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An Element of Controversy

The Life of Chlorine in Science, Medicine, Technology and War

Edited by Hasok Chang and Catherine Jackson

from research by undergraduate students at
University College London

British Society for the History of Science

2007

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The Elementary Nature of Chlorine

Tamsin Gray, Rosemary Coates and Mårten Åkesson

1. Introduction

The idea that chlorine is a chemical element is now so fundamental to chemistry that it is hard for us to imagine quite how contentious this issue once was. It may seem a straightforward thing to decide which chemical substances are elements and which are compounds. That is not so, as the early history of chlorine illustrates with perfect clarity. By around 1800 chlorine was most commonly known as “oxymuriatic acid” or “oxygenated muriatic acid” (henceforth “OMA”), after the demise of the phlogiston-based conception, which was discussed in detail in Chapter 1.¹ The early years of the 19th century witnessed wide-ranging and heated debates concerning whether or not OMA/chlorine should be classified as an element. This lack of consensus amongst the scientists of the day illustrates the difficulties experienced by chemists attempting to apply the new Lavoisierian definition of an element as a substance that could not be decomposed. Repeated failures to decompose OMA were interpreted as supporting either elementary chlorine or compound OMA depending on the theoretical allegiances of the scientists involved, and even Humphry Davy’s apparently conclusive demonstration of the elementary nature of chlorine, based on its failure to be decomposed by hot carbon, did not convince some eminent chemists of the day.

¹ A few words on nomenclature are needed. What modern chemists call *hydrochloric acid* was then known as *muriatic acid* or *marine acid* (which we abbreviate as *MA* in this chapter). What we now know as chlorine was first called *dephlogisticated muriatic/marine acid* by Scheele, its discoverer. Afterwards it was dubbed *oxygenated muriatic/marine acid* by those who rejected the phlogiston theory, and that designation was often shortened as *oxy-muriatic acid* or *oxymuriatic acid* (which we abbreviate as *OMA* in this chapter).

In this chapter, we describe how chlorine came to be considered a chemical element. We begin before Davy's 1810 announcement that chlorine was elementary, when a failed attempt to decompose OMA led Joseph-Louis Gay-Lussac and Louis-Jacques Thenard to countenance the notion that OMA might be elementary. Others including Claude-Louis Berthollet were sceptical, and remained so even after Davy proposed the name "chlorine" for the new element. Berthollet was not the only chemist to resist the idea that chlorine was an element, and in the later sections of this chapter we also discuss the objections of John Murray and Jöns Jakob Berzelius to the new element. Each story highlights a different aspect of scientific controversy and its resolution, but all of them make it absolutely clear that we cannot expect such disputes to be resolved by means of a single, decisive experimental result. The acceptance of chlorine as an element was largely due to the recognition of its chemical similarities to iodine and the consequent accumulation of additional evidence for its elementary nature, rather than to a clear and speedy consensus effected by Davy's decisive experiments.

2. What is (and was) an element?

Today we may feel that we have a clear conception of whether or not a substance is elementary. If a substance contains only one type of atom it is an element. The types of atoms are determined by the number of protons in the nucleus. At the start of the 19th century such definitions were not possible, since atomic theory had not yet been established and the idea of sub-atomic particles was even further off. This was, nevertheless, a time of immense activity in chemistry and, in particular, in the announcements of discoveries of new elements. There must, therefore, have been some operative concept of an element. What was that concept?

Antoine-Laurent Lavoisier (1743–1794) is credited with paving the way for a great deal of modern chemistry, including the definition of an element, articulated in his *Traité élémentaire de chimie* of 1789. In fact, Lavoisier's concept of an element was based upon a principle that had been first articulated in 1661 by Robert Boyle (1627–1691):

I mean by Elements, as those chymists that speak plainest do by their principles, certain Primitive and Simple, or perfectly unmingled bodies, which not being made of any other bodies, or of one another,

are the Ingredients of which all those call'd perfectly mixt Bodies [compounds] are immediately compounded and into which they are ultimately resolved.²

Lavoisier's version of this stated that "substances that could not be decomposed into simpler substances were to be regarded, provisionally at any rate, as elements",³ a definition that has been interpreted by William H. Brock as meaning that an element was "any substance that could not be analysed by chemical means." This definition does not aid any kind of real classification, and is logically dubious if we are to consider the epithet "element" to refer to something fundamental. Perhaps more significantly, Lavoisier himself did not use it consistently, as Brock's description of Lavoisier's table of elements shows:

