few days earlier and Garnett had then repeated them on the 28th. He could not have been in error very long on the matter.

William Cruickshank, "Some Experiments and Observations on

Cruickshank may not have completely shared Nicholson's belief that the Voltaic pile demonstrated that the galvanic influence was electrical in nature, for he noted: "These gentlemen have likewise discovered that galvanism decomposes water with much greater facility than electricity, but with phenomena somewhat different." His article explored the "somewhat different" phenomena attendant to the passage of the galvanic influence through fluids, beginning with "common water."

Although both the conducting wires were actually silver,
Cruickshank designated them with reference to the two metal parts of the
pile. Thus he called the wire connected to the end of the pile terminating in silver the silver wire and the wire connected to the end terminating in zinc the zinc wire. In his experiment with common water, he noted
the production of bubbles and a white cloud "that gradually increased, and
assumed a darker colour, and at last became purple, or even black," at
the silver wire; while at the zinc wire only bubbles were produced. 64 He
repeated the experiment using tincture of litmus in distilled water and
then with tincture of Brazil wood in distilled water. In the first
experiment, the solution became red, just as in Nicholson and Carlisle's
experiments. 65 In the second experiment, Brazil-wood tincture turned
purple; this was the positive test for the presence of ammonia. He
believed that these experiments demonstrated

Galvanic Electricity. By Mr. W. Cruickshank of Woolwich. Communicated by the Author," <u>Nicholson's Journal</u> 4(1800):188. For a discussion of the role of <u>Nicholson's Journal</u> in the publication of the English research on the pile, see S. Lilley, "'Nicholson's Journal' (1797-1813)," <u>Annals of Science</u> 6(1948-1950):83-86.

^{63&}lt;u>Ibid</u>. 64<u>Ibid</u>.

^{65&}lt;sub>Ibid., pp. 188-189</sub>.

Cruickshank then tried the galvanic influence on a solution of lime-water and reported an olive colored cloud, "exactly resembling the precipitate of silver by lime-water."67 He assumed that since hydrogen gas reduces metal calxes, he could use the production of hydrogen from the passage of the galvanic influence through metallic solutions to produce pure oxygen. Using acetite of lead "to which an excess of acid was added to counteract the effects of the alkali" he obtained needles of lead at the silver wire and bubbles and corrosion at the zinc wire. 68 He got similar results with other solutions of metal. Sulphate of copper yielded copper metal while silver in nitrous acid yielded the "most beautiful precipitate" of silver. Although he had reported a little gas and considerable corrosion at the silver wire, none of these experiments produced the quantity of pure oxygen Cruickshank had expected. Asking "what became of the oxygene gas usually produced in these experiments?" he continued his account of his experiments on fluids. Both vinegar in distilled water and sulfuric acid precipitated silver at the silver wire. 69 Muriate of ammonia caused a black substance to be precipitated; Cruickshank thought it was luna cornea.

⁶⁶ Ibi<u>d</u>., p. 189.

^{67&}lt;sub>Ibid</sub>.

^{68&}lt;sub>Ibid.</sub>,

^{69&}lt;u>Ibid</u>., pp. 189-190.

Finally, he passed the galvanic influence through two tubes of water connected in series. At the silver wire in the first tube, bubbles were produced. The zinc wire in the first tube was corroded. The same wire, after it crossed into the second tube, produced bubbles, and the final wire (zinc) of the second tube, was also corroded. Cruickshank found that the results were the same if copper wires were used instead of silver. He wrote, "I make no doubt that a similar effect would be produced, if any number of tubes were connected in a similar manner, . . ."

He did not associate the corrosion with oxidation of the wire.

Other accounts of the Voltaic pile were published in July 1800. In the July 1 Monthly Magazine an account of the experiments performed by Dr. Garnett for the scientific course offered by the Royal Institution revealed that Garnett concluded his lecture by repeating "some curious experiments on galvanism, which had lately been made by Professor Volta. . . ."⁷¹

The same issue of the <u>Monthly Magazine</u> also carried a short description of the Voltaic pile and the information:

Mr. Carlisle has applied this apparatus to the decomposition of water; alcohol has likewise been decomposed by it: it affects the electrometer as common electricity does, and no doubt other coincidents will soon be discovered. 72

^{70 &}lt;u>Ibid</u>., pp. 190-191.

^{71&}quot;Royal Institution of Great Britain," The Monthly Magazine 9(1 July 1800):573.

^{72&}quot;Sixty Articles of Literary and Philosophical Intelligence,"
<u>Monthly Magazine</u> 9(1 July, 1800):586.

Among those sending experiments to <u>Nicholson's Journal</u> in 1800 was Henry Haldane (<u>f1</u>. 1800) who read an account of the history and effects of the pile in the <u>Morning Chronicle</u> of May 30, 1800, and became interested enough to construct his own pile and conduct his own experiments. His experiments were published with Nicholson's comments in the September issue of <u>Nicholson's Journal</u>. Haldane was interested primarily in the action of the pile itself rather than in its action on other substances. By placing the pile under an air pump, he found that the pile would not decompose water in the absence of air. Haldane also varied the composition of the pile noting that an arrangement of iron and silver gave off gas at the silver end and oxidized the iron end while an arrangement of zinc and iron gave off gas at the iron end and oxidized the zinc. 74

The results of Haldane's experiments with the pile contradicted the findings reported by Volta, Nicholson, Carlisle, and Cruickshank, in that Haldane could not produce any phenomena with it that he considered to be electrical. He reported that he was unable to produce sparks with the pile, and that using an electrometer, he was unable to detect that the pile had an electrical charge. In his comparison of the effects of the pile with the effects of electricity, he had inserted needles into each of his hands and connected these needles to the pile in order to

⁷³Henry Haldane and William Nicholson, "Experiments and Observations Made with the Newly Discovered Metallic Pile of Sig. Volta. By Lieut. Col. Henry Haldane. With Remarks by W. N.," Nicholson's Journal 4(1800):241.

^{74&}lt;u>Ibid</u>., p. 242.

form a galvanic circuit. According to Nicholson, Haldane reported that "a sharp irritation was felt at the wounded parts, with a convulsive sensation, extending to the shoulders, and even the neck." In "." Haldane's view, these results did not resemble the electric shock, because they were "more unpleasant, and of longer duration." Haldane's findings may have been affected by a theoretical bias that galvanism and electricity were not the same. 75

Nicholson's theoretical commitment to the electrical nature of galvanic action was at least as strong as Haldane's belief to the contrary. He sought to explain the inconsistencies between Haldane's results and his own and at the same time reaffirmed his belief that the phenomena that Haldane had described were electrical.

I cannot forbear adverting again to the novelty of the field of research in which I have thus ventured to speculate. We may reasonably hope that the discoveries to which this new exhibition of joint actions of chemistry and electricity may lead us, will shew other powers and energies of what is called the electrical fluid, and induce us to reject with gladness the imperfect theories afforded by our present knowledge of the subject.⁷⁶

Haldane continued his researches in August with an investigation of the internal construction of the Voltaic pile. Using piles composed of all the combinations of two metals possible from the following group, zinc, gold, silver, iron, copper, lead and mercury, he found that with zinc, "their powers of acting seemed to be in the order of iron, copper, lead, tin, and mercury" and "with iron the powers of these combinations, appeared to be in the order of mercury, gold, silver, copper, lead, and

^{75&}lt;sub>Тыд.</sub>

^{76&}lt;sub>Ibid., p. 245.</sub>

tin."⁷⁷ He reported that for the remaining permutations of lead, tin, copper, silver, and gold, the operation of the pile was feeble or imperceptible.⁷⁸ He measured the power of each combination by the amount of oxidation and by the amount of gas produced from water by the combination.

Haldane also sought to determine experimentally if the number or size of the pairs affected the power of the cell. He found that while greater power could be obtained with an increase in the number of pairs, the size of the pairs did not affect the power. In other experiments, Haldane examined the gases produced by the action of the Voltaic pile on water and continued his exploration of the relationship between the action of the pile and its ambient atmosphere. In the first one, he collected and ignited the gases produced by the galvanic decomposition of water and declared that by comparison his results were precisely the same as those from the ignition of hydrogen and oxygen. The experiments, using atmospheric air, oxygen, and azotic air, he found that the greatest galvanic activity occurred in oxygen. He wrote:

we may venture to agree in opinion with Cit. Fabroni (Phil. Journal, vol. III, p. 308) that the effects of galvanism depend on a chemical operation, and are produced principally by the attraction of oxygen from the atmosphere, and therefore, on the

⁷⁷Haldane, "Experiments made with the Metallic Pile of Signor Volta, Principally Directed to Ascertain the Powers of Different Metallic Bodies. By Lieut. Col. Henry Haldane," <u>Nicholson's Journal</u> 4(1800):315. This article, dated 3 August 1800, was not published until October 1800.

^{78&}lt;sub>Ibid.</sub>, pp. 315-317.

⁷⁹<u>Ibid</u>., p. 318.

present theory, the whole operation can be received only as a combustion. . $^{80}\,$

The August 1800 issue of Nicholson's Journal included a letter by William Henry (1774-1836) on the chemical action of galvanism. After repeating the experimental findings of Nicholson, Carlisle, and Cruickshank, and alluding to the experiments of Deiman and Pearson, Henry noted that he had little to add to their experiments. 81 He listed seven experiments in which he had passed the galvanic influence through concentrated sulfuric acid, pure and colorless nitric acid, muriatic acid, oxygenated muriatic acid, several gases, volatile alkali, and caustic vegetable alkali. 82 Although he could produce gases from fluids using the galvanic influence, Henry reported that he could not pass the galvanic influence through "aeriform bodies" and that "the deficiency of the property of transmission through gases limits considerably the use galvanic influence through a mixture of hydrogen and oxygen, through phosphorated hydrogen gas, and through a mixture of muriatic acid and oxygen gas. He noted that galvanism and electricity were dissimilar in their effect on these gases. Although he was disappointed by this result, because he had hoped to use galvanism to decompose and thus analyze muriatic acid, Henry did believe the galvanic influence would lead to the analysis of vegetable alkali.84

^{80&}lt;sub>Ibid</sub>., p. 319.

⁸¹ William Henry, "Experiments on the Chemical Effects of Galvanic Electricity," Nicholson's Journal 4(1800):224.

^{82&}lt;sub>Ibid.</sub>, pp. 224-225. 83_{Ibid.}, p. 225. 84_{Ibid.}, pp. 225-226.

In the September issue of <u>Nicholson's Journal</u> more of Cruickshank's experiments were published. He had continued his experiments wishing "to ascertain with some degree of precision, the nature and relative proportions of the gases obtained from water and other fluids" by the galvanic influence. ⁸⁵ He was able to obtain more gas from both ends of the cell by using gold wires and he determined the ratio of the two gases produced to be "nearly two parts hydrogen and one oxygen, mixed with a little azote, being nearly the proportions estimating by bulk, which are said to enter the composition of water."

Cruickshank had also focused his attention on Nicholson's assumption that hydrogen and oxygen were produced from different ends of the pile:

It has been supposed, although not proved by Mr. Nicholson, that the gas which escapes from the wire connected with the silver extremity of the pile is hydrogen, whilst that disengaged by the one connected with the zinc is oxygen gas. 87

He developed a new apparatus to test Nicholson's assumption consisting of a glass tube ten inches long and bent in the middle "until the legs form an accute angle resembling the letter V. . . ." Using this apparatus Cruickshank could and did obtain the gases produced at each wire separately. He determined "that the gas obtained from the silver wire was chiefly hydrogen gas, and that from the zinc wire, nearly pure oxygen." 88

⁸⁵ William Cruickshank, "Additional Remarks on Galvanic Electricity. By Mr. W. Cruckshank, Woolwich. Communicated by the Author," Nicholson's Journal 4(1800):254.

⁸⁶Ibid., p. 255.

^{87&}lt;sub>Ibid</sub>.

^{88&}lt;sub>Tbid</sub>.

Since he had been able to precipitate substances from their solutions in acids in his previous experiments, Cruickshank tried the same with solutions of lime. Using muriate of lime he obtained gas from the zinc side only. Instead of yielding a precipitation of lime, the solution turned yellow and smelled of acqua regia or oxy-muriated acid. Cruickshank interpreted these results by assuming the passage of the galvanic influence through muriate of lime formed oxy-muriatic acid or acqua regia, the only acid capable of dissolving gold. The dissolution of the gold wires would also account for the yellow color of the solution. Moreover, he reported that a yellow color and the smell of oxy-muriatic acid were produced only when he used gold or platina wires. Solumnarizing these experiments and his previously published experiments, Cruickshank listed six points, here paraphrased.

- 1. When the fluid operated on by the galavanic pile is pure water, hydrogen is always produced from the silver end of the pile, no matter what metal the conducting wire is.
- 2. When metallic solutions are used instead of water, the hydrogen produced at the silver wire "revives the metallic calx, and deposits it at the extremity of the wire in its pure metallic state
- When earthy solutions such as magnesia and argill are used,
 they are decomposed at the silver wire.
- 4. When the wire connected to zinc is gold or platina, oxygen, azote, and a little nitrous acid is evolved.

^{89&}lt;u>Ibid</u>., p. 256.

- 5. When the wire connected to the zinc is of an imperfect metal, the wire is oxidated and or dissolved and a little gas is evolved.
- 6. When the gases obtained from water with gold wire are ignited together, "the whole nearly disappears and forms water, with probably a little nitrous acid."⁹⁰

Although he believed that water must have been decomposed in some of his experiments, Cruickshank admitted that there was some difficulty in supporting such an explanation:

In reflecting on these experiments it would appear, that in some of them, the water must be decomposed; but how this can be effected, is by no means so easily explained. For example, it seems extremely mysterious how the oxygen should pass silently from the extremity of the silver wire to that of the zinc wire, and there make its appearance in the form of gas. It is to be observed likewise, that this effect takes place which ever way the wires are placed, and whatever bends may be interposed between their extremities, provided the distance be not too great.

However, Cruickshank did have an explanation of how it could be effected. He considered the simplest explanation

would be, to suppose that the galvanic influence (whatever it may be) is capable of existing in two states, that is, in an oxygenated and deoxygenated state. That when it passes from metals to fluids containing oxygen, it seizes their oxygen, and becomes oxygenated; but when it passes from the fluid to the metal again, it assumed its former state, and becomes deoxygenated.

Cruickshank's theory of the oxygenated and deoxygenated states of the galvanic fluid not only explained the galvanic decomposition of water, including the separation of the production of hydrogen and oxygen, but

⁹⁰<u>Ibid</u>., p. 257.

^{91&}lt;sub>Ib1d</sub>.

^{92&}lt;u>Ibid.</u>, pp. 257-258. See also T. A. Coutts, "William Cruickshank of Woolwich," <u>Annals of Science</u> 15(1959):121-129.

it also provided a mechanism for the transport and release of oxygen some distance from its separation from hydrogen. He found two further arguments for his theory: (1) Fluids that do not contain oxygen do not transmit the galvanic influence. (2) The pile itself exhibits an alternating oxidation and de-oxidation of its parts.⁹³

It was not until September that the other major independent philosophical journal in England, the Philosophical Magazine, began to publish detailed accounts of English experiments with the Voltaic pile. The Philosophical Magazine had published one of the earliest journal accounts of the discovery of the galvanic decomposition of water. However, this account, published in May 1800, mentioned only Carlisle's name in association with the discovery. Once the editors of the Philosophical Magazine learned of Nicholson's role in these experiments, "motives of delicacy" led them not "to give any further particulars till Mr. Nicholson himself . . . should first lay them before the public." Once Nicholson had done so in his own journal, the Philosophical Magazine published an account of the experiments of Nicholson, Carlisle, and Cruickshank which ended with a recommendation that the reader turn to Micholson's Journal for the accounts of the experiments of Henry, Haldane, and Humphrey Davy (1778-1829). The September issue of the

^{93&}lt;sub>Ibid., p. 258.</sub>

^{94&}quot;Intelligence and Miscellaneous Articles. Galvanism," Philosophical Magazine 6(1800):372.

^{95&}quot;Experiments in Galvanic Electricity, by Messrs. Nicholson, Carlisle, Cruickshank, & c.," <u>Philosophical Magazine</u> 7(1800):337.

^{96&}lt;sub>Ibid., p. 347.</sub>

<u>Philosophical Magazine</u> also carried an English translation of Volta's letter, which had been published originally in French in the <u>Philosophical Transactions</u>, and another article that illustrates the widespread interest in the Voltaic pile in England. The article was a letter from Henry Moyes (1749-1807), blind itinerant lecturer, to Maxwell Garthshore (1732-1812), M.D.,F.R.S. Moyes had lectured on natural philosophy in England and America and in 1783, Priestley, in a letter to Banks, commended him as an excellent lecturer.

With the aid of his nephew, William Nicol (f1. 1800), Moyes had built a pile and conducted experiments at his summer residence at Pittenween, Fifeshire. 98 Believing that "the Galvanic action of various fluids upon the whole or most of the oxydable metals, has lately opened a field of research, which seems well entitled to persisting attention," Moyes speculated that the action of the pile would probably lead to a new theory of earthquakes and he promised Gartshore a further account of his projected experiments on fluids. 100

One of the most systematic examinations and accounts of the effects of the Voltaic pile published in 1800 was by Humphry Davy,

⁹⁷ John Anthony Harrison, "Blind Henry Moyes, 'an Excellent Lecturer in Philosophy'," Annals of Science 13(1957):109-125. See also Banks Letters, p. 68 and Robert E. Schofield, The Lunar Society of Birmingham: A Social History of Provincial Science and Industry in Eighteenth-Century England (Oxford: Clarendon Press, 1963), p. 246.

^{98&}lt;sub>Henry</sub> Moyes, "Letter from Henry Moyes, M.D. to Maxwell Gartshore, M.D. Containing an Account of Some Interesting Experiments in Galvanic Electricity. Communicated by Dr. Garthshore," The Philosophical Magazine 7(1800):347-348.

^{99&}lt;u>Ibid., p. 349.</u>

^{100&}lt;u>Ibid</u>., pp. 348, 350.

