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Volta and the Synthesis of Water: Some Reasons for a Missed Discovery

1. The Nature of Airs

Volta officially entered the late eighteenth-century chemical debate in 1776, with the discovery, description and analysis of the inflammable air of marshes (mainly methane). One year later, Volta's observations about this air were published in the form of 7 letters to Father Campi, who originally drew Volta's attention to this area of research. Volta's letters had a remarkable diffusion in Italy and abroad, and were translated into French and German.[1]

By then, Volta had already begun writing a treatise on airs. He revised the text many times, and finally it was published in 1776. The author was officially Volta's pupil Giuseppe Jossi; in reality, it was written by Volta himself.[2] The Swiss natural historian Jean Senebier read this treatise in its manuscript form,[3] and he and Volta began a very interesting correspondence on these subjects. It was this treatise, together with later additions and corrections, that provided the material for Volta's notes and commentaries to the entries on "airs" in the Italian translation of Pierre-Joseph Macquer's *Dictionnaire de chymie*. This translation, hereafter named *Dizionario di chimica*,[4] was edited by Giovanni Antonio Scopoli between 1783 and 1784 on the second edition of Macquer's *Dictionnaire de chymie*.[5]

While studying the inflammable air of marshes, and comparing it with the air obtained by dissolving metals in acids (hydrogen), Volta noticed that the volume of the former diminished when it was ignited by means of an electric spark in a closed vessel (in which common atmospheric air was already present). The decrease in

[1] VOLTA (1777), ID. (1777a). Between 1777 and 1778 four German translations were issued; a French translation was issued in 1778.
[2] VOLTA, (1776); ID. (1776a).
[3] *VO* (see Abbreviations), VI, p. 281.
[4] MACQUER (1783-84).
[5] MACQUER (1778); NEVILLE and SMEATON, (1981). See also the article by Bernadette Bensaude-Vincent in this volume.

volume was also the principle on which the nitrous air eudiometer was based.[6] Volta noticed this one and many other analogies between nitrous air and inflammable air, and only one difference: nitrous air affected pure air (oxygen)[7] by simple direct contact, whereas inflammable air needed to be ignited; so Volta established that:

> All the differences between inflammable and nitrous air can be reduced to the way phlogiston gets combined with the acid [...]: because in the end the acid is a true *constituent principle* both of nitrous and inflammable air, and in both airs it is the *basis* of phlogiston.[8]

Following these analogies, Volta built an inflammable air eudiometer (and an inflammable air "electric gun", which soon became a fashionable trick). Actually he was so convinced himself that this instrument was useless for establishing the degree of salubrity of air,[9] that he decided to call it noncommittally "universal apparatus for the ignition of airs in a closed space".[10]

Volta called the mixture of dephlogisticated and inflammable air "thunder air", "metallic" if the inflammable air was pure inflammable air (hydrogen); "marshy" if the inflammable air was the inflammable air of marshes. The difference between these two airs was determined by the quantity of phlogiston they contained, which was much more abundant in the inflammable air of marshes. By means of his new instrument, which he considered much more accurate than nitrous air eudiometers,[11] Volta noticed that when inflammable metallic air and pure air were burned in due proportions they disappeared completely; at the same time a white vapour was generated, and a humid residue appeared on the internal surface of the glass tube. At this point a crucial problem arose: what was the residue of the combustion of the two airs?

> Reste à savoir si le phlogistique qui passe successivement e.g. dans les inflammations reiterées, à un volume d'air resp. pur se diffond chaque fois dans tout le volume, et le diminue à mesure qu'il y passe, ou vraiment si chaque molecule de cet air chargée du phlogistique qu'elle peut porter, perd l'état aerien et se précipite, laissant le reste de l'air aussi pur et aussi respirable qu'il étoit, jusqu'à ce que chaque portion de phlogistique entrainant une portion d'air, il n'en reste plus. Je croirais ceci plus probable; car autrement le phlogistique ne pourroit diminuer l'air qu'en en [sic] précipitant un des principes constituants, la terre e.g. mais enfin l'autre ou les autres principes s'il y en a plus d'un où iroient-ils pour que tout le volume d'air disparût?[12]

[6] See the article by Marco Beretta in this volume.
[7] In the eighteenth century, oxygen had many names: pure air, dephlogisticated air, fire air, breathable air.
[8] VOLTA (1778a), p. 205.
[9] VOLTA (1783a).
[10] VOLTA (1790), p. 229.
[11] *VO*, VI, pp. 263-4.
[12] *Ibid.*, p. 268.