Lavoisier's table of elements did not include the alkalis, soda and potash, even though these had not been decomposed Lavoisier was so confident that soda and potash would similarly [to ammonia] be decomposed into nitrogen and other unknown principles that he withheld them from the table of simple substances.⁴

The only grounds for calling a substance an element had been disobeyed by the very man who had proposed it, and so we should not consider any chemist who also disobeyed this rule to be unscientific, or working outside Lavoisier's paradigm. Instead, he would be, like Lavoisier, relying on analogy with other substances, rather than a logically unsound rule, as a heuristic to resolve questions about the elementary nature of substances. The case of chlorine allows us to explore the ways in which early 19th-century chemists used the concept of element.

Three chemists in particular made statements about the elementary nature of chlorine early in the nineteenth century: Joseph-Louis Gay-Lussac (1778–1850), Louis-Jacques Thenard (1777–1857), and Humphry Davy (1778–1829).⁵ In February 1809, Gay-Lussac and Thenard published an account of their researches into "oxymuriatic acid" (OMA) in the *Mémoires de la Société d'Arcueil*, in which they detailed the numerous ways in which they had attempted, without success, to decompose it. They concluded that it was possible that OMA might be elementary, on

² Quoted in McKie (1952), p. 29.

³ Douglas McKie, "Introduction", in Lavoisier ([1790] 1965), p. xxv.

⁴ Brock (1992), p. 119.

⁵ For further details on the competition between Davy and Gay-Lussac, see Crosland (1980).

the basis that they had not been able to decompose it, but they were unable to prove that this was the case. In July 1810 Davy announced to the Royal Society of London:

As yet we have no right to say that it [oxymuriatic acid] has been decomposed; and as its tendency of combination is with pure inflammable matters, it may possibly belong to the same class of bodies as oxygene [sic].⁶

By November 1810, when Davy gave his Bakerian lecture to the Royal Society, he had even given this element a new name, Chlorine (from the Greek *chloros*, meaning yellow-green, referring to the colour of the gas). The main reason for Davy's conviction that chlorine should be considered elementary, he said, resulted from one experiment in particular. This was the inability of OMA to react with white hot carbon. In the "old" theory, OMA was, as the name suggests, oxidized muriatic (hydrochloric) acid, and therefore, when OMA was passed over white hot carbon, the oxygen was expected to be extracted from the OMA by carbon's greater affinity for oxygen, yielding muriatic acid (henceforth "MA") and carbonic oxide.⁷ Contrary to this expectation no such reaction occurred, but even this apparently incontestable result did not constitute a crucial experiment in the manner of Francis Bacon or Karl Popper. It could be explained without pronouncing OMA elementary. Davy himself had offered such an explanation one year earlier, in his Bakerian lecture for 1809:

Muriatic acid gas, as I have shewn, and as is further proved by the researches of [Monsieurs] Gay Lussac and Thenard, is a compound of a body unknown in a separate state, and water. The water, I believe, cannot be decomposed, unless a new combination is formed.⁸

His argument was that since MA could not be formed without associated water, it was unable to exist in isolation. If oxygen were removed from dry OMA, dry MA would be formed; since it was impossible for MA to exist without combined water, the reaction could not occur. Scientists on both sides of the debate carried out their experiments in the presence of water, so the experiments could not provide a conclusive proof that OMA was an element, and the decision about whether OMA is an element or

⁶ Davy, H. (1810b).

⁷ In the form of a quasi-modern equation, this reaction would be: $C_{(\text{white hot})} + \text{OMA} \rightarrow \text{CO} + \text{MA}$.

⁸ Davy, H. (1810a).

not had to be made by other means. This is an instructive example of how a scientific theory may be defended from experimental refutation by the construction of appropriate auxiliary hypotheses.