Superintendent of Dr. Thomas Beddoes's (1760-1808) Pneumatic
Institution at Clifton. In 1800 Davy's only other chemical publications were accounts of his experiments on nitrous oxide 101 and his essays on heat and light. In his essays on heat and light he postulated that oxygen and light formed a compound, phosoxygen 102 a view that he had retracted by 1800. By July of 1800 Davy's attention had turned at least partially from nitrous oxide to galvanism. In a letter, dated 3 July to Davies Giddy (1767-1839), later known as Davies Gilbert, P.R.S., Davy referred to the experiments of Nicholson, Carlisle, and Cruickshank, remarking

We have been repeating the Galavanic experiments with success . . . An immense field of investigation seems opened by the discovery: may it be pursued so as to acquaint us with some of the laws of life! 103

An account of these experiments was published in the September issue of <u>Nicholson's Journal</u>. Davy used in his experiments a pile constructed for Dr. Beddoes that always contained at least 110 pairs of metallic plates. For the sake of convenience he adopted, in his discussion of the effects of the Voltaic pile, the nomenclature used by Cruickshank, designating the wire connected to the end of the pile terminating with a silver plate as the silver wire and the wire to the end terminating with a zinc plate as the zinc wire. He wrote that he was

^{101&}lt;sub>June</sub> Z. Fullmer, <u>Sir Humphry Davy's Published Works</u> (Cambridge, Massachusetts: Harvard University Press, 1969), pp. 27-30.

^{102&}lt;sub>Humphry</sub> Davy, <u>The Collected Works of Humphry Davy</u>, ed. John Davy, 9 vols. (London: Smith, Elder and Co., 1839), 2:23.

^{103&}lt;sub>Humphry</sub> Davy, in a letter to Davies Giddy, Esq., Quoted from John Ayrton Paris, The <u>Life of Sir Humphry Davy</u>, 2 vols. (London: Henry Colburn and Richard Bentley, 1831), 2:86-87.

struck with the curious phaenomena noticed by Messrs. Nicholson and Carlisle, namely, the apparent separate production of oxygen and hydrogen from different wires, or from different parts of the water compleating the galvanic circle . . .

Therefore, he directed his experiments toward producing hydrogen and oxygen separately from quantities of water not immediately in contact with each other. Using two glasses about five inches apart connected in a Voltaic circuit, Davy found that he could indeed produce hydrogen and oxygen separately. After a series of experiments on the purity of the two gases, he reported that they were hydrogen and oxygen nearly in the proportions required to form water. In another experiment, in which he used muscle fiber to connect the pile to the water, he showed that conductors made of wire were not essential to the decomposition of water. 105

Davy also related experiments in which he used the galvanic pile to decompose substances other than water, collecting their components separately. His attempt to decompose caustic potash "only enabled the galvanic influence to extricate oxygen and hydrogen more rapidly from water." Davy reported that when he used a solution of caustic ammoniac, the galvanic influence produced oxygen and nitrogen, in a three to two ratio, in the zinc tube and produced only hydrogen in the silver tube. For reasons that Davy did not state, he then tried a solution of caustic ammoniac in one tube and water in the other.

¹⁰⁴ Humphry Davy, "An Account of Some Experiments Made with the Galvanic Apparatus of Signor Volta. By Mr. Davy of the Pneumatic Institution," Nicholson's Journal 4(1800):275.

¹⁰⁵ Ibid., p. 277.

^{106&}lt;sub>Ibid</sub>., p. 279.

^{107&}lt;sub>Ibid</sub>.

In these 1800 articles Davy presented his results in such a consistent and concise manner that his readers are faced with a problem reminiscent of the synthesis of Greek mathematics: no trace of his analysis remains. Consequently the reader is given little insight into how or why Davy chose to proceed in his experiments in the manner which he did. One might suspect that Davy had a strong sense of the orderliness of all natural phenomena and a belief in the chemical nature of galvanism and made these the foundations of his neat and polished presentation.

According to Davy, when the tube containing water was connected to the zinc end of the pile and the one containing caustic ammoniac was connected to the silver end, hydrogen and oxygen were produced in exactly the proportions required to produce water. However, if the ammoniac was connected to the zinc end and the water to the silver end, "hydrogen was produced from the water; the zinc gold wire was corroded, and the mixture of oxygen and nitrogen to the hydrogen, as six to one (one to six?) was produced as before."

When he used sulfuric acid, the zinc side produced oxygen and the silver side produced sulfur and possibly, according to Davy, partially sulphurated hydrogen gas. When he used caustic potash or water in the tube connected to silver and sulfuric acid in the tube connected to zinc, hydrogen was produced at the silver side and oxygen was produced at the zinc side. However, if the sulfuric acid was used in the tube connected to silver and water was used in the tube connected to zinc," the products

¹⁰⁸<u>Ibid</u>. The parenthetical query is Davy's or Nicholson's.

were the same as when pure sulfuric acid was used in both tubes." Davy also used very diluted sulfuric acid and obtained only hydrogen and oxygen.

Trying the experiment with muriatic acid, he reported that no gas was produced in the zinc tube and that hydrogen was produced in the silver tube. He also noted that the gold wire was corroded in the zinc tube when both sides held muriatic acid, but that when the zinc tube held water and the silver one held muriatic acid, both hydrogen and oxygen were produced, and there was no corrosion of either wire. Using water in the silver tube and muriatic acid in the zinc tube, Davy reported "the same phaenomena took place, as when pure muriatic acid was used in both tubes."

Finally, Davy reported that he had tried concentrated nitric acid, obtaining oxygen at the zinc tube, and a little gas and a green color in the nitric acid in the silver tube. When he used water in the zinc tube and nitric acid in the silver tube, the results were the same, but when he used water in the silver tube, and acid in the zinc tube, hydrogen and oxygen were produced. He argued from these experiments that none of the compound bodies had been immediately decomposed by the galvanic influence, but that the sulfuric and nitric acids had been decomposed by the "nascent" hydrogen produced by the galvanic influence. 111

¹⁰⁹ Ibid., pp. 279-280.

¹¹⁰ Ibid., p. 280.

^{111&}lt;sub>Tbid</sub>.

Davy believed these results to be in contradiction with those reported in Henry's article on the same subject and suggested that Henry would alter his conclusions if he repeated the experiment under new circumstances. Henry did indeed retract his conclusions after learning of Davy's results, saying that he had "drawn too hasty a conclusion" and had assumed a black precipitate to be charcoal when it was "merely a metallic oxide."

Davy's next communication on galvanic phenomena was dated 22 September, 1800 and was published in the October issue of <u>Nicholson's Journal</u>. Inspired by Volta's experiments using charcoal to conduct the galvanic fluid, 113 Davy used conductors of charcoal in the galvanic decomposition of water. Although Davy concluded his article by saying, "I shall, at present, offer no theoretical conjectures concerning these experiments . . ., "114 the concise and systematic manner in which he related his experiments reveals a search for select chemical phenomena and thus betrays Davy's theoretical expectations.

Because gas was produced from water on both sides of the galvanic circuit when he used charcoal conductors, Davy assumed that hydrocarbonate gas was produced on the silver side and carbonic acid gas on the zinc side. He based this assumption on "the common phenomena of the action of

^{112&}lt;sub>Henry</sub>, "Extract of a Letter from Mr. William Henry, Dated Sept. 25, 1800, to Correct an Inference in his Paper on Galvanism," Nicholson's Journal 4(1800):336.

¹¹³ Davy, "Additional Experiments on Galvanic Electricity. By Mr. Davy, Superintendant of the Pneumatic Institution," Nicholson's Journal 4(1800):326.

^{114&}lt;sub>Ibid.</sub>, p. 328.

That is, Davy asssumed that the production of gas by the galvanic influence was essentially chemical in nature and therefore analogous to other chemical operations. In order to demonstrate his conclusion, Davy collected the gases produced from each of the two terminals of the galvanic pile and submitted them to chemical analysis. The gas produced from the zinc side clouded lime water, a positive test for fixed air, and contained about as much oxygen as common air. Although the gas produced at the silver side did not contain oxygen, when it was mixed with oxygen it could be ignited by an electric spark. After such an ignition it was reduced in bulk, and the residue from this ignition clouded lime water, indicating that it contained oxygen. Davy reported similar results using one wire conductor and one charcoal conductor. He varied the experiment in a systematic manner to test the effect of charcoal conductors on solutions of lime water, caustic potash, and ammoniac. Using one charcoal conductor connected to the zinc terminal of the pile and a silver wire connected to the silver terminal, Davy reported that lime water produced gas at the wire. He noted that two charcoal conductors in a solution of lime water produced no gas, but that when he used a silver wire and a charcoal conductor in lime water, gas was produced at the wire whether it was connected to zinc or silver terminals. When he used two charcoal conductors in potash, Davy reported the production of gas at the zinc terminal. However, when he used a charcoal conductor at the zinc terminal and a silver wire at the silver terminal, gas was produced at both sides

^{115&}lt;sub>Ibid</sub>., p. 327.

(with more produced at the silver terminal). In addition to the production of gas, Davy reported that the solutions were often clouded or changed in color by the experiments. Although he offered "no theoretical conjectures" to explain his results, his choice of variables in these experiments reveals once more a systematic search for chemical phenomena governing galvanic action.

Davy explicitly revealed his opinion concerning the chemical nature of galvanism, along with his discovery that carbon conductors could be used to decompose water, in a letter to Davies Giddy dated 20 October 1800.

In pursuing experiments on galvanism, during the last two months, I have met with unexpected and unhoped-for success. . . . Galvanism I have found, by numerous experiments, to be a process purely chemical, and to depend wholly on the oxidation of metallic surfaces, having different degrees of electric conducting power.117

He further confided to Giddy that the pile did not act without the oxidation of zinc in the galvanic process.

Zinc is incapable of decomposing <u>pure</u> water; and if the zinc plates be kept moist with <u>pure</u> water, the galvanic pile does not act; but zinc is capable of oxidating itself when placed in contact with water, holding in solution either oxygen, atmospheric air, or nitrous or muriatic acid, &c.: and under such circumstances, the galvanic phenomena are produced, and their intensity is in proportion to the rapidity with which the zinc is oxidated.

The galvanic pile only acts for a few minutes, when introduced into hydrogen, nitrogen, or hydrocarbonate; that is, only as long as the water between its plates holds some oxygen in solution:
...118

^{116&}lt;sub>Ibid</sub>., pp. 327-328.

^{117&}lt;sub>Humphry</sub> Davy, in a letter quoted from Paris, <u>The Life of Sir Humphry Davy</u>, vol. 2, pp. 109-110.

¹¹⁸ Ibid., p. 110.

Davy also related to Giddy that the action of the pile was more powerful in oxygen than in common air and even more powerful in marine-acid and nitrous acid. He wrote that nitrous acid gave the most power and that the shock from twenty plates "was insupportable."

Davy made these conclusions public in an article published in the November issue of <u>Nicholson's Journal</u>. He said he had been inspired by Haldane's observations, "on the non-excitement of galvanism in the vacuum of an air pump" and "began an investigation with the view of ascertaining precisely the influence of the atmosphere on the phenomena."

He believed he could demonstrate experimentally that the galvanic process was chemical in nature and that he had "met with some new facts, which are capable of arrangement, and which will probably lead to a complete explanation of the galvanic effects."

121

"Facts . . . capable of arrangement" is the touchstone of Davy's prominence in the chemical examination of galvanism. His ability to systematize his inquiry and his argument produced an impressive case for the chemical nature of galvanic phenomena. He supported this case by first illustrating that with a zinc and silver pile, that zinc does not appreciably oxidize in the absence of free oxygen. In fact, he argued, zinc will not oxidize in "pure" water, "water holding in solution no

¹¹⁹ Ibid.

¹²⁰ Davy, "Notice of Some Observations on the Causes of the Galvanic Phenomena, and on Certain Modes of Increasing the Powers of the Galvanic Pile of Volta. By Mr. Davy, Superintendant of the Pneumatic Institution. Communicated by the Author," <u>Nicholson's Journal</u> 4(1800): 337.

¹²¹ Ibid.

oxygen gas, no nitrous gas, and no acids." Thus Davy rejected Volta's contact theory, arguing that metals do not oxidize on contact because of "a peculiar electrical influence produced by the contact of metals." 122

Davy also isolated piles in atmospheres of "hydrogen, nitrogen, nitrous oxide, and hydro-carbonate [gas]" and noted that in no case "was the zinc more oxidated than if the pile had been immersed in pure water." He also isolated a pile "in vacuo" for fourteen hours without any noticeable oxidation of the zinc. 124

Davy's second argument was that "the Oxidation of the Zinc

Plates of the Galvanic Pile takes place whenever the Water in contact with

them holds Atmospheric Air, or Oxygen, or Nitrous Gas, or Nitrous Acid,

or Marine Acid, &c. in Solution." He believed these facts to be well

known from previous galvanic experiments. 125

His third argument in favor of the chemical nature of galvanic phenomena pointed out that "When Zinc is in contact with Water, holding in solution Substances containing loose Oxygen, or Acids, is oxidated, these Substances are altered, or they exert some Chemical Affinities." 126 That is, the oxygen necessary for oxidation is provided by these substances, and when they do provide it directly, they are either changed chemically or diminished physically. When the substances provide the

^{122&}lt;u>Ibid., p. 338.</u>

^{123&}lt;sub>Ibid</sub>., p. 339.

¹²⁴тыід.

^{125&}lt;sub>Ibid</sub>.

^{126&}lt;sub>Ibid</sub>.

oxygen necessary for oxidation indirectly, they do so through the exertion of chemical affinities. According to Davy, an example of a chemical change resulting from the provision of oxygen would be the decomposition of water or of nitrous acid. An example of a physical change would be a decrease in the quantity of atmospheric air or oxygen surrounding the water of the cell. On the other hand, marine or sulfuric acid would provide oxygen by "predisposing" affinity. 127

In his fourth argument, Davy demonstrated that the pile was incapable of acting without the oxidation of zinc by showing that the pile did not act in pure water. Fifthly, and conversely, he demonstrated, by experiment, that the pile did act in cases where its zinc was being oxidized, specifically in solutions containing atmospheric air, oxygen, nitrous acid, or marine acid. Moreover, he could demonstrate by experiment that the action of the pile lasted only as long as did its supply of oxygen, and that a pile stopped by the deprivation of oxygen could be restored to action by the addition of further oxygen. 128

Finally, Davy related the power of the pile to the ability of the conducting fluid to oxidize zinc. He found that zinc oxidizes more rapidly in oxygen than in atmospheric air and more rapidly in atmospheric air than in nitrous air. Therefore, the power of the Voltaic cell is greatest in pure oxygen and greater in atmospheric air than in nitrous oxide. He also noted that the power of the cell is greater in marine

¹²⁷ Ibid., pp. 339-340.

^{128&}lt;u>Ibid.</u>, pp. 340-341.

acid than in nitric acid because marine acid enables zinc to oxidize more rapidly. 129

Davy's arguments for the chemical nature of galvanism were persuasive and repeatedly stated:

Of two phenomena, or of two series of phenomena, we can only affirm that the one is the cause of the other when it uniformly precedes it, and when their modifications are connected. But it appears from all the foregoing facts, that the galvanic pile of Volta acts only when the conducting substance between the plates is capable of oxidating the zinc; and that in proportion as a greater quantity of oxygen enters into combination with the zinc in a given time, so in proportion is the power of the pile . . . greater. It seems therefore reasonable to conclude, though with our present quantity of facts we are unable to explain the exact mode of operation, that the oxidation of the zinc in the pile and the chemical changes connected with it are some how the cause of the electrical effects it produces. 130

His theory of the chemical nature of the pile allowed him to predict that a more powerful pile might be constructed using another fluid more capable of oxidizing zinc in place of water. From his experiments, he reported that a pile of only eighteen plates in muriatic or dilute nitrous acid was stronger than a pile of seventy plates in water. The verification of his prediction could be viewed as Davy's final demonstration of the validity of his arguments. 131

On October 23, shortly after he had written Giddy, Davy wrote a supplement to these experiments, and it was also published in the November 1800 issue of Nicholson's Journal. In it Davy described how he had, at Dr. Beddoes' suggestion, tested the effects of the pile in an

¹²⁹ Ibid., p. 341.

¹³⁰ Ibid.

^{131&}lt;sub>Ibid</sub>., p. 342.

atmosphere of oxygenated muriatic gas. He found that the pile would not act in the gas alone, but that it would act when immersed in water under an atmosphere of this gas. Davy summarized:

This experiment not only arranges with the facts of Fabroni and Colonel Haldane, and those I have before stated; but likewise seems to prove that the chief use of the large surface of water required in the pile of Volta is to oxidate a larger quantity of zinc: . . . 132

Davy intended to determine experimentally if there were differences in the gases produced by the galvanic pile when different oxidating substances were the "medium of communication between the plates." On the completion of these experiments he expected to "offer some observations on the peculiar affinities which enable iron, zinc, &c, to decompose water only when it holds in solution atmospheric air, acids, or other bodies containing oxygen." 133

Davy continued his examination of galvanism as a chemical phenomenon in the December 1800 issue of Nicholson's Journal. In this article he reaffirmed through experiment that certain galvanic phenomena could be predicted from the principle that he had advanced. Namely, assuming that the power of the Voltaic pile was based on the oxidation of its zinc plates, the pile should and did work more powerfully in dilute sulfuric acid than in concentrated sulfuric acid. In fact, he reported that concentrated sulfuric acid produced no galvanic action or oxidation of zinc. 134

¹³² Davy, "Extract of a Letter from Mr. Humphry Davy, Dated October 23, Supplementary to his Paper on Galvanism, in the Present Number," <u>Micholson's Journal</u> 4(1800):380-381.

^{133&}lt;sub>Ibid</sub>.