Volta was almost obsessed with the problem of the residue. Implicitly, he was guided by the law of conservation of matter, which did not allow him to believe that these airs were merely destroyed during their combustion:

> With regard to this wondrous decrease, I am not without hope that eventually I shall make perceptible what separates itself from these airs and precipitates. Because *it is quite clear that these airs are not annihilated and nothing material is lost*; but only that a lot of their volume disappears, as a result of many parts abandoning the aeriform state and condensing in drops, in powder or in something else. My aim is to perform the experiment on as large a scale as possible and to collect the airs over mercury. In this way, any *precipitate*, fluid or solid, salty or earthy, will stick to the walls of the jar or will gather on the surface of the mercury.[13]

Volta knew that in another kind of combustion, namely respiration, fixed air (carbon dioxide) was formed:

> Lorsque l'air resp. se phlogistiquant diminue de volume, il se fait une précipitation. Qu'est ce donc qui se précipite, est-ce de la terre, ou l'acide? [...] je suis donc persuadé que c'est l'acide en plus grande partie qui est précipité avec un peu de terre phlogistiquée qu'il entraine avec lui, et qu'un tel acide lié à ce peu de terre phlogistiquée constitue l'air fixe.[14]

Initially, Volta thought like Priestley that the earth was one of the principles composing breathable air, and that an acid was one of the principles composing inflammable air.[15] Hence, the residue of the combustion between dephlogisticated and inflammable air was likely to come from the former air and to be an earth. However, Volta abandoned this hypothesis, because the dephlogisticated air completely disappeared,[16] and this led him to suppose that the residue could be an acid.[17]

Volta knew Carl Wilhelm Scheele's theory, according to which, in this kind of combustion, pure air and phlogiston constituted the matter of heat, capable of passing through the pores of the experimental apparatus and so dispersing in the atmosphere. However, according to Volta, there was an obscure point in this interpretation:

> But we cannot conceive how the air, which cannot pass through the glass, by supercomposing itself with phlogiston is able to become so subtle as to penetrate it, as well as all the solid bodies that heat penetrates. [...]. Does it lose the aeriform state and change itself into that vapour, that subtle fume we observed after the ignition? And of which air will this fume be the residue, of the inflammable or the dephlogisticated?[18]

[13] VOLTA (1778a), pp. 196-7 (the first italics are mine), originally published as VOLTA (1778).
[14] *VO*, VI, p. 285.
[15] See the article by Frederic L. Holmes in this volume.
[16] *VO*, VI, p. 262.
[17] *Ibid.*, p. 271.
[18] VOLTA (1783d), p. 397.

But what did Volta think about the nature of the different kinds of air? The answer is in the correspondence with Senebier, during the second half of the 1770s.

Acids

Experimentally, when the water in which acids are diluted is removed, acids assume the aeriform state but still preserve their acidity: hence – according to Volta – acids are the simplest airs and the aeriform state is their natural, original state. All the other airs are thus composed of acids combined with other principles, e.g. an earth and/or phlogiston. The (dephlogisticated) earth, combined with an acid, makes this acid capable of maintaining combustion and respiration. On the other hand, when the acid is combined with phlogiston, this acid gives a kind of "aerial sulphur", whose different properties depend on the acid used in the reaction.

Thus Volta, like many other contemporaries interested in chemistry, believed in the existence of a universal acid, from which all the other acids derived, and he thought that perhaps this universal acid was the vitriolic one. The alkalis, too, derived – in his view – from this universal (acid) salt,[19] probably when it was joined with both earth and phlogiston.[20]

Inflammable Air

Since 1777, Volta thought that:

> it needs nothing but a combination of an elastic, dry acid with phlogiston to form inflammable air; it is a kind of *aerial sulphur*. [...]. The nature of every acid is the dry aerial state, and the spirits or liquid acids are nothing but water impregnated with *this or that acid air*. In this way, the aerial nature of fixed air will no longer be surprising, because this is the nature of all acids. So, fixed air will no longer be a different species but only a particular kind of acid.[21]

Thus, inflammable air was composed of acid plus phlogiston. However, in his notes on airs in Macquer's Italian translated *Dizionario di chimica*, Volta abandoned the denomination "aerial sulphur" in favour of "aerial salt", because no acid was obtained by burning dephlogisticated, inflammable air, and the aqueous vapour obtained in this combustion was not acid either.[22]

[19] In the eighteenth century all the acids belonged to the broader category of salts.
[20] *VO*, VI, pp. 283-5.
[21] *Ibid.*, pp. 282-3.
[22] VOLTA (1783d), pp. 389-90.

Dephlogisticated Air

As I mentioned earlier, Volta initially thought that dephlogisticated air was an acid combined with an earth. However, since no earth was obtained by burning this air with inflammable air, he abandoned this interpretation[23] and stated that dephlogisticated air was:

> [...] a salty, primitive, elementary principle, an aeriform substance by its nature, it neither mixes itself with water nor with the earths, it is greedy for phlogiston because it contains none or almost none, whereas it is rich in pure elementary fire. It can easily reconvert itself into fixed air [...] by losing this pure fire and acquiring phlogiston.[24]

In 1779 the theory of acidity based on oxygen, formulated by Lavoisier three years earlier, became public, and in 1783 Volta had to come to terms with it:

> Meanwhile, after the hypotheses of others [Volta had just quoted above A.F. Fourcroy, *Leçons de chimie*: dephlogisticated air can be found in any acid], and wishing to put forth one of our own, we propose that fixed air is hosted in all the acids; if not in all, at least in those from which one can release dephlogisticated air. By this theory we reduce to only one principle the many different ways of obtaining dephlogisticated air.[25]

Now we see that, according to Volta, dephlogisticated air was no longer composed of earth, as he thought earlier, but only of fixed air deriving from an acid when it loses its phlogiston.

Fixed air

According to Volta, fixed air was dephlogisticated air containing a considerable amount of phlogiston. He reached this conclusion because, when burning pure air (oxygen) and inflammable air obtained from the distillation of oils, he obtained fixed air.

As for the many chemical procedures by which one could obtain fixed air, Volta concluded:

> Alors, reflechissant, que les vapeurs du charbon, la calcination des métaux, la putrefaction, et la respiration changent de même une portion d'air dephlogistiqué en air fixe, je vis que c'étoit plutot un cas particulier celui où cet air au lieu de subir en recevant le phlogistique ce changement, disparoit entierement, comme s'il étoit aneanti, mais qu'il n'en étoit pas moins vrai en general, que l'air fixe est de l'air dephlogistiqué, qui a cessé d'être tel par l'addition du phlogistique, et une certaine combinaison avec lui.[26]

[23] *VO*, VI, p. 262.
[24] VOLTA (1783c), p. 366.
[25] *Ibid.*, p. 365.
[26] *VO*, VI, p. 315.

So, Volta did not believe, as Lavoisier did, that metallic calces were full of dephlogisticated air in its pure state, but that they were full:

> [...] de cet air changé en air fixe par le phlogistique que les métaux mêmes ont fourni en se calcinant, ces chaux dis-je jouissant d'une grande affinité avec le phlogistique aidées par la chaleur dans des vaisseaux clos en depouillent le même air fixe, qui est chassé alors dans sa pureté naturelle, c'est à dire en forme d'air dephlogistiqué.[27]

In this way he established a graduated scale going from dephlogisticated to phlogisticated air, passing through fixed air:

> We have already suggested, as we think, that fixed air is intermediate between dephlogisticated and phlogisticated air [with regard to the quantity of phlogiston contained].[28] This fixed air is in an intermediate state and close to the two extremes, so that one step forward or backward brings it to one or to the other: it is a true Proteus.[29]

2. The Nature of Water

The problem of the residue of the combustion between dephlogisticated and inflammable air occupied Volta till 1783, when Cavendish, Monge, Lavoisier, and Meusnier discovered that this residue was pure water. Different natural philosophers gave different theoretical explanations of this phenomenon: Cavendish and Watt thought that water was composed of phlogiston and dephlogisticated air that had lost much of its heat or elementary fire[30] Priestley and the followers of his phlogiston theory claimed that water was already present in the two airs, oxygen being dephlogisticated water and hydrogen being phlogisticated water. Lavoisier, on the other hand, formulated a revolutionary theory, according to which water was no longer a simple element but rather a compound of hydrogen and oxygen.