 $^{^{134}}$ Davy, "An Account of Some Additional Experiments and

Davy also reviewed the inaction of the Voltaic pile in a vacuum, pointing out that "no phenomenon is more constant than the cessation of the action of the common galvanic pile in a vacuum when the gauge is below one-tenth." He was careful to point out that the pile acted a short while in a vacuum and then ceased, once all traces of oxygen were used up. However, his experiments showed that free oxygen was not essential to galvanic action in that a drop of sulfuric acid in water moistening the pile under a vacuum would activate the pile in the absence of oxygen and oxidate it "as vividly as in the atmosphere." Davy was not yet sure if water was absolutely essential to the action of the pile, but he noted that a "compound of concentrated sulfuric acid and oxigenated muriatic acid" capable of strongly oxidizing zinc did not produce strong galvanic effects when used as "the communicating medium of the cells of a pile." 136

In addition to his chemical examination of the cause and power of the Voltaic pile, Davy had also examined the action of the pile on fluids. He suspected an analogy between the action of the pile on water and the interaction of the parts of the pile. That is, he believed that when the zinc terminal was oxidized and hydrogen was produced at the silver terminal, an analogous effect took place at each zinc-silver interface of the pile. 137

Observations on the Galvanic Phenomena. By Mr. Davy, Superintendant of the Pneumatic Institution. Communicated by the Author," <u>Nicholson's</u> <u>Journal</u> 4(1800):394.

^{135&}lt;sub>Ibid., p. 395.</sub>

^{136&}lt;u>Ibid</u>., p. 396.

^{137&}lt;sub>Ibid</sub>.

Davy failed in his initial experimental attempt to demonstrate this analogy. This failure led him to vary the size and shape of the silver plates in the pile, and by doing so, he not only found the demonstration he sought, 138 but also he determined that the hydrogen produced "was in some measure, and to a certain point, in the inverse ratio of the quantity of the surface of the silver plates." Davy attributed his initial difficulty to the formation of ammoniac at the larger silver plates. He believed the ammoniac resulted from the union of the hydrogen produced and impurities of nitrogen provided by the atmospheric air. 140

In the same article, Davy described the previously promised experiments on the nature of the gases produced from water when the pile was oxidized by different substances. With these experiments he illustrated that the action of the pile on water always produces hydrogen at the silver terminal and oxygen at the zinc terminal, regardless of how the zinc was oxidized and regardless of how many containers of water were connected in series to the pile. 141

Although Davy had presented an arrangement of the phenomena of galvanism in which a "chemical action generates . . . an influence capable of increasing all analogous actions, and of generating new and similar actions," he refused "to speculate" further "on these facts." He could not commit himself to declare that water was decomposed galvanically

¹³⁸ Ibid., pp. 397-398.

¹³⁹ Ibid., p. 398.

^{140 &}lt;u>Tbid., p. 399</u>.

¹⁴¹ Ibid., pp. 399-400.

because:

Supposing its decomposition, we must assume, that at least one of its elements is capable of rapidly passing in an invisible form through metallic substances, or through water and many connected organic bodies; and such an assumption is incommensurable with all known facts. 142

However, he was more than optimistic that the laws of galvanism would be discovered in "a number of new experiments." Davy wrote:

But a short period is elapsed since philosophers beheld with wonder, solid and fluid substances assuming new modes of existence in different gases. Do not the new phaenomena of galvanism authorize us to hope that at no very distant time they will behold even those gases undergoing novel changes, and existing in new and unknown forms?¹⁴³

Thus he assumed that the phenomena of galvanic decomposition of water "incommensurable with all known facts," because of the production the two components of water at distance from each other, might be explained by the discovery of a new form of matter that would be to gases as gases were to solids and liquids.

He ended his article with remarks on the powers of different galvanic combinations, noting that increases in the oxidation of the zinc would not increase the power of the pile beyond a certain extent. 144

Davy represents the pinnacle of English research on the Voltaic pile in 1800. 145 Yet he, like others before him, was unable to explain how the action of the pile on water produced the two constituents of water separately and at some distance from each other. With the exception of Cruickshank's theory of the deoxygenated and oxygenated

^{142 &}lt;u>Ibid.</u>, p. 400. 143 <u>Tbid.</u> 144 <u>Ibid.</u>, p. 401.

¹⁴⁵ For other accounts of Davy's electrochemical researches, see Colin A. Russel, "The Electrochemical Theory of Sir Humphry Davy. Part I: the Voltaic Pile and Electroylsis, Part III: The Evidence of the Royal Institution Manuscripts," <u>Annals of Science</u> 15(1959):1-13 and 19(1963): 255-271.

states of the galvanic fluid, no other English natural philosopher offered a published explanation of the matter at that time. The problem which the galvanic decomposition of water posed for antiphlogistic chemistry is best summarized by an anonymous letter to Nicholson's Journal dated 21 December 1800. After pointing out that the new system of chemistry could be applied to a wide range of phenomena with fascinating ease and that one who even questioned its application might suffer derision, the unknown correspondent reviewed the phenomena of the galvanic decomposition of water and asked:

Now, Sir, I wish to know how it happens, according to any system, that the two component parts of water should be made to appear at such distances from each other. Does the hydrogen of the decomposed particle of water on the zinc side of the pile, fly away instantly as the oxygen is produced on that side, to the wire connected with the silver? If it does, why do we not see the bubbles in its passage? Or does the oxygen pass from the wire connected with the silver to that connected with the zinc? Or are there two currents?

In the ordinary modes of reasoning on these subjects, we generally suppose that when one of the component parts of a substance is separated or is fixed, the other appears instantly in some way or another, and close to it... It is a new principle for it insensibly to hurry through the water for a distance of six inches or more, and there to make its appearance in the character of gas. 146

Nicholson seized the editorial opportunity presented by this

letter to add further remarks of his own. After admitting the difficulty

of explaining these phenomena and leaving an elucidation of them to "those

able men who are now employed upon it," Nicholson pointed out that some

distance of time and space may intervene between all chemical phenomena.

For instance, the precipitations of a metal from its solution in acid by

^{146.} On the Chemical Effects of the Pile of Volta. By a Correspondent, Nicholson's Journal 4(1801):472-473.

the addition of another metal, according to Nicholson, involved an interval of distance. 147

The historical situation in England is clear. The reception of the Voltaic pile there was associated with Nicholson and Carlisle's discovery of the action of the pile on water. The published accounts of experiments with the pile conducted from May 1800 until January 1801, with the exception of Haldane's, all explicitly accepted galvanism as electrical or electro-chemical in nature, and all were concerned with the chemical effects of the pile. With a few exceptions, the English writers also accepted the galvanic, or electrical, decomposition of water.

The chemical implications of the separate production of hydrogen and oxygen were also recognized as posing a problem that contemporary electro-chemical theory could not explain. Only Cruickshank offered a theory to explain this problem, while the anenymous critic used the problem to question the validity of the new chemical theory. Both Nicholson and Davy were optimistic that the problem soon could be resolved. The transmission of the knowledge of the Voltaic pile and its effects on water back across the channel 148 reveals that Davy's optimism proved unwarranted; the effects of the pile on water were not soon reconciled with the new chemical theory.

 $^{^{147}}$ Nicholson, in a note to "On the Chemical Effects," p. 473.

¹⁴⁸ Volta often chose to introduce his discoveries through the <u>Philosophical Transactions</u>, perhaps because he believed that the <u>English</u> would be more favorable to his theories. For this reason, the knowledge of the Voltaic pile was, formally, introduced into Europe via England.

CHAPTER VI

THE RECEPTION OF THE VOLTAIC DECOMPOSITION OF WATER ON THE CONTINENT

Although many English natural philosophers accepted the electrical decompostion of water, and therefore, accepted Nicholson and Carlisle's experiments with the pile as a crucial instance illustrating the electrical nature of galvanism, the inability of the theory of Lavoisier, upon which they based their assumption of the decomposition of water, to explain the separate production of hydrogen and oxygen in a Voltaic circuit reinforced the beliefs of those who viewed electricity and galvanism as separate phenomena. The decomposition of water was a necessary assumption to Nicholson and Carlisle's identification of electricity with galvanism, and it was an assumption that many continental natural philosophers did not share.

The questions raised by Davy's unknown critic were echoed by these continental natural philosophers who used the galvanic production of hydrogen and oxygen at separate locations to argue for their conception of the nature of electricity and galvanism. Because their conception often differed from that of English natural philosophers and the followers of Volta, the Voltaic action on water was often used as a crucial instance to demonstrate either the unique nature of the galvanic

influence or the compound nature of subtile fluids such as electricity and galvanism and the elemental nature of water, instead of the electrical nature of galvanism.

There were those continental natural philosophers who believed in the electrical nature of galvanism. Like Nicholson, and Davy, they were not shaken in their assumption of the galvanic decomposition of water merely because contemporary electro-chemical theory could not explain the separate production of hydrogen and oxygen.

The English investigations of the Voltaic pile were widely known in Europe by September 1800. Most of the transmission of this knowledge was accomplished by the publication in continental journals and newspapers of extracts, summaries, or accounts of the discovery of the pile. However, private correspondence also entered into the transmission of this knowledge. Sir Joseph Banks wrote Van Marum on 14 June 1800 and informed him of Volta's discovery. By 1801 Van Marum had published an elaborate series of experiments on galvanic electricity. Moreover, the prize contest for the Hollandsche Maatschappij der Wetenschappen, of which he was secretary, announced that the prize question for 1801 was "Can the action of the Galvanic pile of Volta be explained lucidly by the well-known laws or properties of electricity (Electrische kracht), or does it teach us about the existence of a separate fluid distinct from

British Museum (Natural History), Warren R. Dawson, ed.,
The Banks Letters: A Calendar of the Manuscript Correspondence of Sir
Joseph Banks Preserved in the British Museum, the British Museum (Natural
History) and Other Collections in Great Britzin (London: by the order of
the Trustees of the British Museum, 1958), p. 586.

the electric fluid?"² Although Van Marum did not publish on the subject in 1800, he was one of the many who turned their attention to the investigation of the Voltaic pile in Europe that year.

An announcement of the Voltaic pile was published in <u>Le moniteur</u> on 17 August 1800 in the form of an account, extracted from the <u>Courier de Londres</u>, of Doctor Garnett's repetition of Nicholson and Carlisle's experiments in his public lectures? The same summary of Garnett's experiments was also published in the <u>Journal de Bruxelles</u> of 21 August.

One journal that was very important in the transmission of scientific knowledge from England to the continent in the late eighteenth century and the early nineteenth century was the <u>Bibliothèque britannique</u> edited by Marc-Auguste Pictet (1752-1825), a Geneva lawyer. Pictet, through the influence of Horace Bénédict de Saussure (1740-1799), had become interested in natural philosophy, and upon Saussure's retirement, had taken his chair at the Geneva Academy. In 1796 he founded the <u>Bibliothèque britannique</u> with the expressed intention of making developments in Britain in literature, science and art known in Europe. Pictet himself wrote of the Bibliothèque britannique

²Quoted from W. D. Hackmann, "Electrical Researches," Chapter 15 of Martinus Van Marum, Life and Work, vol. 3, p. 359. Hackmann discusses Van Marum's research in galvanic electricity on pp. 357-370.

^{3&}quot;Extérieur Angleterre, (Extrait du Courier de Londres du 8 aout, 20 thermidor) [on the galvanic decomposition of water]," Gazette nationale ou le moniteur universel, no. 329, monidi, 29 thermidor an 8.

⁴Journal de Bruxelles no. 333 (fridi 3 fructidor an 8): 503-504. Although the source of the article is not identified, it was probably taken from <u>Le Moniteur</u> since the wording is the same.

^{5&}quot;Robert Fox, "Marc-Auguste Pictet," DSB, 10:602-603.

Au travers de mille difficultés dont les circonstances de la guerre ont entravé notre entreprise, nous sommes parvenus à la sixième année avec un succès toujours croissant. 6

He went on to discuss the major events of each field of endeavor that his journal had covered in 1800.

Mais deux découvertes importantes ont surtout enrichi cette année la partie physique de nos Annales. L'une est cette singulière modification du Galvanisme qui produit la commotion électrique, l'étincelle, la décomposition de l'eau; et qu'on obtient par une pile de rondelles de deux métaux différens. . . . La simplicité de cet appareil, qu'on doit au célèbre VOLTA, contraste singulièrement avec l'intensité et la permanence de ses effets.

Pictet was right on the first point as well as the second.

Beginning with its first article of 1800, an extract of Nicholson and Carlisle's experiments with the Voltaic pile, the <u>Bibliothèque</u>

<u>britannique</u> contributed to the transmission of the news of the Voltaic pile. Immediately following this extract, Pictet published extracts of Cruickshank's experiments from the July issue of <u>Nicholson's Journal</u>8

Marc-Auguste Pictet, "Préface," <u>Bibliothèque britannique.ou</u> recueil extrait des ouvrages Anglais périodiques et autres; des mémoires et transactions des sociétés et académies de la Grande-Bretagne, d'Asie, d'Afrique et d'Amérique, en deux series, intitulées: <u>Littérature et Sciences et arts</u>. <u>Sciences et arts</u> 16(an 9 or 1801):3. (Journal hereinafter referred to as <u>Bibliothèque britannique</u>). "Through thousands of difficulties by which the circumstances of war have hindered our enterprises, we have reached a sixth year with ever increasing success, . . .'

^{7 &}lt;u>Ibid.</u>, p. 12. "But two important discoveries have especially enriched the physical part of our Annales this year. One is the singular modification of galvanism that produces the electric commotion, the spark, the decomposition of water; and which one obtains by a pile of discs of two different metals. . . . The simplicity of the apparatus, that we owe to the celebrated Volta contrasts singularly with the intensity and permanence of the effects." Pictet considered the other major discovery of 1800 to be John Hershel's discovery that the solar spectrum contained "invisible rays" of "radiant heat" beyond the red. <u>Ibid.</u>, pp. 12-13.

⁸Cruickshank, "Some Experiments and Observations, etc. Quelques expériences et observations sur l'électricité galvanique; par Mr. W. Cruickshank de Woolwich, communiquées par l'auteur." (Journal de

and of Henry's experiments from the August issue of <u>Nicholson's</u>
<u>Journal</u>.

Although the <u>Bibliothèque</u> <u>britannique</u> was not devoted to giving accounts of original experiments made in Europe, through the editorial commentary one can gain insight into the European reactions to the English experiments with the Voltaic pile. In the first article on Nicholson and Carlisle's experiments, Pictet noted that he himself had constructed a pile using "piastres," and that the pile seemed to increase in power as more pairs of metal discs were included in the circuit. One of the reasons that Pictet was so ready to identify the action of the pile as electrical was that, although Volta and Nicholson had used a condenser with the pile to obtain sparks, Pictet had obtained sparks from a pile of fifty-seven pieces of silver and zinc without using a condenser. Using a pile of 112 piastres, he found the spark produced when his eyes were connected in series with the pile "si fort . . . qu'on ne répète pas volontiers l'expérience."

Nicholson juillet 1800)," <u>Bibliothèque britannique</u>. <u>Sciences et arts</u> 15(1800):23-34.

Henry, "Experiments on the Chemical Effects, etc. Expériences sur les effets chimiques de l'électricité galvanique; par Mr. William Henry. (Journ. de Nicholson, août 1800.)," <u>Bibliothèque britannique</u>. Science et arts 15(1800):35-45.

Pictet in editor's note to "Account of the New Electrical, etc. Description du nouvel appareil electrique, ou galvanique de Mr. Alex. Volta, et expériences faites avec cet appareil." (Journal de Nicholson, juillet 1800.)," <u>Bibliothèque britannique</u>. <u>Sciences et arts 15(1800):5.</u>

^{1&}lt;u>Ibid.</u>, p. 6. 12<u>Ibid.</u>, p. 7.

 $^{^{13}}$ <u>Ibid.</u>, p. 8. "so strong . . . that one does not willingly repeat the experiment."

Pictet's notes to the extract revealed that he had repeated Nicholson and Carlisle's experiments on the decomposition of water, and experiments on the effect of the galvanic influence on acid-base indicators as well, at a séance of the "société de physique et d'histoire naturelle de Genève."

According to his notes, he had also repeated some of Cruickshank's experiments before the Société de Genève and was surprised to find that a pile of 112 piastres directly affected an electrometer. 15

Among the other experiments that Pictet repeated before the Société de Genève was the one in which Cruickshank had passed the galvanic influence through water containing tincture of Brazil wood. Whereas Cruickshank had explained his results by assuming that an acid was formed at the zinc end and that ammoniac was formed at the silver end, Pictet commented,

Ce vert indiquoit, ou la formation d'un réactif alkalin, ou celle d'un acide. . . . L'ammoniaque, ajouté à la liqueur verte conservée quelques jours, ne la fit point passer au bleu; et cette circonstance nous fit considérer la première des deux suppositions comme la plus probable. $^{16}\,$

Pictet had also repeated Cruickshank's experiments in which metals were

^{14&}lt;u>Ibid</u>., p. 14.

¹⁵ Pictet in a note to "Some Experiments and Observations, etc. Quelques expériences et observations sur l'électricité galvanique; par Mr. W. Cruickshank de Woolwich, communiquées par l'auteur. (Journal de Nicholson, juillet 1800)," Bibliothèque britannique. Sciences et arts 15(1800):25.

¹⁶_<u>Ibid.</u>, p. 28. "This green indicated either the formation of an alkaline reactant or of an acid. . . . Ammonia, added to the green liquor preserved [it] several days, without turning it blue; and this circumstance made us consider the first of the two suppositions as the most probable."

dissolved in acid using the galvanic influence, and he had continued one experiment for twelve hours, only to report that he had observed "précisément les mêmes phénomènes" as Cruickshank. 17

Pictet was not so agreeable in his commentary on Henry's experiments. Unlike Henry, Pictet was surprised that enough oxygen could be produced from an aqueous solution of oxygenated muriatic acid to indicate both the decomposition of water and the deoxygenation of the acid, even when the conducting wires were coated with shellac to prevent their oxidation. Pictet inferred from these results that the same effects could be produced with nonmetallic conductors, 19 a conclusion that Davy had also reached in a different manner.

Pictet rejected Henry's contention that the galvanic production of hydrogen from caustic alkali indicated that hydrogen was one of its constituents, saying, "doit-il être plutôt attribué à la décomposition de 1'alkali qu'à celle de 1'eau dans laquelle celui-ce est dissous . . . ?"²⁰ Henry had asserted that although azote was also a component of caustic alkali, it was not produced from it in gaseous form by the galvanic influence because it immediately united with the oxygen also

^{17 &}lt;u>Ibid.</u>, p. 29. "precisely the same phenomena."