This discovery was communicated to Volta by Landriani at the end of 1783. Volta replied to Landriani on the 11th of December:

> As far as the synthesis [of water] is concerned, I understand that [Lavoisier] obtained this water by burning the mixture of those airs [dephlogisticated and inflammable]. I understand it, I say, because I almost achieved this result, since I discovered that, when inflammable air disappears by means of ignition, it does not change any portion of dephlogisticated into fixed air, as all the other inflammable airs and all the other phlogistic processes do. On the contrary, it destroys a volume of dephlogisticated air that is half of its own, which destruction goes together with the appearance of a fume or nebulous humid vapour. [...]. It is true that I doubted that it was not a purely aqueous vapour, because it is difficult to condense it in drops: however, I excluded any acid and

[27] *Ibid.*
[28] VOLTA (1783c), p. 372.
[29] *Ibid.*, p. 373.
[30] VOLTA (1784), p. 101.

> salt. [...]. As far as the theoretical consequence is concerned, i.e. that water is composed of the two airs dephlogisticated and inflammable, my view is different; I think that water is a simple element, or at least simpler than the two airs, and that water is contained in them, and not them in water. [...]. This is what makes me wish to know whether and how Mr. Lavoisier succeeded in analysing water and separating the claimed constituent principles, i.e. pure air and inflammable air. I believe that he was able to obtain the one and the other air, but not from simple water, i.e. not without the intervention of some other body, that would have enriched water with fire or phlogiston.[31]

A few months later, Lavoisier provided an answer to Volta's remarks, albeit indirectly, in a note sent to D'Arcet and enclosed in a letter written by the latter to Volta.[32]

Why did Volta not recognise the formation of water, after having actually synthesised it so many times by means of his eudiometer and his electric gun? Eudiometers consisted of tubes plunged in water, and of course the residue of the combustion of dephlogisticated and inflammable air could not be detected this way. Volta realised the necessity of performing this kind of experiment over mercury instead of water, and the reason he alleged in his many letters on this subject – trying, in other words, to explain the reason why he missed the discovery of the synthesis of water – was that he never had enough mercury for this kind of experiment.

But the historian can hardly be satisfied with this explanation. In Abbri's view, Volta did not "see" water for theoretical reasons, in particular because he was mainly concerned with the study of the phlogistication of airs.[33] I agree with Abbri that Volta did not see water for theoretical reasons, but I think that the explanation is more complex. I have already explained what Volta thought about airs; however, in order to make my claim clearer, it is useful to examine his views about heat and phlogiston as well: in other words, about the other two substances involved in this kind of experiments.

In 1779 Adair Crawford published a work on heat and respiration; his theory stirred much heated debate in the scientific community, but in the end it was accepted by many of his contemporaries.[34] Volta was among them:

> J'ai adopté la théorie de Mr. Crawford sur la chaleur pour ce qui regarde le feu elementaire contenu abondamment dans l'air dephlogistiqué, qui s'en échappe et se manifeste en qualité de chaleur sensible à mesure que cet air se charge de phlogistique, qui est son précipitant (précipitant, dis-je, par cela même qu'il est de nature analogue, de la maniere qu'un acide précipite un autre acide, une terre une autre terre ec.).[35]

[31] *VO*, VI, pp. 410-2.
[32] D'ARCET (1784).
[33] ABBRI (1984), pp. 278, 282. See also Abbri's article in this volume.
[34] CRAWFORD (1779); a summary in Italian appeared in *Opuscoli scelti sulle scienze e sulle arti*, 3 (1780), pp. 39-98.
[35] *VO*, VI, p. 315.