Pictet in a note to "Experiments on the Chemical Effects, etc. Expériences sur les effets chimiques de l'électricité galvanique; par Mr. William Henry, (Journ. de Nicholson, août 1800)," <u>Bibliothèque britannique</u>. <u>Sciences et arts</u> 16(1800):36 reveals that he did repeat Henry's experiments.

^{19&}lt;sub>Tbid., pp. 39-40.</sub>

²⁰_<u>Ibid.</u>, p. 44, note 1. "Should it be attributed to the decomposition of alkali rather than to the water in which it [the caustic alkali] is dissolved. . ?"

produced at the same time by the galvanic decomposition of the water in the caustic alkali solution. Pictet disagreed:

Si l'azote est ainsi oxigéné on devroit appercevoir, ou du gaz nitreux, ou de l'acide nitrique, qui s'unissant à la potasse formeroit du nitre, lequel paroitroit en nature dans la solution.

Finally, Pictet, like Davy, rejected Henry's suspicion that the precipitate formed galvanically from caustic vegetable alkali might be a third component of the alkali. Pictet, unlike either of the English writers, named this component "potasse"; however, he believed that the black precipitate was "un simple oxide dû à l'oxigène de l'eau qui dissolvoit la potasse," rather than "la potasse" itself. 22 When Henry admitted his mistake in response to Davy's criticism, Henry attributed the precipitate to an oxide of mercury and mentioned that he believed the third component of vegetable alkali to be charcoal. 23

Just as the <u>Bibliothèque</u> <u>britannique</u> extracted articles from English journals, other French scientific journals (Geneva was a part of France in 1800) made extracts of articles from the <u>Bibliothèque</u> <u>britannique</u>. An extract of the <u>Bibliothèque</u> <u>britannique</u>'s description of the Voltaic pile and of Nicholson and Carlisle's experiments with it, complete with Pictet's notes reporting similar results at a séance of

²¹<u>Ibid.</u>, p. 44, note 2. "If azote is thus oxygenated, one should notice either from nitrous gas or nitric acid, which uniting to the potassium would form nitre, and which would appear naturally in the solution."

 $^{^{22}}$ Tbid., p. 45, note. "A simple oxide due to the oxygen of the water in which the potassium was dissolved." For Davy's criticisms of Henry's conclusion, Supra, p. 226.

²³Henry, "Extract of a Letter from Mr. William Henry to Correct His Paper on Galvanism," <u>Nicholson's Journal</u> 4(1800):336.

the Societe de Genève, was published in the October 1800 issue of the <u>Journal de physique</u>. ²⁴

Although Pictet believed the galvanic influence to be electrical, others did not. Perhaps it is only coincidence, but the first <u>Journal dephysique</u> article on the action of the Voltaic pile, an extract of Cruickshank's article published in the July 1800 issue, ²⁵ discussed the galvanic influence as if it were not electrical. There was also a mixed reception of Volta's discovery in the Institut National.

On 16 fructidor, an 8, according to the <u>Procès-verbaux de</u>

<u>l'Institut national</u>, "Le Cn Hallé rend compte des expériences que la

Commission du Galvanisme a faites, pour vérifier les phénomenes annoucés nouvellement par les papiers anglais."

An account of the Voltaic pile and of experiments made with it by Etienne-Gaspard Robertson (1763-1837) had been read to the Institut National five days earlier. Robertson

²⁴ Nicholson and Carlisle, "Description du nouvel appareil ou galvanique de M. Alexandre Volta, et d'expériences faites avec cet appareil par MM. Nicholson et Carlisle (Journal de Nicholson). Extrait de la Bibliothèque britannique," Journal de physique 51(1800):344.

²⁵ Cruickshank, "Expériences et observations sur l'électricité galvanique, par M. Cruickshanks, de Woolwich," <u>Journal de physique</u> 51 (1800):164. Because this article contains no notes by Pictet, it may have been translated directly from <u>Nicholson's Journal</u> rather than from the <u>Bibliothèque britannique</u>.

^{26&}lt;sub>Procès-verbaux</sub> de l'Institut National, 2(16 fructidor an 8):221.
"Citizen Hallé reported on the experiments that the Commission on Galvanism has made in order to verify the phenomena newly announced by the
the English papers."

^{27 &}lt;u>Ibid.</u>, p. 218. See also Etienne-Gaspard Robertson, "Expériences nouvelles sur le fluide galvanique; par Robertson, lues à 1'Institut National de France, le 11 fructidor an 8," <u>Annales de chimie</u> 37(1800-an 9):132.

had read of the pile in the <u>Courier de Londres</u> and he began his own experiments, publishing part of those read to the Institut National in the <u>Journal de Paris</u> 10 fructidor an 8. 28 The remainder of Robertson's experiments were published in the <u>Journal de Paris</u> on 15²⁹ and 17 fructidor. 30 Robertson, formerly a professor of physique at the Ecole Centrale, Département de l'Ourthe, was no amateur at galvanic and electrical experiments. According to daily ads in the <u>Journal de Paris</u>, Robertson entertained nightly at 7:30 at the Cour des Capucines. Only Robertson's ad best imparts the nature of his enterprise:

FANTASMAGORIE DE ROBERTSON, cour des Capucines, place Vendôme.— Auj. APPARITIONS de FANTOMES . . . ILLUSIONS, OPTIQUES, HARMONICA; Expériences sur les GAZ, l'AIR, le GALVANISME, ou l'ELECTRICITE; . . . Séance tous les jour à $7^{\rm hl}_2$. On y jouira de l'Expérience & de l'explication de la FEMME INVISIBLE. 31

^{.28} Robertson, Journal de Paris no. 340(10 fructidor an 8):1691-1692.

²⁹ Robertson, Journal de Paris no. 345(15 fructidor an.8):1722-1723.

³⁰ Robertson, Journal de Paris no. 347(17 fructidor an.8):1736-1737.

³¹ Robertson, <u>Journal de Paris</u> no. 273(6 messidor, an 8):1282.
"Phantasmagoria Robertson, court of the Capucines, place Vendôme. —
Today Apparitions of phantoms . . . Illusions, optics, harmonica; experiments on gases, air galvanism or electricity; . . . Seance every day at 7 PM. You will enjoy the experiment and the explication of the invisible woman."

³² Robertson, <u>Journal de Paris</u> no. 120(30 nivôse an 9):928.

Robertson, Journal de Paris no. 359(29 fructidor an 8):1810.

brother of Jacques-Alexander-César Charles (1746-1823) who wrote on the expansion of gases. Robert Charles's "SALON DE PHYSIQUE ACOUSTIQUE, D'INVISBILITE & D'ORACLES" held at the "passage Longueville, en face des Tuileries.—Tous les jours, depuis 10^h du matin jusqu'a 3^h apres midi, & depuis 5 jusqu'a 9 du soir, sans interruption," was also advertised in the <u>Journal de Paris</u>. ³⁴ Charles's ad once noted in what may have been a jab at Robertson, "L'air & la fraicheur qui règnent dans le salon, permettent aux curieux de jouir des expériences sans être incommodés par la grande chaleur." Later, Robertson's ad proclaimed, perhaps in reply to his competitors, that he was convinced by "les essais maladroits qui ete offerts au public" that the experiments of the <u>FANTASMAGORIE</u> were not mediocre. ³⁶

Robertson differed with Volta and Nicholson on one important point concerning the action of the pile—he did not believe the galvanic influence to be electrical in nature. Instead, he defended the views of Galvani, Humboldt, and Aldini, which were quite popular in France. After testing the effects of the Voltaic cell on the human body, Robertson presented results no different from those of Volta, Nicholson and Pictet, but Robertson believed these results only proved the difference between the galvanic and electric fluids. He argued that, although the effects of the galvanic fluid had been confused with the effects of electricity, the

³⁴ Robert Charles, <u>Journal de Paris</u> no. 291(21 messidor an 8):

 $^{^{35}}$ <u>Ibid</u>. "The air and the coolness which prevails in the salon, permits the curious to enjoy the experiments without being inconvenienced by great heat."

³⁶Robertson, <u>Journal de Paris</u> no. 106(16 nivôse an 9):644. "convinced by the maladroit essays offered to the public."

galvanic shock was weaker, more localized, continuous, and only affected the nervous system. Electricity, conversely, was stronger, instantaneous, affected the whole body, and ceased as soon as it reached equilibrium. The also argued that since the pile would not influence an electrometer, it was not electrical. Robertson was in partial agreement with English investigators because Nicholson had not been able to detect directly any signs of electricity from the pile. Instead, he was only able to influence an electroscope with the pile by the intermediate use of a doubler. However, Pictet reported that a pile of 112 piasters would affect an electrometer.

The most striking difference that Robertson found between the effects of electricity and the effects of galvanism was that the galvanic column had an acidic taste when touched to the tongue while electricity "n'offre aucun goût sur la langue." Although his belief that electricity had no acid taste ran contrary to the writings of three generations of French chemists, it encouraged Robertson to speculate that the galvanic fluid was perhaps "le premier agent du mouvement vital, et que l'on désignait dans l'ancienne école, sous le nom de fluide

³⁷ Robertson, "Expériences nouvelles," <u>Annales de chimie</u> 37 (1800-an 9):134-135.

³⁸Ibid., p. 138.

³⁹ Nicholson, "Account of the New Electrical or Galvanic Apparatus of Volta, Nicholson's Journal 4(1800):182.

^{40&}lt;sub>Supra</sub> , p. 244.

 $^{^{41}}_{\rm Robertson,"Expériences nouvelles,"}$ p. 138. "Offers no taste to the tongue."

nerveux."⁴² He believed that the actions of this nervous acid were sometimes overlooked because they were weakened by the epidermis which broke the connection between the Voltaic column and the nervous system.⁴³ Accordingly he related an experiment that illustrated the effects of the galvanic fluid after the epidermis had been bypassed.

In another experiment he cut the skin of his hand and of his little finger with a razor and connected a Voltaic column to these cuts so that his hand completed the circuit. Again Robertson found the pain "insupportable," and that it ceased when he broke contact with the column. He concluded from this experiment that a continuous galvanic current existed from one end of the pile to the other, a phenomenon that Robertson believed to illustrate further the difference between galvanism 45 and electricity, for an electrical shock would have been almost instantaneous while the galvanic shock lasted as long as his hand completed the circuit. It might be noted that in England Haldane had published a similar

 $^{^{42}}$ <u>Ibid.</u>, p. 139. "the first agent of vital mouvement, and that which one designated in the old school, with the name the nervous fluid."

^{43&}lt;sub>Ibid</sub>.

^{44 &}lt;u>Ibid.</u>, p. 140. "After having peeled the skin of the finger or of any other part of the body with the point of a needle, while you touch the summit of the galvanic column, you instantly experience an insupportable feeling that is very much similar to the burning produced by fire or acids; this pain lasts even after the experiment, and seems to change into a light inflammation."

^{45&}lt;u>Ibid</u>., pp. 140-141.

argument. Robertson claimed that this conclusion led him to experiments on the galvanic decomposition of water that he considered to be proof of the existence of such a continuous current. 46

In his experiments on the galvanic decomposition of water Robertson used a tube of water six lines in diameter and eight inches long with wires of tin inserted through corks in each end. He left a gap of about one inch between the wires, and after connecting the wires to a galvanic column and placing the tube perpendicularly, he noted bubbles continuously forming at the upper wire and rising to the surface of the water. Robertson identified these bubbles as being hydrogen by mixing them with oxygen and electrically igniting the mixture to form water. He repeated the whole experiment several times using wires of different metals with the same results. He also noted that the lower wire was in each case oxidized and did not give off any bubbles. 47

Robertson argued that his experiments indicated the existence of a fluid generated by the contact of two heterogeneous metals, an acid so powerful that it extended even to the limits of life, capable of profound effects upon the nervous systems of dead animals. To illustrate the existence of such an acid, he had added a colored indicator to the water in his galvanic decomposition of water and obtained a positive test for the presence of acids. Believing that further repetitions were necessary to better study the galvanic fluid, or the nervous acid, and that

⁴⁶Ibid., p. 141. <u>Supra</u>, p. 214.

⁴⁷ Robertson, "Experiences nouvelles," pp. 141-142.

^{48&}lt;u>Tbid., pp. 143-144.</u>

they would only add to the analogy between the galvanic fluid and the nervous acid. Robertson promised to repeat his experiments "les 1^{er} et 5 de de [sic] chaque décade, à mes séances du soir, cour des Capucines." He added that his arguments were supported by a multitude of new facts and observations and enumerated four of these:

- Tincture of violets or of tournesol were colored by the passage of the galvanic fluid.
- Touching heterogeneous metals oxidized rapidly and produced a white salt.
- 3. The wire used in the galvanic decomposition of water deposited a substance that appeared to be a type of "galvanade."
- 4. The galvanic fluid offered "au microscope et au sentiment" effects similar to those of acids.⁵⁰

After commenting on the construction of the galvanic column and explaining how to produce the strongest galvanic effects, Robertson suggested that the power of any galvanic column could be measured by a Galvanomètre consisting of the one apparatus sensitive enough to clearly indicate galvanic activity, the apparatus used in the galvanic decomposition of water. He assumed that the greater the quantity of bubbles produced, the greater the activity of the column. Haldane had made a

⁴⁹<u>Ibid.</u>, p. 144. "The first and fifth of each decade at my evening seances at the courtyard of the Capucines." The revolutionary calendar consisted of three ten day periods or decades per month.

⁵⁰ Ibid., p. 145. "to the microscope and to the feeling."

similar assumption and measured the power of the pile by the amount of gas it could produce from water. 51

Finally Robertson admitted that the cause determining at which wire the bubbles would originate in galvanic decompositions

embarrassera sans doute les phisiciens. Son principe tient peut-être à la nature du métal, à sa masse, à sa qualité, ou même à l'état hygrométrique ou barométrique de l'atmosphère. 52

On 21 frimaire an 9, or 13 December 1800, Charles Jean Lehot (fl. 1800), engineer to the Corps Royal des Ponts et Chaussées began reading an account of his galvanic experiments to the Institut National. 53 Lehot supported Volta in the belief that the contact of different conductors excited the galvanic fluid, a point that was conceded even by Robertson. Lehot argued that one could not use an electroscope to know the true direction of the galvanic current because one could not know which of two electrified bodies is truly charged or deficient in electric fluid. 54 However, given certain rules, he believed that indisputable signs existed that indicated the true direction of the galvanic fluid and that "on peut déterminer à priori" for a number

^{51 &}lt;u>Ibid.</u>, p. 148. <u>Supra</u>, p. 215.

 $⁵²_{\rm Robertson}$, "Expériences nouvelle," p. 150. "will no doubt embarass physicists. Its principle is due perhaps to the nature of the metal, its mass, its quality, or even to the hygrometric and barometric state of the atmosphere."

⁵³Procès-verbaux de l'Institut National, 2(21 frimaire an 9):278-280. According to A. Fourcy, <u>Histoire de l'Ecole Polytechnique</u> (Paris: Chez l'auteur, à l'Ecole Polytechnique, 1828), p. 401, Lehot began at the Ecole Polytechnique as a student in 1796 and later taught there.

⁵⁴C. J. Lehot, "Extrait d'un mémoire du citoyen Lehot, sur le galvanisme; lu à l'institut le 26 frimaire an 9," <u>Annales de chimie</u> 38 (1801):42. Lehot continued the account of his experiments at the séance of 26 frimaire (17 December) an 9.

of different galvanic circuits the direction of the galvanic $_{\rm fluid}$. 55

Like Volta, Lehot believed that the galvanic fluid resulted from an imbalance in the exciting or conducting substances and that compared to metals, wet substances or animal tissue had little capacity for generating the galvanic fluid. Most of Lehot's experiments treated simple galvanic chains of metals and animal tissue, and he mentioned the pile of Volta only in passing by pointing out that Volta had built an apparatus based on the principles examined in Lehot's own experiments. Lehot considered the chemical effects of this apparatus to be related to the direction of the current and the very principles of galvanic excitation that he had just discussed. Now that he had established the laws of movement of the galvanic fluid "il resterait a en examner la nature, et à le comparer au fluide électrique: . . ." He concluded by admitting that several natural philosophers, particularly Volta, had done so and appeared to have proved that the galvanic fluid was electrical in nature. 57

Beginning in the fall of 1800, experiments with the Voltaic pile were performed at the Paris Ecole de Médecine by various natural philosophers. The accounts of these experiments published in 1800 included articles in the Magazin encyclopédique, the Bulletin des sciences de la Société Philomatique, and summaries of these articles translated into

⁵⁵ Ibid., pp. 42-43. "one can determine à priori."

⁵⁶<u>Ibid</u>., p. 48.

 $^{^{57}\}underline{\text{Tbid}}$, pp. 64-65. "It would remain to examine its nature and to compare it to the electric fluid."

German for Voigt's <u>Magazin für der neuesten Zustand der Naturkunde</u> and into Italian for Brugnatelli's <u>Annali di chimica</u>. 58

According to an article written by Pierre-Roland-François Butet de la Sarthe (1769-1825) for the <u>Bulletin des sciences de la Société</u>

<u>Philomatique</u>, Hallé and Pierre-Simon Laplace (1749-1827) performed experiments at the Paris Ecole de Médecine that established "l'identité des phénomènes de la pile . . . avec ceux des attractions et répulsions électriques."

In other experiments performed at the Ecole, Jean-Baptiste-Jacques Thillaye (1752-1822) used a pile to produce visible sparks, and Butet identified the silver terminal of the pile as being positively charged and the zinc terminal as being negatively charged. Together

Thillaye and Butet used the pile to decompose water and noted that the oxidation in their experiments always occurred at the positive terminal of the pile while hydrogen was always produced at the negative terminal.

A more detailed and systematic account of the experiments performed at the Ecole de Médicine was published in the Magazin Encyclopédique of nivôse an 9 (December 1800-January 1801). This unsigned article, probably written by Hallé, 61 describes experiments to determine

⁵⁸ For a summary of all these experiments see Pierre Sue, <u>Histoire</u> du galvanisme; et analyse des différens ouvrages publiés sur cette découverte, depuis son origine jusqu'à ce jour, 2 vols. (Paris: Chez Bernard, an 10-1802), v. 1, pp. 1-13.