Volta discussed Crawford's theory in detail in the entry "Calore" of the *Dizionario di chimica*.[36] He was very interested in the study of heat, notably because he was a physicist by training, but also because this fluid was directly involved in the phenomena relating to inflammable airs; and, last but not least, because Volta was much interested in the study of vapours, mainly of the aqueous vapour.

Volta became interested in this subject in the early 1780s. During his stay in Paris in 1781-82 he attended the course of chemistry taught by the "phlogistonist" Balthazar Georges Sage,[37] and performed some experiments with Lavoisier and Laplace, (who, in those years, were engaged in research on heat), in order to detect the presence of electricity by means of the simple evaporation of bodies.[38] His subsequent studies on vapours eventually brought Volta to formulate the law of the uniform dilation of air in 1793.[39]

We can find a comprehensive theory of all these phenomena in many of Volta's letters, as well as in the notes to some entries of the *Dizionario di chimica*. Since the dictionary is in alphabetical order, the first volume (1783) contains the notes regarding airs and water (*acqua*, in Italian). The discovery of the synthesis of water, which came about in the same year, was thus discussed in the second volume, within the note to the entry "Volatilità".

The studies on heat and on vapours led Volta to formulate a theory, mainly related to water, according to which gases were characterized as mature and immature airs, according to the quantity of heat they contained and the way it was combined. If the gases were permanently elastic they were "mature airs"; if they were not permanently elastic they were "immature". This theory is explained in the entry "Vapore" of the *Dizionario di chimica*:

> Mr. De Saussure believes, as some others do, that this calorific fluid, or elementary fire is properly combined with the molecules of water, and it is a true constituent principle of vapour. We do not think so but that it is simply joined to vapour in proportion to its capacity, which has become very large. If it were really combined, it does not seem that this calorific fluid would abandon the vapour, when we condense it, for example by means of a piston. However, by this means, which is not a decomposing means, the vapour increases its heat without addition of fire, only because a part of it loses the vapour state and becomes water again. In doing this it also loses that extraordinary capacity it had. So the fire, now redundant, raises the sensible heat (cit. art.).
>
> We do not think that an intimate combination between the calorific fluid and water rarefied to vapour, and a certain fixation of the calorific fluid would be impossible. Even if in the quoted entry *Heat* we showed ourselves not much in favour of that fixation which we did not think necessary for explaining the phenomena of heat discussed there,

[36] VOLTA (1783), pp. 5-47.
[37] *VE* (see Abbreviations), II, p. 79.
[38] *VE*, II, pp. 103-5; *VO*, III, pp. 303-5; *VO*, III, p. 306.
[39] GUARESCHI, (1914).

> we were not far from adopting it, when other phenomena would prove it, or would make it likely. Now some new discoveries relating to airs, which we will discuss in the article *Volatility*, make this intimate combination of the calorific fluid with vaporised water more than likely. Then, according to Mr. Volta, the vapour is no longer a simple vapour, [...], an *immature* air, as he calls it, but a *mature* air, permanently elastic, true air, better said, very pure breathable air (see the mentioned article *Volatility*).
> Now, back to the simple vapours: the elementary fire transforms water in them. First it expands water and raises its sensible heat; then it inflates it in a strange form and turns it into an elastic fluid, without, or nearly without raising its sensible heat, thanks to the extraordinary capacity that water acquires passing into the aeriform state, as we said before. Before reaching this state, water must be warmed to 80° R, as we said before. This is meant under the ordinary weight of the atmosphere [...].[40]

But in the entry "Volatilità", Volta made some different statements:

> Before the publication of those [Lavoisier's] experiments, our Mr. Volta carried out some analogous experiments, producing inflammable air by plunging a big red-hot piece of iron or charcoal into water [...]. The experiment with charcoal was also made by the distinguished Abbot Fontana. Mr. Volta performed those experiments to prove that water vapour, in order to pass into the state of air, i.e. of a permanently elastic fluid, needs only to combine itself in a proper way with a sufficient amount of phlogiston, this having been his opinion for a long time. Now who cannot see how the success of these experiments confirms this idea?[41]

Following his ideas on the different degree of maturity of vapours, he thought that water vapours reached permanent elasticity whenever they got combined in a particular (chemical) way with phlogiston:

water :: heat ? aqueous vapour
aqueous vapour + phlogiston ? inflammable air
(:: = physically combined; + = chemically combined).