Pierre-Roland-François Butet de la Sarthe, "Note sur le galvanisme, par le C. Butet," <u>Bulletin des sciences de la Société Philomatique</u> 43(vendémiaire an 9-Sept. and Oct. 1800):151. "established the identity of the phenomena of the pile . . . with those of electrical attraction and repulsion."

^{60&}lt;sub>Tbid</sub>.

⁶¹ This article, "Ecole de Médecine. Expériences galvaniques

the best arrangement of the pile and experiments to verify its effects on "corps bruts" and on animal bodies. Although the article is unsigned and contains no references to specific experimentors or publications, its author in a lone footnote revealed that "L'appareil de ces expériences est tenu journellement en activité dans les cabinets de l'Ecole de médecine, par le C. Thillaye fils, aide conservateur.

Divers savants, entr'autres les CC. La Place, Butet, etc."63
had concurred in the "vérification de faits qu'elles constatent."64 He also noted that several of the facts in these experiments had already been announced in the Bibliothèque Britannique's accounts of the experiments of "Volta, Nicholson, etc." However, because of "quelques différences qui, sans doute, ne sont qu'apparentes, nous ont déterminés à décrire la formation de notre pile avec plus d'exactitude que ne l'ont fait les auteurs de cet excellent recueil."65

vérifiées jusqu'à présent à l'Ecole de Médecine, au moyen de l'appareil imaginé par le D.r Volta," Magazin Encyclopedique (16 nivôse, an 9 or December 1800-January 1801):521-529, and an account by Hallé in Sue, Histoire, 1:3-12, are similar enough to have been written by the same person. However, there is one anomaly, if one assumed that Hallé wrote both articles. On pp. 2-3 in Sue, there is a footnote almost identical to the only footnote in "Expériences galvaniques," but which contains one very important difference, an extra line reading "Ces premières expériences ont eu lieu en floréal et en prairial de l'an 9." Unless this reference is in error, the experiments described by Hallé were made in April, May, and perhaps June of 1801 or months after the publication of "Expériences galvaniques."

^{62&}quot;Expériences galvaniques," pp. 521-523.

^{63 &}lt;u>Ibid.</u>, p. 522. "The apparatus for these experiments is held in activity daily in the cabinets of the Ecole de Médicine by citizen Thillaye, the son, <u>aide conservateur</u>. Many scholars, among them citizens La Place, Butet, etc."

 $^{^{64}\}underline{\text{Ibid}}$. "verification of the facts they [the experiments] had established."

⁶⁵ Ibid., "Several differences which, without doubt, are only

As the author noted, ⁶⁶ the account of these experiments added little to that which had already been published on the matter, but the concise and systematic relation of the three effects of the pile on corps bruts—the decomposition of water, the production of sparks, and the attraction or repulsion of an electrometer by the terminals of the pile ⁶⁷—could have only strengthened the position of those who argued that galvanic phenomena were electrical or chemical in nature.

The interest in German-speaking areas of Europe in the Voltaic pile and the proliferation of experiments with the Voltaic pile parallels the reception of the Voltaic pile in France. An announcement of the discovery of the Voltaic pile and of Nicholson and Carlisle's experiments with it extracted from Nicholson's Journal was published in the second 1800 volume of the Annalen der Physik. The editor's notes to this extract were predominantly in reference to articles on galvanism published in German journals prior to the discovery of the Voltaic pile and furnished no commentary of the galvanic decomposition of water. 68
This article was immediately followed by an account of Cruickshank's experiments 69 and an account of Henry's experiments, 70 both extracted

apparent, we have decided to describe the form of our pile with more exactitude than had the authors of this excellent journal."

^{66&}lt;sub>Tbid.</sub>, p. 524. 67_{Tbid.}, pp. 524-526.

⁶⁸ Nicholson, "Beschreibung des neuen electrischen oder galvanischen Apparats Alexander Volta's, und einiger wichtigen damit angestelten Versuche, von Will. Nicholson," <u>Annalen der Physik</u> 6(1800):340-359.

⁶⁹ Cruickshank, "Versuche und Beobachtungen über einige chemische Wirkungen der galvanischen Electricität, von W. Cruickshank zu Woolwich," Annalen der Physik 6(1800):360-368. The editor was probably Gilbert.

⁷⁰ Henry, "Versuche über chemische Wirkungen der galvanischen

from <u>Nicholson's Journal</u>. Like the first article, they contained no editorial commentary except for references to earlier articles on galvanism.

The only discussion of the English experiments or mention of local experiments in the 1800 volumes of <u>Annalen der Physik</u> occurred in a supplement included at the end of the second 1800 volume. Gilbert, in commenting on the experiments of Nicholson, Carlisle, Cruickshank, and Henry, questioned Nicholson's identification of the galvanic fluid as electricity:

Den englischen Physikern scheinen die Untersuchungen deutscher und französischer Naturforscher über den Galvanismus noch ganz unbekamt seyn. Kein Wunder daher, dass sie über die Identität oder Vershiedenheit desselben von der Electricität so leicht fortgehen . . . und die Identität beider als unbestritten ausgemacht, in den Ueberschriften ihrer Abhandlungen galvanisch oder electrisch annehmen. 71

Gilbert preferred to use the term "galvanische Electricität" that he believed indicated the "grosse Aehnlichkeit" between the two without giving their identity as "völlig ausgemacht." His caution was based upon the prevalent German approach to galvanism prior to 1800, typified by the ideas and researches of Humboldt and Johann Wilhelm Ritter (1776-1810). Ritter, like Humboldt, emphasized the chemical

Electricität, von William Henry zu Manchester," Annalen der Physik 6(1800):369-375.

^{71&}lt;sub>Gilbert</sub>, "Zusätze und Verbesserungen zu den Annalen der Physik," <u>Annalen der Physik</u> 6(1800):469. "English physicists appear to be yet wholly unaware of the researches of German and French natural philosophers on galvanism. No wonder that accordingly they so easily pass over its identity with or its difference from, electricity; . . . and have assumed the identity of both as undisputed, using galvanic or electric in their writings about their proceedings.

^{72 &}lt;u>Thid</u>. "great similarity" "completely settled."

aspects of galvanism and, because of these chemical aspects, was unwilling to identify galvanism as electricity.

Gilbert believed that continental physicists such as Fabbroni, Humboldt, and Ritter had just claims for the priority of the discovery of the galvanic decomposition of water and pointed out that prior to 1800 Fabbroni had reported the galvanic decomposition of water to the Academy of Florence in 1792, Dr. Ash of Oxford had reported the same to Humboldt in 1795, and Ritter had referred to the chemical nature of galvanism in an article published in the 1799 Annalen der Physik and to the galvanic decomposition of water in his Beyträge zur nähern Kenntniss des Galvanismus of 1800.73

The first account of Volta's discovery of the galvanic cell published in <u>Voigt's Magazin für den neuesten Zustand der Naturkunde</u> was contained in the summary of a letter from Marsilio Landriani (1751-1816?) to "Hofrath Dr. Mayer in Prag" communicated to Voigt by Ritter. Hofrath Mayer was probably Johann Mayer (1754-1807) of Prague, the author of several articles on galvanism. 74 Landriani's letter was one of the few announcements of Volta's discovery of the galvanic cell which was not transmitted via England. It describes Volta's "chain of cups" apparatus and contains no references to the experiments of Nicholson and Carlisle or to the galvanic decomposition of water. 75

⁷³Ibid., pp. 469-470.

⁷⁴Poggendorff, 2:93-94. Hofrath Mayer could also be Johann's brother Joseph Mayer (1752-1814) who taught at Prague beginning in 1800.

^{75&}quot;Auszug eines Schreibens des Hn. Ritters von Landriani, an Hn. Hofrath Dr. Mayer in Prag, über einige Versuche des Hn. Volta, die

However, in the same volume of Voigt's Magazin there were three other letters on the subject that did. Two of these letters were from Joseph Banks to Johann Friedrich Blumenbach (1752-1840). In the first letter, dated 13 May 1800, Banks described the construction of the Voltaic cell and the effects he considered to demonstrate that the cell produced an amount of electricity analogous to that stored in a weakly charged Leyden jar. In the second letter, dated 11 July, 1800, Banks described Nicholson and Carlisle's 76 experiments and the apparatus they used in the galvanic "decomposition of water." The fourth and last letter, dated 3 August, 1800, was from Dr. Ash of London to Blumenbach. In this letter, Edward Ash, identified by Humboldt as one of the first to discover the galvanic decomposition of water, described the discovery of the Voltaic cell and its ability to decompose water as having proved "die Idee die ich vor mehrern Jahren gegen Sie äusserte, dass die Decomposition des Wassers eine von den Hauptursachen der Phänomene beym sogenannten Galvanismus sey."78 Ash, without mentioning Nicholson or Carlisle, reported that "einige unserer genauesten Physiker"

Theorie der von Galvani entdeckten electrischen Ersheinungen in thierischen Körpern zu erklären. Aus der französichen Handschrift übersetzt und dem herausgeber vom Hn. Hofr. Mayer mitgeheilt," Magazin für den neuesten Zustand der Naturkunde mit Rücksicht auf die dazu gehörigen Hülfswissenschaften herausgegeben von Johann Heinrich Voigt 2(1800):215-219.

(Journal hereinafter referred to as Voigt's Magazin.)

^{76&}quot;Naturhistorische Miscellen. Aus Briefen an J. F. Blumenbach. 1. Ueber Hrn. Volta's electrische Säulen-Maschine, oder Galvanische Batterie," <u>Voigt's Magazin</u> 2(1800):292.

⁷⁷ Ibid., p. 293.

^{78 &}lt;u>Ibid.</u> "The idea that I expressed to you for many years that the decomposition of water is one of the essential phenomena with the so-called galvanism." Also <u>Supra</u>, p. 192.

had produced a "Funken" with a cell of 80 to 100 plates, detected that the silver terminal of the pile was negative and that the zinc terminal was positive in charge, decomposed water, and produced a change in the color of a litmus solution by making the solution part of the galvanic circuit. Ash also noted that depending on the nature of the conducting wires, either hydrogen and calcination or hydrogen and oxygen were produced from the galvanic decomposition of water and that these results occurred at some distance from each other. 79

Another announcement of the galvanic decomposition of water by the Voltaic cell was also published in the 1800 Zeitschrift für speculative Physik in the form of an extract from the Journal de Bruxelles.

The extract mentioned Volta's letter to Banks, Nicholson and Carlisle's experiments, and Dr. Garnett's demonstrations of them. 80 The editor labeled the pile itself as a new discovery and the decomposition of water with it as "nur eine neue und glückliche Modification der schon längst bekannten des Hernn Ritter, welchem die Ehre des ersten Erfinders gebührt."81

Indeed, Ritter had made a detailed examination of galvanic phenomena before 1800 and argued from his experiments that galvanism was a chemical phenomenon. He had published these experiments in his

 $^{^{79}}$ "Naturhistorische Miscellen," p. 294. "One of our more precise physicists."

^{80.} Machricht von neuen Entdeckungen über den Galavismus,"

Zeitschrift für spekulative Physik 1, Bk. 2 (1800):149-151. The Journal

de Bruxelles article was taken from Le moniteur which was in turn taken
from the Courier de Londres. Supra, p. 241.

 $⁸¹_{\underline{\mathrm{Ibid}}}$., p. 152. "only a new and fortunate modification of what has already long been known by Herr Ritter, to whom the honor of [being] the first discoverer is due."

Beyträge zur nähern Kenntniss des Galvanismus along with the report of the Institut National on galvanism. 82 In 1800 Ritter's attention turned toward experiments with the Voltaic cell, and, according to his own account and to some of his contemporaries, he had already accomplished the greatest part of the discoveries made by English experimenters before he had learned of them. 83 Despite Ritter's activity in galvanic investigation, his experiments with the Voltaic cell were not widely published in 1800.

The only reference to Ritter's experiments with the Voltaic cell published in the 1800 Annalen der Physik was in the supplement to the sixth volume. Although Ritter had not communicated his experiments to Gilbert, Gilbert was able to give a short account of these experiments by quoting parts of a letter from Ritter to Dr. Johann Horkel (1769-1846) of Halle. Which is letter, Ritter spoke of using a battery of sixty-four plates and of planning experiments with a battery of three hundred plates. Be not only reported the galvanic decomposition of water using the battery, but he also noted that "Es ist keine Flüssigkeit, die nicht

⁸² Johan Wilhelm Ritter, <u>Beyträge zur nähern Kenntniss des Galvanismus und der Resultate seiner Untersuchung</u>. Herausgegeben von J. W. Ritter, vol. 1, Bks. 1 and 2, (Jena: Friedrick Frommann, 1800).

Michael Friedländer, "Précis des expériences faites en Allemagne avec l'appareil galvanique de Volta; communiquées à l'Institut par le docteur Frudlander, de Berlin," <u>Journal de physique</u> 52(1801):102.

^{84&}lt;sub>Gilbert</sub>, "Zusätze und Verbesserungen," <u>Annalen der Physik</u> 6(1800):470.

⁸⁵ Ritter quoted by Gilbert in "Zusätze und Verbesserungen," Annalen der Physik 6(1800):470-471.

... ihre Luft gäbe" under the battery's influence. 86 Like Cruickshank, Ritter found that he could decompose and precipitate metals from acids using the Galvanic influence. He believed these phenomena to be exclusively chemical in nature, and therefore he concluded "ist es nicht Electricität." 87

Ritter's principal 1800 publication on galvanism and the Voltaic cell was published in Voigt's Magazin. In this article, dated from the 28th to the 30 September, 1800, Ritter took care to establish that although Nicholson had discovered the phenomena much earlier, he had discovered the galvanic decomposition of water independently and prior to his knowledge of the English experiments. According to Ritter, he first knew of the experiments of Nicholson, Carlisle, Henry, and Cruickshank on the 24th of September, when the proofs of letters to Blumenbach from Ash and Banks were sent to him prior to their publication in Voigt's Magazin. He had not actually read an account of the English experiments until 27 September when he received a "Nachricht" of the articles in Nicholson's Journal from Dr. Horkel.

Ritter noted that he had already performed most of the English experiments before the 24th and that his experiments were so similar to

 $⁸⁶_{\underline{\text{Ibid}}}$., p. 471. "There is no fluid that would not . . . give its air."

⁸⁷ Ibid. "it [galvanism] is not electricity."

⁸⁸ Ritter, "Volta's Galvanische Batterie; nebst Versuchen mit derselben angestellt von J. W. Ritter," <u>Voigt's Magazin</u> 2(1800):360.

⁸⁹Ibid., p. 359.

^{90&}lt;sub>Ibid., p. 360.</sub>

those of Nicholson, Carlisle, Henry, and Cruickshank that one might believe "wie sich Hr. D. Horkel gegen mich ausdrückte, die ersten fast nur für eine Wiederholung der letzern halten könnte." That is, if one did not know better, they might take his experiments as a continuation of the English ones. Ritter's experiments did greatly resemble the English ones, but there were important differences between his views on the subject and those published in England. Ritter did not believe that galvanism was an electrical phenomenon or that water was actually decomposed by the galvanic pile.

Using a pile or a galvanic chain, as he preferred to call it, of sixty plates, Ritter had tested the galvanic influence on his body and had also sought to produce the sparks reported by Nicholson (and others). 92 Although Ritter did report that the galvanic chain would produce flashes of light when touched to the eyes, 93 he noted that it could not produce sparks between two conductors. 94 Ritter considered his inability to produce sparks as evidence that galvanism was not electricity. However, like Humboldt before him, Ritter believed that the most striking difference in galvanism and electricity was in their ability to be conducted. He found that hot glass would conduct electricity but would not conduct galvanism. 95

<u>91 Thid.</u> "as Dr. Horkel expressed it to me, the first almost could be taken as a mere repetition of the last."

^{92&}lt;u>Thid.</u>, p. 361. Ritter pointed out that his term chain, agreed with Volta's term for the Voltaic cell.

^{93&}lt;u>Ibid</u>., pp. 361-365.

^{94&}lt;u>Ibid.</u>, p. 367. 95<u>Ibid.</u>, pp. 366-367.

Ritter repeated Nicholson's galvanic decomposition of water and reported that the galvanic influence did produce hydrogen and oxygen from water in the ratio of two-and-one-half to one. However, Ritter also mentioned that the volumes of the two gases were 1-2/3 cubic inches, which would yield a ratio of 3:2. He had arrived at the first ratio, two-and-one-half to one, by reasoning that 1/3 of the 2/3 of a cubic inch was due to impurities. He used 1/3 because a residue of nearly 1/3 the original amount was left after he had tested the gas for oxygen. Ritter assumed that since it did not unite with phosphorous, the residue probably originated from impurities of nitrogen (Stickstoff gas) dissolved in the water which could have avoided by boiling the water and subjecting it to the action of a vacuum pump. 96

Although Ritter did not doubt that the galvanic chain produced hydrogen and oxygen from water, he did doubt that water was decomposed in the process. This doubt arose from the separate production of hydrogen and oxygen at a distance from each other.

Die Producte der beyden Dräthe sind dieselben, die man den der sogenannten Zersetzung des Wassers erhält, Oxygen und Hydrogen. Jedem Atom entbundenen Oxygen muss ein Atom entbundenes Hydrogen correspondiren, und beyde machten in der Vereinigung vorher Ein Atom Wasser. . . . Kann sich aber das nemliche Atom Wasser in einem und dem nemlichen Augenblick zugleich an diesem und wieder an jenem Drathe befinden? Und doch müsste das der Fall seyn, wenn beyde Gasarten, beyde Stoffe, das Oxygen und Hydrogen, von einer wirklichen Zersetzung des Wassers herrührten. 97

⁹⁶ Ibid., pp. 373-374.