The air which was generated by this combination of phlogiston with water vapour was inflammable air, and when it gave off the phlogiston, as happened when ignited, it became water again, passing through the intermediate state of vapour:

> But the weight of the water obtained by means of this ignition is greater than the weight of the inflammable air alone, and is approximately equal to the weight of the dephlogisticated air which disappeared together with the inflammable air. So, we can conclude that dephlogisticated air, too, has water as its basis. But what is the other constituent principle, responsible for the aerial state and the permanent elasticity of dephlogisticated air? It cannot be phlogiston, otherwise there will be no difference between this air and inflammable air. On the other hand, the fact that it greedily attracts phlogiston from the other bodies demonstrates that it contains none or very little. And yet,

[40] VOLTA (1783b), pp. 87-8.
[41] VOLTA (1784), p. 99.

> we have many proofs of an exceedingly great quantity of the calorific principle (a substance very different from phlogiston) contained in dephlogisticated air (see *Heat*). When free and producing sensible heat, this igneous fluid is the cause of any fluidity, of any volatility and expansibility. When united in sufficient amount, without entering into combination, this igneous fluid keeps water in the elastic vapour state and, by simply departing from it, makes it return to the state of incompressible fluid. But what if this igneous fluid intimately combines with water? Will it not bestow on water permanent elasticity? If phlogiston does so much in combining with water, much more rightly will the elementary fire do the same.[42]

At this point Volta faced the problem of the combustion of oxygen with impure inflammable air, i.e. that of marshes: in this case the residue was not water, but fixed air:

> If the phlogiston released from this inflammable air decomposes the dephlogisticated [air], and sets free the calorific principle or igneous fluid, and precipitates its water, and the flame is the result of the conflict and union of this phlogiston with this igneous fluid, why does not the same happen when the phlogiston coming from other inflammable airs and other combustible bodies discharges itself into the dephlogisticated air? And why does the dephlogisticated air not decompose itself and become water? Why does it become fixed air instead? To these questions Mr. Volta answers that, by hitting against the dephlogisticated air, a portion of phlogiston decomposes the quantity of this air required to produce the observed flame; but another portion of phlogiston, which is not flung with so much impetus or is impeded in whatever manner from penetrating so deeply, does not decompose an additional portion of dephlogisticated air, but does simply get united and joined to it, thus forming some fixed air, which is indeed, by myriad proofs, demonstrated to be really composed of pure air and phlogiston (see the notes to the articles on *Airs*). Thus, dephlogisticated air is affected by phlogiston in different ways, depending on the circumstances; sometimes it is decomposed by phlogiston and sometimes it is supercomposed with phlogiston.[43]

Volta confirmed this theory in a letter to Senebier in the same year 1784:

> [...] pour l'alterer, pour le transformer [the dephlogisticated air] en air fixe il faut un phlogistique libre, tel que celui qui émane du sang, de plusieurs corps en combustion, du foye du soufre ecc.: ce phlogistique libre s'attachant alors à l'air déphlogistiqué, et s'y combinant d'une certaine maniere, forme cette autre espece d'air que nous appelons air fixe. Je dis en *se combinant d'une certaine maniere*; parceque une autre combinaison, vraisemblement à plus grande dose, forme l'autre espece d'air qu'on nomme phlogistiqué; et dans un cas, qui est celui de l'inflammation de l'air inflammable plus pur, c'est-à-dire métallique, l'action du phlogistique de cet air sur l'air pur dephlogistiqué, dissout ce dernier, et détruit entierement sa forme aërienne, formant un precipité d'eau pure.[44]

[42] *Ibid.*, p. 101.
[43] *Ibid.*, p. 104.
[44] *VE*, II, p. 193.