^{97 &}lt;u>Ibid.</u>, p. 380. "The product of both wires are the same when one obtains hydrogen and oxygen from the <u>so-called</u> (italics mine) decomposition of water. Each component atom of oxygen must correspond to a component atom of hydrogen and both made in conjunction an atom of water... Can the same atom of water in one and the same instant be at this

Thus Ritter argued that the production of hydrogen and oxygen from water were two processes, independent of each other and not connected with the decomposition of water. The alternative for Ritter, the rapid transmission of one of the gases through the water to another point before its release, was absurd. In order to demonstrate that no such transmission occurred and that the processes were indeed independent of each other, he sought to isolate the production of hydrogen from that of oxygen. He believed that he could do this by separating two quantities of water by an intervening fluid that would conduct the galvanic influence without itself producing gas. He determined that both the spirit of wine and sulfuric ether would transmit the galvanic influence without gas production, but only when they were free of water. After also rejecting concentrated alkalis because they produced gas when connected in a galvanic circuit, Ritter settled on concentrated sulfuric acid. 98

The apparatus he designed for his experiments consisted of a "V" shaped glass tube partially filled with concentrated sulfuric acid. By adding water to each leg of the "V" so that the acid intervened between the two quantities of water and inserting the wires connected to the galvanic chain in each leg of the "V," he found that he could indeed produce hydrogen and oxygen separately and that no bubbles of gas moved through the acid. 99 To further illustrate his point, he linked two straight tubes in series with a galvanic chain and added a layer of

and then that wire? And yet this must have been the case, when both gas species, hydrogen and oxygen, originate from a true decomposition of water."

^{98&}lt;u>Tbid., pp. 380-383.</u>

^{99 &}lt;u>Ibid</u>., pp. 384-385.

sulfuric acid and a layer of water to each. Hydrogen was produced in one tube and oxygen in the other. 100 According to Ritter's arguments, the decomposition of an "atom" of water certainly could not produce one component in one tube and the other in a different tube. Finally, he used a single tube containing a layer of acid and a layer of water and reported that, depending on its orientation to the galvanic chain, either hydrogen or oxygen was produced. 101 Ritter considered this experiment to be a demonstration that the production of either gas was independent of the other and certainly not dependent on the decomposition of water. 102 Thus he could transform water into either hydrogen, or oxygen, or both. In Ritter's words.

Es war mir also wirklich gelungen . . . darzuthun, dass die beyden entbundenen Gasarten, deren gewichtige Grundlagen man bis daher gewöhnlich als heterogene Bestandtheile eines und desselben Wassers angesehen hatte, keinesweges von einer Zersetzung des Wassers, wie man nach der neuern chemischen Theorie wohl glauben mochte, sondern durchaus von zwey ganz von einander verschiedenen Processen herrührte, deren jeder für sich isolirbar sey, und auf keine Weise mit dem andern zusammenhänge.103

Ritter also related other experiments including ones similar to those of Cruickshank in which he was able to precipitate copper, silver,

^{100&}lt;sub>Ibid.</sub>, pp. 385-386.

^{101&}lt;sub>Ibid., pp. 386-387.</sub>

^{102&}lt;sub>Ibid., p. 390.</sub>

¹⁰³_<u>Ibid.</u>, p. 385. "Thus I truly succeeded . . . in proving that both the gas species produced, whose significant basis one usually had considered until now as heterogeneous component parts [of] one and the same water, [in] no way [originated] from a decomposition of water as no doubt one liked to believe according to the new chemical theory, but on the contrary were produced through two processes wholly different from one another each of which is in itself capable of isolation and in no way connected with others."

and zinc from their solutions in dilute acid. Moreover, he noted that in certain cases the conducting wire oxidized and dissolved on one side and the metal in solution was deposited on the other wire. 104 Finally, Ritter discussed experiments on litmus similar to those of Ash 105 and experiments showing that impurities of water would allow even concentrated sulfuric acid to produce gas under the galvanic influence. 106

Although Ritter's claim for priority in his experiments, based on his contention that he independently made the greater part of the discoveries published by Nicholson, Cruickshank, Carlisle, and Henry before he read of them, must be taken on faith, it is certain that he firmly believed that galvanic phenomena were chemical, that he knew of the galvanic"decomposition of water, and that he was interested in the same phenomena as other natural philosophers of his time, including Ash, Humboldt, Fabbroni, and Volta.

Ritter's influence upon his contemporaries is difficult to gauge. Prior to 1801, there is little published evidence of his influence other than his own <u>Beyträge zur nähern Kenntniss des Galvanismus</u> and a few articles in German journals about his experiments. In a letter to William Babington (1756-1833), dated 17 December 1800, a Freiberg correspondent identified only as "Doctor G. M." described Ritter as "the principal galvanic discoverer here" and as having priority in important galvanic experiments. However, the correspondent then described Ritter's previous publications

^{104&}lt;sub>1<u>bid</u>., p. 393.</sub>

^{105&}lt;u>Ibid., p. 394.</u>

^{106&}lt;sub>1bid</sub>., p. 397.

as obscurely written, "little known and less noticed." The picture painted of Ritter in the letter is of an author "having neither enemies who were interested in bringing him into discredit, nor friends who were desirous of drawing him out of obscurity. . . ."107

On the other hand, Dr. Michael Friedländer (1769-1824), in a communication to the Institut National summarizing Ritter's experiments, pictured him quite differently.

M. Ritter, bien connu en Allmange par ses <u>Beitrage zur nahern</u> <u>kenntniss der galvanismus</u> n'en connoissoit que la première notice qui en a été donnée dans le journal de Bruxelles. Il avoit déja fait la plus grande partie des découvertes des savans cités plus haut [Nicholson, Carlisle, Cruickshank, and Henry], lorsqu'il les a reçues. 108

There is one important difference in Ritter's account of his experiments and in the accounts of his experiments made by others. In the articles published in 1800, Ritter did not explain how the galvanic fluid could produce gases from water; he only claimed that the galvanic production of hydrogen and oxygen from water were independent processes and did not result from the decomposition of water. He did note that the gas produced was dependent on which end of the galvanic chain was connected to water and which one was connected to the acid layer.

^{107&}quot;Extract of a Letter from Doctor G. M. to Dr. William
Babington, Dated Freiberg, Dec. 17, 1800. On the State of Galvanism and
Other Scientific Pursuits in Germany. Communicated by Dr. Babington,"
Nicholson's Journal 4(1800):512.

¹⁰⁸ Michael Friedländer, "Précis des expériences faites en Allemagne," <u>Journal de physique</u>, 52(1801):102. "Mr. Ritter, well known in Germany for his <u>Beitrage zur nahern kenntniss der galvanismus</u> only knew about the first notice that had been given in the journal of Brussels. He had already made the greater part of the discoveries of the scholars cited above, when he learned of them." (The <u>Journal de Bruxelles</u> article was published 21 August 1800.)

When the zinc end was connected to acid and the silver end to the water, only hydrogen was produced. When the zinc end was connected to water and silver to acid, no trace of hydrogen was produced. 109

Although Ritter offered no published explanation for these results in 1800, according to other writers of the time Ritter believed that the gases produced in these experiments were compounds of the galvanic fluid and water. For instance, Dr. Friedländer wrote that Ritter

In G. M.'s letter to Babington of December 17, 1800, he wrote:

the rationale of this phaenomenon is as yet in obscurity. One philosopher accounts for it thus; that water + light gives oxygen. . . , and water + heat hydrogen Others propose the following; that oxygen gas is water + positive electricity; and hydrogen gas, water + negative electricity.

¹⁰⁹ Ritter, "Galvanische batterie," <u>Voigt's Magazin</u> 2(1800): 389.

¹¹⁰ Friedlander, "Précis des expériences faites en Allemagne,"

Journal de physique 52(1801):105. "draws the conclusion, that the two airs cannot be regarded as the constituent parts of water, but as two materials that are produced by a part of the water combined with the galvanic fluid. . . ."

^{111&}quot;Extract of a Letter from Dr. G. M. to Dr. William Babington," Nicholson's Journal 4(1801):513. Note that Babbington did not identify Ritter with either of those accounts. A more modern writer, J. R. Partington, in his History of Chemistry, 4:21, cites Ritter's article in Voigt's Magazin 2(1800):356 and Babbington, Nicholson's Journal 4(1801):511, saying "he thought the gases are compounds of electricity and water: H = water + E, oxygen = water - E." No such claim exists in Die Begründung der Elektrochemie und Entdeckung der Ultravioletten Strahlen von Johann Wilhelm Ritter. Eine Auswahl aus den Schriften des romantischen Physikers, ed. with commentary by Armin Hermann, Ostwalds Klassiker der Exacten Wissenschaften n.s., No. 2 (Frankfurt am Main: Akademische Verlagsgesellschaft, 1968) or Robert J. McRae, "Johann Wilhelm Ritter," DSB., 11:473-475, or in Wilhelm Ostwald, Elektrochemie: Ihre Geschichte und Lehre (Leipzig: Veit & Comp., 1896), pp. 67-71, 158-5, 162.

Thus Ritter's contemporaries differed in their interpretation of his work and of his influence. This difference of opinion also exists among historians. It has been suggested that the crux of this difference is in Ritter's relationship to German romantic Naturphilosophie. 112 Naturphilosophs such as Friederich Wilhelm Joseph von Schelling (1775-1854), Ritter's friend, and the editor of the Zeitschrift für spekulative Physik, had found Ritter's writings up to 1800 supportive of the dynamic theory of nature integral to Naturphilosophie. If Ritter was a Naturphilosoph and a romantic, a word of elusive meaning, it should not diminish his importance in the history of science. The idea that water and electricity, through their positive and negative polarities, might be the basis of certain chemical compounds would fit the schema of the Naturphilosoph as described by both historians and Naturphilosophs themselves. 114 Moreover, the idea that electricity plus water yielded gas fit with one of the traditional reactions to the chemical theories of Lavoisier by chemists who accepted the phlogiston theory. 115 Other German physicists, such as Gren and Lichtenberg, might

¹¹² See McRce, "Ritter," <u>DSB</u>., 11:473-475, and also Dorothee Hüffmeier, "Johann Wilhelm Ritter, Naturforscher oder Naturphilosoph?" <u>Sudhoffs Archiv für Geschichte der Medizin und der Naturwissenschaften</u> 45(1961):225-234.

¹¹³ Friederick Wilhelm Joseph Von Schelling, "Allgemeine Deduction des dynamischen Processes," <u>Schelling's Zeitschrift</u> 1, Bk. 2(1800):68-72, 110-111.

¹¹⁴ In Addition to sources already cited, see Henrik Steffens (1773-1845), "Recension der neuern naturphilosophischen Schriften des Herausgebers von Dr. Steffens, aus Coppenhagen," Schelling's Zeitschrift 1, Bk. 1(1800):45-58 and Barry Gower, "Speculation in Physics: The Eistory and Practice of Naturphilosophie," Studies in History and Philosophy of Science 3(Feb. 1973):301-356. For a discussion of the interpretation of Romanticism and Science, see David M. Knight, "The Physical Sciences and the Romantic Movement," History of Science 9(1970):54.

^{115&}lt;sub>Supra</sub>, pp. 115-126, 165-173.

have suggested such an idea, but Ritter did not publicly propose it in $1800. ^{116}$

Voigt argued from Ritter's experiments that because vital air and inflammable air ("entzündbare Luft") could be produced separately and at some distance from each other by connecting one or several bodies

^{116&}lt;sub>Supra., p. 268.</sub>

¹¹⁷ Johann Heinrich Voigt, "Nachschrift des Herausgebers," <u>Voigt's Magazin</u> 2(1800):400. "lectures upon experimental physics."

 $[\]frac{118}{\text{Ibid.}}, \text{ p. 401.}$ "Ritter, my one time pupil and since then established friend, who, as one knows from his classic writings is very knowledgable in this domain, to undertake this task."

 $[\]frac{119}{\mathrm{Tbid}}$. "The previous account is the fine fruit of his work and his sagacity."

of water in series with a Voltaic battery, water was not decomposed by the action of the Voltaic cell. Indeed, Voigt believed that water was an element and incapable of being decomposed, and instead that the galvanic fluid was decomposed. Thus Voigt used Ritter's results to illustrate his own theory "des Feuers" in which he conceived of fire as a compound of two component parts ("Bestandtheilen") in conflict that he depicted as "+ F u. -F."

Voigt's view of nature as a dynamic and interlocking series of polar phenomena, such as positive and negative electricity, heat and light, acidicity and alkalinity, and the opposition between the two poles of a magnet, 122 can be described as "romantic" or by the term Naturphilosophie. If applied to Voigt, these terms would only reflect that Voigt assumed nature to be unitary and dynamic and that he sought to relate the phenomena of galvanism with other diverse phenomena of this unitary nature in terms of recurring polarities. In doing so, he appealed to the recently published discovery of Herschel on the nature of light to suggest that the Voltaic battery was an apparatus which could also be used to separate sunlight ("Sonnenstrale") into its two component parts, heat and light. That is, Voigt considered the production of inflammable air by the Voltaic battery to result from the union of a small portion

 $^{120\}underline{\text{Lbid}}$., pp. 402-403. (Voigt also uses the term "wasserstoff" occasionally.)

¹²¹ Ibid., p. 402. "+F and -F."

 $^{122\}frac{\mathrm{Tbid}}{\mathrm{Tb}}$, p. 403. Voigt uses the two poles of a magnet as an example of the polarity in nature.

of water with heat and the production of vital air to result from the union of a small portion of water with light. 123

Thus Voigt identified the two imponderable components of the galvanic fluid as being the two components of sunlight, a "wärmende Theil" dependent upon or originating in the "Expansivkraft" of light and a "leuchtende Theil" dependent upon or originating in the "Vibrationen" of light. These two components were essentially the same as those of fire, and he depicted them as such with -F and +F. Voigt's explanation of the metal galvanic battery went beyond relating it to fire, sunlight and their mutual components. He explained phenomena associated with galvanism in a manner consistent with other chemical and physical phenomena that he believed to be related to the dynamic process of life. 124

Voigt could explain the greater weight of vital air produced in Ritter's experiments by assuming that a smaller amount of light (than heat) would serve to unite with water. Since water was the only ponderable component of either of the compound gases produced in Ritter's experiments, if more water was united to light, the amount of vital air produced would be heavier than the amount of inflammable air produced. And it was. Libble He further explained that the "warmenden Bestandtheile" was separated at the silver terminal of the battery, because silver was a better conductor of heat than was zinc. Likewise, the "leuchtenden Bestandtheile" was separated at the zinc terminal, because zinc, as evidenced by the burning of zinc or of a zinc amalgam with a very bright

^{123&}lt;sub>Ibid.</sub>, pp. 402-403.

¹²⁴ Ibid., p. 403.

^{125&}lt;sub>Ibid., p. 404.</sub>

light, had a stronger relationship with light than had silver. 126
Voigt also pointed out that when these two compound gases, inflammable air and vital air, were ignited together, the original components were separated out and produced. That is, the inflammation of the two airs produced heat, light, and water. 127

Finally, Voigt drew an analogy between the action of the Voltaic battery and an important life process, the production of vital air by plants. He suggested that the Voltaic battery, like plants, combines one part of the sun's rays, light, with water to produce vital air. 128 From this analogy he concluded:

Ob nun auch in Thierreich ein ähnlicher Process vorgehe, davon kann kaum die Frage seyn, zumal wenn mann die Rittersche Schrift: Beweiss, dass ein beständiger Galvanismus den Lebensprocess in Thierreich begleite-mit dem Geiste liest, in welchem sie geschrieben ist! 129

In his postscript Voigt cited the experiments of Robertson from the September issue of the <u>Journal de Paris</u>, ¹³⁰ and following his postscript he gave a short account of Robertson's "galvanometer." ¹³¹ Voigt described the rest of Robertson's experiments as containing nothing else new. ¹³² Because many of the ideas that Voigt advocated,

^{126&}lt;sub>Ibid.</sub>, pp. 404-405. 127_{Ibid.}, p. 402. 128_{Ibid.}, p. 405.

^{129 &}lt;u>Ibid.</u>, pp. 408-405. "One can scarcely ask the question whether or not a similar process exists in animals when one reads Ritter's writings with the spirit, in which they are written: [they] prove that continuous galvanism balances the life process in animals!

¹³⁰ Ibid., p. 404.

^{131&}lt;sub>Voigt</sub>, "Nachricht von einem Galvanometer," <u>Voigt's Magazin</u> 2(1800):409-410.

^{132&}lt;sub>Ibid., p. 409.</sub>

including the elemental nature of water and the compound nature of imponderable fluids, were very similar to the ideas that had been important to phlogiston theory for the previous two decades, one might apply a similar verdict, containing nothing new, to Voigt. Moreover, although his ideas are explicit and they contain none of the vague abstractions that have supposedly characterized the writings of others supporting Naturphilosophie, Voigt's utilization of the idea of polarity bears a striking resemblance to the "romantic" writings of the Naturphilosophs of his own time. Despite the possibility that Voigt's ideas are less than original, Voigt's writings influenced Ritter to the extent that Ritter, because of Voigt's insistence on the ability of the galvanic cell to produce light, reexamined the galvanic apparatus in this respect and then changed his original opinion that the Voltaic cell did not produce fire. 133

Other than the accounts of Ritter and Voigt's experiments and the references to Ritter's experiments, there was little published in 1800 about the Voltaic cell or experiments with it. The only other mention in the 1800 Annalen der Physik of German experiments was a short reference to the experiments of Sigismund Friedrich Hermbstädt and to experiments made in Halle with a cell of 200 plates. According to Gilbert, Hermstädt had repeated the experiments with the Voltaic cell and had established that water and acid were decomposed by the galvanic influence. Gilbert promised an account of the experiments made in Halle with "einer Säule von 200 Lagen, in den flogenden Heften," but no account followed in the next

¹³³ Ritter, "Fernere Versuche mit Volta's Galvanischer Batterie, angestellt von J. W. Ritter," <u>Voigt's Magazin</u> 2(1801):495-496.

volume of Annalen der Physik. 134 However, in 1801, Gilbert did outline experiments that he had made in conjunction with Horkel with a cell of 150 plates, some of which may have been performed in 1800. 135

One should not mistake the delay in publication for a lack of interest. Letters and articles published in 1801 reveal that there was a great interest in experiments with the Voltaic cell in Germany in 1800. In a letter to Gilbert dated Brieg, November 1, 1800, Christian Heinrich Müller (1772-1849) related that he had conducted Voltaic experiments in Breslau with a cell of 600 pairs of plates, constructed with the help of "Herr Münzwardeins Unger." After Herr "Mechanikus Klinger" and "Herr Apotheker Paricius" had prepared the necessary instruments and chemicals, Müller reported that he had conducted experiments decomposing water, dissolving alkalis, earths and acids, precipitating metals from acids and studying the gases given off in the various processes. He also mentioned experiments on animals. Müller closed his letter announcing plans for further experiments and requesting that platina wire be sent to him because it could not be found in Breslau. 136

In another letter to Gilbert written on 26 September 1800,

Carl Wilhelm Böckmann (1773-1821) professor of physics at Carlsruhe,

described experiments that he had conducted after reading "mit grossem

^{134&}lt;sub>Gilbert</sub>, "Zusatze und Verbesserungen," <u>Annalen der Physik</u> 6(1800):472.

^{135&}lt;sub>Gilbert</sub>, "Beobachtungen über die Voltaische Säule and deren Wirkungen, besonders über ihre Funken, vom Herausgeber," Annalen der Physik 7(1800):158.

¹³⁶ Christian Heinrich Müller, "Auszug aus einem Briefe des Hrn. Heinr. Müller in Brieg an den Herausgeber," Annalen der Physik 7(1801): 134-135.

Interesse . . . die wichtigen Nachrichten von der galvanischen

Electricität" in the Annalen der Physik. Böckmann had used Voltaic cells of nine, twenty four, and sixty plates and produced hydrogen and oxygen in a ratio of three to one by volume. 137 He had also connected six or twelve cups in series with a Voltaic cell, noting that hydrogen and oxygen were produced in each. 138 When he used iron wire instead of gold, he reported that hydrogen was produced at one end and the wire was oxidized at the other. 139 Böckmann noted that the smell of nitric acid accompanied the passage of the galvanic discharge through water and through "Sperrwasser." He speculated that "wird vielleicht durch diese Art von Electricität, welche an dem Drahte hinströmt, die umgebende atmosphärische Luft leichter als sonst gewöhnlich, in Salpetersäure umgewandelt?" 140

When Böckmann tried a gold wire at the non-silver terminal of the pile, he observed that the surface of the silver often became covered with a dark brown oxide, whereas the other end of the pile did not. 141 Finally, he attempted to report the effects of the cell on his own body. When he connected the cell to his ears and eyes he was able to see the

¹³⁷ Carl Wilhelm Böckmann, "Auszüge aus Briefen an den Herausgeber. 2. Von Herrn C. W. Böckmann", Annalen der Physik 7(1801):242-243.

¹³⁸ Ibid., pp. 243-244.

¹³⁹ Ibid., p. 245.

 $[\]frac{140}{\text{Lbid.}}$, pp. 245-246. "Perhaps in this way the surrounding atmospheric air, lighter than usual, is changing into nitric acid by the electricity, which streams out of the wire."

¹⁴¹ Ibid., p. 246.

"electrischen Blitze," but then explained "Ich könnte Ihnen noch mancherlei sonderbare Effecte beschreiben!" 142

Christian Heinrich Pfaff (1773-1852), one of several brothers known for their activities in natural philosophy or mathematics, wrote Gilbert from Kiel on 3 December 1800 explaining that his interest in the English experiments published in the Annalen der Physik and in Ritter's experiments published in Voigt's Magazin had led him to construct a pile of sixty plates. With it he produced "alle die Erscheinungen, die von andern Physikern beobachtet worden find, in ausfallendem Grade."

Initially he sought "die Analogie mit der Electricität in ihrem ganzen Umfange auszumitteln."

Pfaff differed with Ritter in this respect and argued that, unlike Ritter, he had "da Aehnlichkeit entdeckte, wo sie Diversität hinausbrachten."

The first similarity in the electric and galvanic fluid that he reported was that with a "Batterie" of fifteen plates, "kleine Funken von einem glünzend weissen Lichte" was produced, and that with a battery of twenty plates, it became quite apparent. However, he believed that the best analogy between electricity and galvanism was "ein gleiches

 $[\]frac{142_{\hbox{\sc Ibid.}}}{\hbox{\sc Ibid.}}$, pp. 247-248. "I could still describe many peculiar effects to you!"

¹⁴³ Christian Heinrich Pfaff, "Auszüge aus Briefen an den Herausgeber. 3. Von Herrn Professor C. W. Pfaff," <u>Annalen der Physik</u> 7(1801):247-248. "All the results that other physicists have observed, in striking degree."

¹⁴⁴ Tbid., p. 248. "to determine the analogy with electricity in its [galvanism's] every circumstance."

 $¹⁴⁵_{\mbox{\sc brought}}$. "indeed found similarities, where others brought out differences."

¹⁴⁶ Ibid., pp. 248-249. "a small fire from a glowing white light."

Verhältniss beider gegen verschiedne Körper in Rücksicht auf ihre Durchleitung oder Nichtdurchleitung durch dieselben." Although Ritter had reported experiments demonstrating a difference between the ability of hot glass to conduct electricity and galvanism, Pfaff claimed that he found experimentally that hot glass did not conduct either very well. Therefore, Pfaff concluded that the Voltaic battery was analogous to a "schwach geladnen Leidener Flasche." 149

Having assumed the galvanic effect to be electrical, Pfaff sought then the laws that governed its production. He believed "ohne Zweifel" that it was a chemical process. In order to demonstrate this conclusion, he used different fluids to moisten the pile and found that the pile worked better in a solution of salt (Kocksalz) then in one of vegetable or mineral alkali. 150 Although Pfaff had not tried acids, he expected them to likewise "weniger wirksam sind." He based this expectation on his own electro-chemical theory: that alkalis "das -enthalten, und in vorzüglicher Menge hergeben," while "Sauren das +, und Neutralsalze, (die bekanntlich in diesen Versuchen zerstezt werden),

 $[\]frac{147}{\text{1bid.}}$, p. 249. A like relationship of both in comparison with bodies in respect to their conduction or nonconduction through the same."

^{148&}lt;sub>Ibid.</sub>, pp. 249-250.

¹⁴⁹ Ibid., p. 250. "weakly charged Leyden jar."

¹⁵⁰ Ibid., p. 251. "without [a] doubt."

¹⁵¹ Ibid., pp. 251-252. "be less workable."

^{152 &}lt;u>Ibid</u>., p. 252. "contain minus (-) and in predominating quantities."

das + -."¹⁵³ Although Pfaff is not explicit on this point, he implies that the chemical production of electricity in galvanic phenomena depends upon the ability of the fluid used in the galvanic cell to provide both positive and negative electricity. Fluids such as water, neutral and "Mittelsalze" having a balance of positive and negative are therefore more "wirksam" in the galvanic cell. According to Pfaff, if an acid solution (+) is used, the water in the solution must provide the necessary negative, and if an alkaline solution (-) is used, the water in the solution must provide the balance of positive and negative capable of producing galvanic electrity. Pfaff believed that he could even feel the difference in the positive and negative ends of the battery. ¹⁵⁴

He repeated "Ritter's sinnreiches Verfahren" in which two bodies of water were connected in series so that one produced only hydrogen and the other only oxygen. 155 He also confirmed "Ritter's schöne Versuche über den positiven und negativen <u>Lichtzustand</u>, so wie über die <u>Farben</u>, "156 but he was unable to reproduce the "Blitzerscheinung" that Ritter had reported for a weakly charged Leyden jar. In other words, Pfaff confirmed all the reported similarities between electricity and galvanism but was unable to confirm any of their reported diversities.

^{153 &}lt;u>Thid.</u> "acids [contain] the plus (+), and neutral salts, (that are known be decomposed in these experiments,) [contain] plus-minus (+ -)."

^{154&}lt;sub>Ibid</sub>.

¹⁵⁵ Ibid., p. 253. "ingenious process."

^{156 &}lt;u>Thid.</u> "Ritter's beautiful experiments on the positive and negative states of light, as well as on colors."

¹⁵⁷ Ibid. "Appearance of a spark."

Accompanied by Dr. Horkel, Gilbert had conducted experiments with the Voltaic cell in 1800. 158 Because he did not publish his experiments with the cell until 1801, it is difficult to determine which experiments were conducted in 1800 and which experiments were conducted after 1800. However, the general tone of his article reveals that he was concerned with the reports that the Voltaic cell could produce an electric spark and that he had sought to resolve the difference in the experiments of Nicholson and Ritter on this matter. 159 Much of his article is devoted to a description of his initial difficulty in constructing a strong cell, a difficulty that he resolved only with the help of a friend with a talent for mechanics, Herr Schimming of Danzig. 160

Although the pile was Volta's discovery, the English experiments with the pile put Italian natural philosophers on the same footing with other continental natural philosophers in replying to, expanding upon, and reporting the English developments. Volta himself was informed of the English discovery of the galvanic decomposition of water in a letter dated 17 August 1800, from Marsilio Landriani in Vienna. Landriani had, in turn, learned of the English experiments from Nikolas Josef Jacquin (1727-1817), professor of chemistry and botany at the Medical faculty of Vienna. 161 In Landriani's letter to Volta, he suggested that the

¹⁵⁸Gilbert, "Beobachtungen über die Voltaische Säule," Annalen der Physik 7(1801):158.

¹⁵⁹ Ibid., pp. 158-160.

¹⁶⁰ Ibid., pp. 161-163.

¹⁶¹ Landriani to Volta quoted from Opere di Alessandro Volta ed. nazionale, vol. 2, pp. 3-4.

decomposition of water could be used as a means of determining the power of the Voltaic pile, and he described an instrument to do so. 162 His suggestion is similar to the ideas of Haldane and Robertson.

Volta replied to Landriani on 22 September of the same year and indicated that he had read initially of the English discoveries around the last of August in "un foglio periodico de Parigi intitolato le Moniteur num. 329." Although Volta termed the calcination of one wire and the production of inflammable air at the other "un fenomeno inaspettato," he then proceeded to explain to Landriani that Nicholson's discovery was not wholly new, and that he himself had not been very far from such a discovery in that his experiments would have soon led him to it. he had noticed in the previous winter the phenomena of the oxidation or calcination of the metal plates and the production of many bubbles. he Moreover, Volta wrote that his "collega e amico" Professore BRUGNATELLI" also had brought the chemical action of the pile to his attention in April. Volta also mentioned in his letter the "belle sperienze dei celebri Fisici Olandesi DEIMAN e TROOSTWICH."

^{162&}lt;sub>Ibid</sub>., pp. 4-5.

¹⁶³ Volta, "Lettera del Prof. Alessandro Volta al Consig. Marsilio Landriani," <u>le Opere de Alessandro Volta</u>, vol. 2, p. 7. "A Parisian newspaper, number 329 of <u>le Moniteur.</u>"

^{164 &}lt;u>Ibid</u>., p. 6. "an unexpected phenomena."

¹⁶⁵ Ibid., pp. 7-8.

^{166&}lt;sub>Ibid., p. 8.</sub>

 $[\]frac{168}{\text{Lbid.}}, \text{ p. 9.}$ "beautiful experiments of the famous Dutch physicists, DEIMAN and TROOSTWIJK."

There is no reason to disbelieve Volta; he certainly knew the experiments of Van Marum, and probably he knew long before 1800 those of Deiman and Paets van Troostwijk concerning the electrical decomposition of water. His friend and colleague, Brugnatelli, had written on the electrical decomposition of water in 1795 and had also discussed the electrical dedomposition of water in his Annali di chimica prior to 1800. In addition, the production of bubbles and the oxidation of metal in Volta's chain of cups are prominently visible phenomena and had been observed in analogous experiments by Fabbroni, Ash, Ritter, and Humboldt even before the invention of the pile. Although Volta could have easily discovered the phenomena reported by Nicholson and Carlisle, he did not because the matter of chemical action was of secondary importance and interest to him. Volta intended his pile as a proof that galvanic phenomena were electrical in nature and that they could be excited merely by the contact of different conductors. Because he considered the pile to be solely an electrical device, chemical phenomena were of secondary importance in the action of the pile to Volta. In contrast, Brugnatelli seized upon the chemical implications of the pile, because he believed electricity to be in the realm of chemical phenomena.

Brugnatelli had written Volta on 26 April 1800, according to Volta's account, and reported that he had found that the use of alkaline solutions in Volta's "chain of cups" was impractical. When he has used oxymuriate of soda, it was changed into soda after standing in contact with the zinc. Moreover, when he used salt solutions in the cups, they

were changed into alkaline solutions, and the free soda could be seen rising up the metal arcs in the form of salt crystals. 169

Thus, Volta knew of the chemical action of the pile in May of 1800. However, he offered no experiments on the subject to scientific journals, nor did he discuss it in writing with anyone until he wrote Landriani in September, some four months later. The publication in Italy of Volta's discovery of the pile further reveals Volta's inaction on the matter and perhaps his disinterest in the chemical phenomena associated with the pile.

In his letter of the 26th of April, Brugnatelli had also asked Volta to send him the first part of the memoir describing his new electrical experiments, because he intended to publish it as the lead article in the eighteenth volume of the Annali di chimica, and he needed enough time to prepare it for printing. Although Brugnatelli did not specifically ask for a description of the pile, he did write in the very next sentence that he kept one handy at all times and that it aroused his interest whenever he saw it. 170

Volta did not write Brugnatelli on the matter until after the 22nd of September, resulting in another four-month delay. In his letter to Brugnatelli, Volta disclosed that in lieu of a description of his new apparatus, he was sending him Landriani's letter of 17 August 1800 and his own letter written in answer to it. 171 In his letter, Volta noted

^{169&}quot;1139 Luigi Valentino Brugnatelli al Volta. Pavia, 26 Aprile 1800," <u>Epistolario di Alessandro Volta</u>: vol. 4, 1800-1805, ed. nazionale (Bologna: Nicola Zanichelli, 1953), pp. 1-2.

¹⁷⁰ Ibid., p. 1.

¹⁷¹ Volta to Brugnatelli, Opere de Alessandro Volta, ed. nazionale,

that Landriani's letter contained an account of "la scoperta di alcuni fenomeni chimica mirabilissimi" made with his apparatus that

per altro non debbono comparirvi del tutto nuovi, dono l'osservazione che faceste, son ora cinque mesi, e ch'io avea fatta gia prima, come vi comunicai a voce, della pronta decomposizione del sal comune, e di altri sali disciolti nell'acqua, in cui pescano i due metalli dissimili, p.e. rame e zinco, e di detto apparato, e della cotanto promossa termossidazione di esso zinco. 172

Brugnatelli printed Volta's short letter and the enclosures to it as the first article in the eighteenth volume of Annali di chimica. In his only note to the letters, Brugnatelli explained that he had noticed that when the "chain of cups" contained oxymuriate of soda and water, the soda was decomposed. In addition, he had noticed that a white jelly was formed on the zinc arc. Believing this jelly to be oxymuriate of zinc, he had tested it only to discover that it was oxycarbonate of zinc. Brugnatelli further reported similar results with oxymuriate of marine salt. 173 He did not point out, however, that he had written to Volta about the chemical action of the "chain of cups" on the 26th of April, long before Volta had claimed to have first noticed the chemical action of his apparatus.

^{2:3} or "Lettera del Prof. Alessandro Volta al Prof. Brugnatelli sopra alcuni fenomeni chimici ottenuti col nuovo apparecchio elettrico," Annali di chimica 18)1800):3-4.

^{172.} Volta al Brugnatelli, "Opera 2:3 or Annali di chimica 18 (1800):4. "the discovery of some notable chemical phenomena." "however ought not [to have] appeared wholly new, since I already made the observations first, some five months ago, and which I related to you in person, that the rapid decomposition of common salt and of other salts dissolved in water, in which dissimilar metals are immersed, for instance, copper and zinc of the said apparatus, and which at the same time promoted so much oxidation of the zinc."

^{173,} Lettera del Volta al Brugnatelli, Annali di chimica 18(1800): 14-15 note.

If Volta had conducted experiments on the chemical action of the pile, why did he not communicate them to Brugnatelli and note that he had received a letter from Landriani on the same subject? The answer is that he did not because he had not considered the matter. Volta was aware that the pile exhibited chemical action, but not that it decomposed water into gases. When he fully learned of the chemical action of the pile from others, he could only write that he had already noticed its chemical effects, and that he soon would have discovered that it decomposed water. When this reply is considered in conjunction with Volta's inactivity for four months on the subject, it becomes an implicit admission on his part that he did not investigate the chemical phenomena associated with the pile. In fact, he was disinterested in the chemical aspects of his pile, and probably he would not have discovered soon that it decomposed water. Such an admission is consistent with Volta's interest in electrical phenomena and his struggle to prove his contact theory of electricity. Chemical phenomena were of secondary value in this struggle. 174

On the other hand, Brugnatelli, who was interested in chemical phenomena, used Volta's discovery as an argument for his very own theory of the chemical nature of electricity. Brugnatelli believed electricity to be an acid, the <u>ossielettrico</u>, a view that unified the long known acidic phenomena connected with electricity with Lavoisier's conception of an acid as a substance that oxidized other substances. Thus

¹⁷⁴ George Sarton discusses this aspect of Volta's interest or disinterest in "The Discovery of the Electric Cell," <u>Isis</u> 15(1931):126. Sarton wrote, "Volta gave a purely electrical theory of his pile, the 'contact theory.' He did not pay attention to the chemical changes."

Brugnatelli accepted galvanism as an electrical and chemical phenomenon. In his arguments for the <u>ossielettrico</u>, Brugnatelli pointed out that, like Henly, "Gli Staliani lo riguardarono come <u>flogisto</u> o almeno come un fluido ricco di questo supposto principio," hale others such as Gardini, working in the context of the antiphlogistic theory, had thought electricity "un composto di calorico e flogogeno (idrogeno v.s)." However, he believed that the odor, taste, and action of electricity revealed it to be an acid. Not only could it decompose water, "come hanno osservato VOLTA e NICHOLSON," but it was capable of dissolving metals and carrying them "considerabili distanze" and depositing them "sopra altri metalli." 178

The only other article on the Voltaic apparatus in the 1800 issue of Annali di chimica was an extract of an article from the Magazin encyclopédique relating the experiments with the pile, performed at the Paris school of medicine by Thillaye, Butet, and Hallé. The article included the experimental verification of the ability of the pile to decompose water, to produce sparks, to affect an electrometer, and to affect the human body as reported by Nicholson, Carlisle, and others. 179

¹⁷⁵ Brugnatelli, "Osservazioni chimiche sopra l'ossielettrico. Di L. Brugnatelli," <u>Annali di chimica</u> 18(1800):136. "The Stahlians regarded it [electricity] as phlogiston, or at least as a fluid rich in this supposed principle."