In the same letter, Volta delineated more precisely his view on the composition of these two airs, which I will try to summarize as follows:

inflammable air = water + phlogiston
dephlogisticated air = water + heat
phlogiston + heat = flame
inflammable air + dephlogisticated air ? water + flame
[water + phlogiston] + [water + heat] ? [water + water] + [phlogiston + heat]

The role of phlogiston, too, was better clarified:

> On sçait que la chaleur seule et libre met en état aeriforme élastique l'eau; mais cette élasticité est fugitive comme la chaleur elle-même: la vapeur refroidie retombe en eau. Or si l'élement de la chaleur, ou vraiment le phlogistique puvoient se combiner et contracter une forte union avec cette même eau, je pense qu'elle acquerroit une élasticité permanente, c'est-à-dire la véritable forme aêrienne, et constitueroit avec le premier de ces principes l'air pur resp.e, avec le dernier l'air inf.e.[45]

When phlogiston does not completely replace the element of heat in pure air, it forms fixed air.

As can be seen from the texts, Volta's theory of heat was no longer the same as Crawford's. In 1783 Volta had written:

> Let the fire be fire and the phlogiston be phlogiston, and we can explain the main phenomena very well, by means of the simple and unique principle of the greater or lesser capacity to contain that elementary fire which many bodies have, and also the same body in the different states of solidity, fluidity, phlogistication or dephlogistication.[46]

But in the light of the new events, Volta believed that, in the explanation of the variations in the sensible heat, the principle of changes in the capacity for heat no longer accounted for all the phenomena. He had to admit that fixed fire was also necessary as another concurring element:

> Alors il y a production de chaleur, non pas à cause d'une *diminution de capacité* dans le corp qui devient chaud, mais par une augmentation réelle de la quantité de feu libre. Souvent ces deux causes concourent ensemble à la génération de la chaleur; souvent la premiere seule: l'air respirable e.gr. reçoit-il du phlogistique, et est-il converti en air fixe? La diminution de capacité qu'il souffre, fait, qu'il ne peut plus contenir la meme quantité de *chaleur absolue* libre, sans que sa *chaleur sensible* augmente. Le meme air respirable est-il surpris par le phlogistique de maniere, qu'au lieu de se combiner avec celui-ci, et former le composé que nous appellons *air fixe*, il soit au contraire decomposé et un des ses principes constituants, qui est le feu fixe, sois mis en liberté? Ce developpement qui augmente réellement la quantité de chaleur libre, produit nécessariement une augmentation de chaleur sensible, qui éclat en flamme par le

[45] *Ibid.*, pp. 194-5.
[46] VOLTA (1783), p. 41.

conflict même du phlogistique.[47] [...]. Mais nous ne connoissons pas, nous ne pouvons pas même supposer que l'eau puisse prendre la forme aërienne, sans qu'un autre principe s'y mêle, un principe qui lui donne la volatilité et l'elasticicité. La matiere de la chaleur à la verité lui fait prendre la forme vaporeuse élastique, lorqu'elle s'y trouve accumulée en quantité suffisante; mais tant que cette matiere de la chaleur ou feu est libre et dans le mouvement calorifique, si par la rencontre d'un corp froid il vient à quitter la vapeur, celle-ci se condense, et retombe en eau; l'air au contraire a une élasticité permanente qui brave le plus grand froid qu'on connoisse: on doit donc dire que si c'est l'élément de la chaleur de qui il tient son état aëriforme constant, cet élément n'y est pas libre et dans le mouvement calorifique, mais fixé et combiné, en qualité de principe constituant ce meme air. Le phlogistique ressemble à l'élément de la chaleur, en ce qu'il est aussi un principe de la volatilité des corps: on peut donc très-bien supposer, que ce principe en se combinant à l'eau la fait passer non pas seulement à l'état de vapeur, mais a celui de fluide élastique permanent, à une espece veritable d'air, qui est l'air infl. le plus pur que nous connoissions.[48]

3. Conclusion

Volta repeatedly claimed that he had almost discovered the nature of water, in fact he claimed that he had shown the disappearance of the two airs in his eudiometer to Lavoisier during his stay in Paris in 1781-82 However, he never failed to acknowledge the merits of the French scientist:

> Lavoisier est veritablement parvenu, il a trouvé ce qui étoit seulement indiqué, il a fixé la verité.[49]

The fact is that Volta never "saw" what Lavoisier "had seen" when he observed the combustion of inflammable and dephlogisticated air.