^{176 &}lt;u>Ibid</u>. "a compound of caloric and hydrogen". By Gardini, Brugnatelli probably referred to Giuseppe Francesco Gardini (1740-1816).

¹⁷⁷ Ibid., p. 138. "as Volta and Nicholson have observed."

¹⁷⁸ Ibid. "considerable distances" "on other metals."

^{179&}quot;Esperienze galvaniche verificate finora alla scuola di medicina per mezzo dell' apparecchio immaginato dal Prof. Volta," Annali di chimica 18(1800):175-185. Supra, pp. 256-258.

In addition to the article published in <u>Annali di chimica</u> on galvanism and the Voltaic apparatus, Volta's letters reflect the state of Italian investigation of the matter. His correspondence on the matter was mainly confined to Brugnatelli and Landriani in 1800. Landriani had known of Volta's discovery in early May, probably through reading of it in the <u>Philosophical Transactions</u>. On May 8, 1800, he wrote Volta that he had constructed a chain of cups, but that instead of cups he had used a box of excellent wood, lacquered and divided into compartments so that the metal arcs rested on the dividing walls. He reported that with this apparatus he had verified all the phenomena which Volta had described, and that he found the results surprising. He further explained that he intended to build a pile of thirty-six plates of zinc and silver and also to test nickel and cobalt for their ability to generate electricity by contact. 180

Landriani also confessed that although he had read Volta's memoir in the "Transaz," he still did not completely understand the theory involved. Nolta wrote him in return sometime after July and sent him a corrected memoir that he had published in the Annali di chimica explaining the contact theory. 182

In a letter to a noted publisher, Johann Ambrosius Barth (1760-1813), Volta reviewed the published descriptions of his pile and

^{180&}lt;sub>"1141</sub>. Marsilio Landriani al Volta. Vienna, 8 Maggio 1800," Epistolario di Alessandro Volta, ed. nazionale, 4:5-6.

¹⁸¹ Ibid., p. 6.

^{182&}quot;1142. Volta a Marsilio Landriani. Anteriore al Luglio 1800," Epistolario di Alessandro Volta, ed. nazionale, 4:7.

the experiments of Nicholson and Carlisle saying:

Cette description, et les principales expériences avec cet appareil . . . qui ont porté le dernier coup mortel à la prétendüe <u>électricité animale</u>, et confirmé d'une maniere si éclatante les principes que j'avois avancés depuis quelques années et soutenus toûjours sur les <u>Galvanisme</u>, et d'autres expériences electro-chymiques de NICHOLSON et <u>CARLISLE</u> . . . ont été surement publiées à Londres, et à Paris; mais je n'ai encore rien reçu de là. Il devroit avoir paru quelque chose encore en Allemagne. Voudriez vous bien m'en informer, et m'envoyer ce qu'on a publié sur cette matiere?183

Thus, following Nicholson and Carlisle's discovery of the chemical action of the Voltaic pile, even Volta himself, although he continued to correspond on the matter, was outside the main realm of activity with regard to the new and exciting electro-chemical developments that gripped the rest of Europe. Volta's discovery became not only an important point in the dispute over the electrical or non-electrical nature of galvanism, it also had already provided in the first year of its inception, arguments against Volta's own contact theory of galvanism. The electro-chemical investigations that stretched from London, to Paris, Jena, Halle, Berlin, and Vienna signaled that the belief in the chemical nature of galvanism had already provided a serious alternative to the contact theory of electricity.

In retrospect, the use of the galvanic decomposition of water as a crucial instance further illustrates the fate of eighteenth-century

^{183&}quot;1156a. Volta a Ambrogio Barth. Como, 28 Dicembre 1800,"

Epistolario di Alessandro Volta, ed. nazionale, 4:29. "This description, and the principal experiments with the apparatus . . . that have dealt the mortal blow to the so-called animal electricity and confirmed in so clear a manner the principles that I have advanced for the last few years and have always sustained in galvanism, and other electro-chemical experiments of Nicholson and Carlisle . . . have surely been published in London and Paris; but I still have not received anything of them. Something should have also appeared in Germany. Would you please inform me of it and send me whatever has been published on this matter?"

attempts to provide crucial experiments in order to decide between competing theories. Nicholson and Carlisle's argument that electricity and galvanism were the same because they both decomposed water did not meet with universal acceptance. Prior to Nicholson and Carlisle's experiment, Volta, Wells, Darwin, and others had agreed that electricity and galvanism were the same, but they had appealed to electrical experiments (such as determining whether galvanism produces an electric charge or spark and whether galvanism and electricity share the same conductors) in order to demonstrate their claim. Although Nicholson and Carlisle expanded the Galvani-Volta controversy to the consideration of the chemical properties of electricity, natural philosophers, including Nicholson, Pictet, Halle, Robertson, and Ritter, continued to base at least part of their arguments on electrical experiments and continued to disagree on the ability of a galvanic battery to produce electrical phenomena.

Moreover, galvanism, the production of animal electricity by the contact of animal tissue and a conductor (or by the contact of two dissimilar conductors according to Volta), was known to possess chemical properties similar to those of electricity. Prior to 1800, Humboldt, Ash, and Ritter had discussed the galvanic production of hydrogen and oxygen from water and, even after Nicholson and Carlisle argued that the galvanic decomposition of water identified galvanism as being electricity, Robertson, Ritter, and Voigt accepted the chemical action of galvanism on water without believing that it demonstrated that electricity and galvanism were the same.

Indeed, Nicholson and Carlisle's experiments raised the problem of the separate production of hydrogen and oxygen from water in a Voltaic circuit. With a few exceptions, such as Cruickshank, Pfaff, and Voigt, neither side in the Galvani-Volta debate could explain this problem in terms of electrical or chemical theory. Although Ritter and others believed the separate production of hydrogen and oxygen from water established the electricity and galvanism were not the same and that water was not decomposed in a Voltaic circuit, those who believed in the new chemistry and the electrical nature of galvanism were not daunted in their identification of galvanism as being electricity.

Finally, there was not only a disagreement over the interpretation of the action of the Voltaic pile on water, there was also disagreement among those natural philosophers who identified electricity as galvanism. Some, like Volta, attributed the origin of galvanic electricity to physical causes (such as the contact of two dissimilar conductors), while others, like Davy, attributed the origin of galvanic electricity to chemical causes (such as the oxidation of a conductor).

The varying interpretations of the production of gas from water in a Voltaic or galvanic circuit illustrate that, although natural philosophers did not refer always to this oft-repeated experiment as an "experimentum crucis," they did appeal to this experiment in order to argue their theories on the nature of water, electricity, and galvanism. That is, even when they did not appeal explicitly to crucil experiments, they did accept experimentation as a means to decide between competing theories. Therefore, while these eighteenth-century natural philosophers

accepted the idea that crucil experiments did exist and some even identified Nicholson and Carlisle's experiments as such an experiment that could provide the Baconian "sign post" between two theories, their preconceptions concerning the nature of electricity and chemistry allowed them to interpret this sign post differently and thus arrive at different (and distant) destinations.

CHAPTER VII

CONCLUSION

The passing of electricity through water was an oft-repeated experiment in the eighteenth century. Although there was consistent agreement on what phenomena were associated with the passage of electricity through water, the interpretation of these phenomena varied a great deal from 1746 to 1800. Initially the passage of electricity was examined and explained by making reference to the properties of electricity and its mechanical effects upon conductors. In the context of this examination, natural philosophers sought to describe the properties of water as a conductor and the effects of electrification upon water. One major result of this kind of inquiry was the association of electrification with evaporation in order to account for certain experimental results. Both Nollet's theory of effluent and affluent electric matter and Franklin's one-fluid theory of electricity made this association.

Natural philosophers such as Franklin and Beccaria also discussed the rapid "dispersion" of water by the passage of electricity through it and they assumed that the electric fire, like common fire, is able to change water into vapor. Others such as Priestley and Lane discussed the electrical dispersion of water in more mechanical terms. Some natural philosophers such as Cavendish simply ignored the effects of the passage of electricity on water and examined the passage of electricity through

water only to ascertain water's ability to conduct electricity as compared with other conducting substances.

The identification of the electric fire with fire and the examination of the action of electricity upon metals and their calxes led to the identification of electricity as phlogiston which was part of and contributed to the examination of the chemical properties of electricity. In the context of this examination natural philosophers sought to determine the chemical effects of electricity upon various substances and to reconcile these effects with the identification of electricity as phlogiston.

It was not until the experiments of Van Marum that the chemical effects of electricity on water were considered. Van Marum argued that electricity decomposed water into hydrogen and oxygen, but perhaps because Van Marum's experiments were just a small part of the experiments he published in 1787, they remained in relative obscurity until 1789 when Deiman and Paets van Troostwijk published the article in Observations sur la physique arguing that they had accidentally discovered the electrical decomposition of water and that this discovery left no doubt as to the truth of Lavoisier's new chemical theory. Without mentioning their friend and colleague Van Marum, they described a series of experiments that reflected a knowledge of the experimental difficulties which he had encountered before them. Schurer's eyewitness acount also reveals that their experiments required too much contrivance to be accidental. Perhaps they were invoking a fashion of the time by presenting this highly contrived experiment derived from their knowledge of Van Marum's Similar experiment as an accidental but decisive discovery.

Regardless of its origin, Deiman and Paets van Troostwijk portrayed their experiment as a crucial instance demonstrating that water was a compound and it behooved partisans of the phlogiston theory to refute their arguments.

The phlogiston theory and the traditional exploration of the chemical properties of electricity had not considered the chemical action of electricity on water prior to the advent of Lavoisier's new theory because in in phlogiston theory there was no special significance to the phlogistication of water. But, once the action of electricity on water was used as an argument for Lavoisier's theory, phlogiston chemists sought to provide an explanation within the framework of phlogiston theory of the action of electricity on water.

Just as there had been no lack of explanation of the electrical and mechanical effects of electricity on water prior to the consideration of the chemical properties of electricity, there was also no lack of phlogistic explanations of the chemical effect of electricity on water. After attacking the initial assumptions of the antiphlogistic explanation of the effect of electricity on water, partisans of the phlogiston theory argued that:

- Any inflammable air produced electrically from water comes from the phlogiston in the electric fluid.
- Any vital air produced electrically from water either had been absorbed by the water from the atmosphere or was produced by the union of water and electricity <u>qua</u> phlogiston.

The phlogistic and antiphlogistic interpretations of the Dutch experiment were published repeatedly in the decade following 1789. Despite the phlogiston theory's ability to explain electro-chemical phenomena, Priestley and others described the revolution in chemistry as sweeping and complete, and by 1799, the new chemical theory of Lavoisier had gained a general, albeit not universal, acceptance.

With this general acceptance of the new chemical system of
Lavoisier, Nicholson and Carlisle were able to <u>assume</u> that the Voltaic
pile decomposes water into hydrogen and oxygen, and they argued that
since both electricity and the galvanic fluid decompose water, electricity and galvanism are the same. Thus, the electrical decomposition of
water became part of a second crucial experiment designed to illustrate
the electrical nature of galvanism. The phenomena associated with the
galvanic fluid's passage through water had been examined prior to
Nicholson and Carlisle's experiments: Humboldt and Ash had even discussed the galvanic decomposition of water without arguing that it
demonstrated that electricity and galvanism were the same. Again varying conceptions of the role of electricity in chemical phenomena
resulted in differing interpretations of the same experiment.

Moreover, Nicholson and Carlisle's discovery of the separate production of hydrogen and oxygen from water in a Voltaic circuit raised problems concerning their initial assumption that water was decomposed in their experiment. Some natural philosophers who believed that the galvanic fluid was a fluid <u>sui generis</u> interpreted Nicholson and Carlisle's experiment as contradicting the identification of galvanism as electricity. Others, including Ritter and Voigt, used the separate

production of hydrogen and oxygen from water in a Voltaic circuit to question the compound nature of water and to refocus traditional questions about the chemical nature of the electric fluid.

While eighteenth-century natural philosophers only occasionally appealed explicitly to crucial experiments, they did accept experimentation as a means to decide between competing theories. In this tradition of crucial experiments the electrical production of air from water was used as a crucial experiment for two different theoretical debates. Those who believed in Lavoisier's new chemistry, such as Van Marum, Deiman, Paets van Troostwijk, Schurer, Hermbstaedt, Pearson, and Brugnatelli, used the phenomena to argue that electricity decomposed water. Those who believed that galvanism was electrical in nature, such as Nicholson, Carlisle, Ash, Davy, Pictet, Lehot, Cruickshank, and Butet de la Sarthe, used the phenomena to argue that galvanism and electricity must be the same because they both decomposed water.

In both cases, other theoretical assumptions played an important role. The electrical production of gas from water could be used as a crucial experiment illustrating the compound nature of water only by those who believed that electricity did not enter materially into the experiment. Because there were differing views in the eighteenth century on the nature of electricity and its role in chemical action, the electrical decomposition of water was not universally agreed upon. Once discovered, the galvanic production of hydrogen and oxygen from water could not be used as a crucial experiment illustrating the electrical nature of galvanism except by those who agreed that water could be

decomposed. For instance, natural philosophers such as Ritter and Voigt were reinforced in their bias against the compound nature of water by the separate production of hydrogen and oxygen from water in their experiments with the Voltaic pile, and they rejected the identification of galvanism with electricity.

In both cases the crucial experiment was securely based in a pre-existing theory. It was deliberately employed to disprove a competing theory. The contrivance of a crucial experiment in itself is in no way contrary to Bacon's crucial instances "expressly and purposely sought and applied, or after due Time and Endeavors, discovered," but these eighteenth-century examples illustrate that, unlike Bacon's conception of a crucial instance, these crucial experiments were based in pre-existing theory, and that usually they were accepted only by those natural philosophers who already accepted that pre-existing theory. Thus the proponents of competing theories often interpreted the same so-called crucial experiment in a contradictory manner, each arguing the experiment to be a demonstration of the theory that he championed.

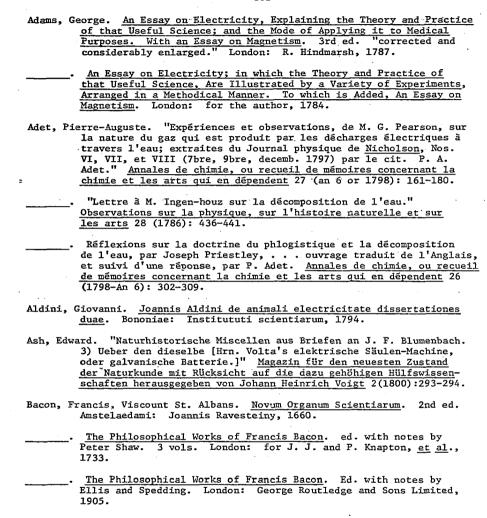
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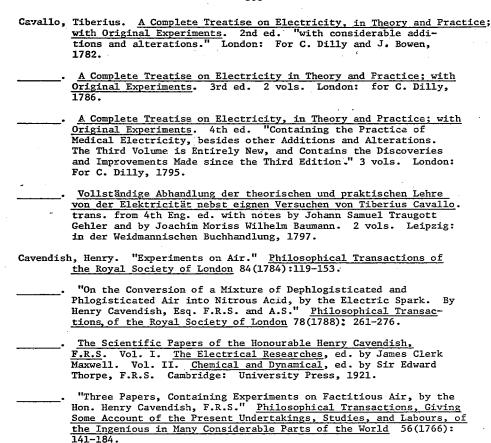
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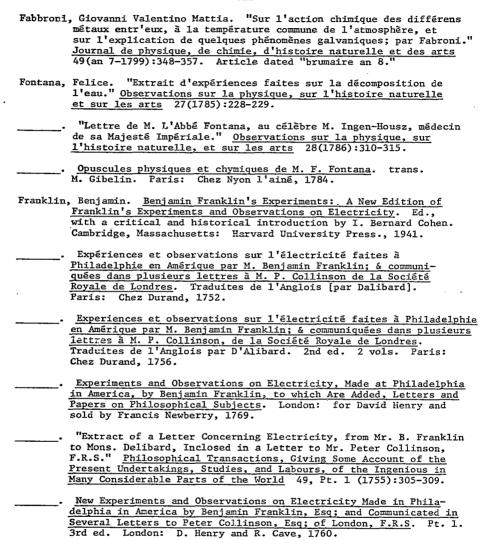
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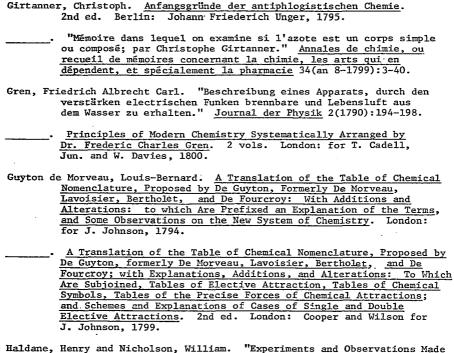
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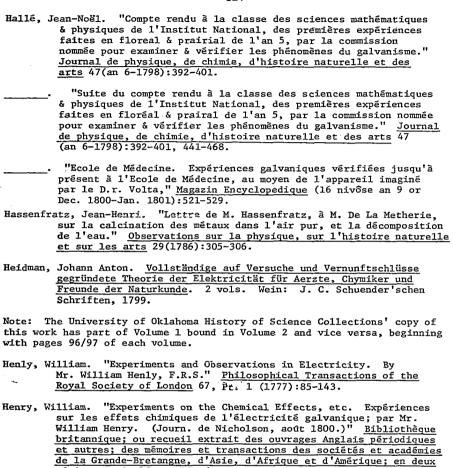
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