Needless to say, the secondary literature on Lavoisier is immense, and I do not intend to summarize it.[50] However, there is one point that I would like to recall. It has been observed that already ten years before the crucial date of 1783, Lavoisier began "educating" himself to do without phlogiston, in his theories of combustion, calcination, and acidity, all based on oxygen.[51] The synthesis and analysis of water, according to his theories, turned out to be a resounding confirmation of the correctness of those theories.

The case of Volta is completely different. The above quoted texts suggest that Volta was guided by some fundamental ideas:

[47] *VE*, II, p. 198.
[48] *Ibid.*, p. 200.
[49] VOLTA (1798), p. 270.
[50] See for example BRET (1995).
[51] See HOLMES (1998).

1) the idea of gradualness in the chemical modification of matter was extended by Volta also to the passage through different physical states. As we have seen, this idea applied in two cases:

a) fixed air was an intermediate stage between dephlogisticated and phlogisticated air,

b) the vapour state was an intermediate stage between the liquid state (water) and that of permanently elastic fluid (gas).

2) heat was responsible for the physical states of matter. It was able to combine "physically", thus generating water vapour, but it was also able to combine "chemically", thus generating airs, as phlogiston did.

Within this theory, water was a simple element that could be found in different physical states.

All these ideas were already present in Volta's interpretation before 1783, and his explanation of the origin of the residue of the combustion of inflammable and dephlogisticated air was conceived within this interpretative framework.

The problem of the nature of the residue entails three levels of explanation:

1) experimental: Volta did not lack experimental skills but he lacked the appropriate experimental apparatus; in particular, as he repeatedly wrote, he did not have a pneumato-chemical apparatus working with mercury,

2) methodological: although experiments came first, Volta always sought a theoretical confirmation of his results,

3) theoretical: within the current theories, the residue should have been an earth or an acid. The vapour obtained by Volta was due to the impurity of the samples. The available theories did not predict the presence of water. Thus, Volta searched for an earth and for an acid, but, rightly, he did not find them.

Once the nature of the residue became clear, some *a posteriori* adjustment of the theory was necessary. Crawford's theory of heat stated that the temperature of bodies increased when their capacity for heat diminished but, in the light of the new facts, Volta had to modify this theory and to find out a new role for phlogiston: the temperature increased because some fixed fire became free. In this way phlogiston became responsible for the permanently elastic fluid state of water,[52] according to the new scale:

water = simple element
water :: heat = not permanently elastic aqueous vapour
[water :: heat] + heat = permanent aeriform fluid = dephlogisticated air
[water :: heat] + phlogiston = permanent aeriform fluid = inflammable air
(:: = simply joined; + = strongly combined)

[52] *VE*, II, pp. 198-200.

In this way, the differences between phlogiston and heat became very blurred, and analogies prevailed, to such extent that on closer examination one looked like a copy of the other. Nevertheless, Volta continued to consider phlogiston and heat as two different fluids, even if they were analogous:

> But even if there is antagonism and reciprocal opposition between these two principles, because they are mutually exclusive, in the end there is some analogy between them: as one acid drives out another of a different kind and replaces it, as the fixed alkali removes the volatile alkali from a base and gets united to it, as one earth precipitates another earth, a metal another metal, in the same way one can understand that phlogiston is no more different from the fire that it drives out and replaces than vitriolic acid from fixed air or fixed alkali from volatile alkali; and that phlogiston differs from fire only by a particular modification or composition, but sufficient to have phlogiston and fire as two absolutely distinct substances.[53]

To conclude, the important point I want to highlight here is the fact that Volta was able to conceive the same substance – the igneous fluid – both physically and chemically, even in the same context. Of course, this was due, at least partly, to his training as a physicist. However, the fact that he was able to switch easily from chemistry to physics, and vice versa, reminds the historian that disciplinary boundaries are often *a posteriori* artifacts and that perhaps, if we were to read Volta's writings keeping in mind both their physical and chemical dimension, we could achieve a better understanding of his work.

[53] VOLTA (1783), pp. 40-1.

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