In Gay-Lussac and Thenard's experiments of 1809, the attempted decomposition of OMA failed except in the presence of water or hydrogen (and they concluded that MA gas could not exist without water). Perhaps the most significant of their experiments was the failure to decompose carefully dried OMA gas passed in a porcelain tube over white hot charcoal. At first a little MA gas was produced, but after a short while the OMA passed over the charcoal unchanged. The MA gas was thought to be produced because there was some moisture contained in the charcoal, providing the water necessary for the existence of MA gas. When the supply of moisture was exhausted MA could no longer be produced so OMA ceased to be decomposed. Gay-Lussac and Thenard were very aware, however, that the failure to decompose OMA could also be explained if OMA was a simple substance, as the conclusion to their paper showed:

It might be supposed, from this fact [failure to decompose OMA by charcoal] and those which are communicated in this Memoir, that this gas is a simple body. The phenomena which it presents can be explained well enough on this hypothesis; *we shall not seek to defend it however, as it appears to us that they are still better explained by regarding oxygenated muriatic acid as a compound body.*⁹

The italicized passage was added to the original conclusion prior to public presentation, upon the urgent advice of Berthollet, who was an important mentor to Gay-Lussac and Thenard. Berthollet had recognized that the key fact that provided continuing support for the compound nature of OMA was the discovery that MA gas always contained water (or the constituent parts of water). This allowed Berthollet the freedom to interpret experiments that would otherwise be taken as conclusive proof of the elementary nature of chlorine, in terms of his preferred view of compound OMA.¹⁰

⁹ Gay-Lussac and Thenard [1809] (1897), p. 48; emphasis original.

¹⁰ Berthollet would have used this new fact to explain the problem discussed in Chapter 1: pure chlorine undiluted with water could not be induced by any experimental means to give up oxygen. Berthollet would simply say that oxygen cannot be removed from the MA unless the water (or hydrogen) essential to its constitution is present.

3. Chlorine and Lavoisier's oxygen theory of acidity

Conflicting beliefs about the elementary nature of chlorine did not, of course, exist in isolation, but formed part of larger systems of chemistry. As in Chapter 1, the story of chlorine will provide an interesting example of the philosophical problem of theory-choice. Here we must begin by dispelling a common misconception, that the acceptance of the elementary nature of chlorine sounded the death knell for Lavoisier's oxygen theory of acidity (henceforth "LOTA"). As a convenient expression of this view, we can cite a statement by Homer Le Grand, one of the leading experts on the history of LOTA:¹¹

The recognition of the elemental nature of oxymuriatic acid and the consequent establishment of the correct composition of muriatic acid *effectively destroyed* not only *Lavoisier's theory that oxygen was the unique 'acidifying principle'*, but also the exalted role of oxygen in his whole chemical system.¹²

The idea of OMA as an element affected Lavoisier's chemical system as a whole, as we will discuss later (see Section 7 especially), but first we argue against the view that elementary chlorine "effectively destroyed" LOTA. Our thesis is that LOTA had ceased to be a central component of French chemistry well before Davy's pronouncement of the elementary nature of chlorine. Le Grand does acknowledge that there were pre-chlorine doubts raised about LOTA, but he argues that the majority of chemists *did* consider oxygen to be the unique acidifying principle in the years leading up to the discovery of chlorine, on the basis of a survey of a large sample of chemical texts he carried out:

This group of five chemists and popularizers of chemistry [Richard Chenevix, Frederick Accum, Thomas Thomson, Samuel Parkes, and Martin H. Klaproth] constitutes a distinct minority of the some 120 French, German, and British chemists consulted for the years 1790–1807. Excluding a few "cranks," the remainder employed the oxygen theory of acidity in an uncritical fashion.¹³

It is quite curious that Le Grand chooses to omit Claude-Louis Berthollet (1748–1822) from his list of dissenters, since he is well aware of the case. Before we discuss others, we must take full account of

¹¹ See also Brooke (1980), pp. 121–123. Crosland (1973, p. 322) gives a more nuanced view.

¹² Le Grand (1974a), p. 213.

¹³ Le Grand (1976), p. 232, footnote 17.

Berthollet's views, not only because he was the leading French expert on OMA (see Chapter 1, Section 3), but also because he was the most influential chemist in France after Lavoisier's death. When Berthollet rejected phlogiston in 1785, he did not blindly accept all of the key ideas of Lavoisier's new oxygen-centered chemistry. His experiments on acids quickly led him to raise a series of objections to LOTA. His four main objections were:¹⁴

- (1) Prussic acid and sulphuretted hydrogen (also an acid) had been analyzed, and shown not to contain any oxygen.
- (2) Muriatic, fluoric and boracic acids, had not been analyzed, therefore not proven to contain oxygen.¹⁵
- (3) Oxymuriatic acid contained more oxygen than muriatic acid, but was less acidic.
- (4) Many compounds of oxygen, such as water and metallic oxides, were not acidic.¹⁶

In 1803 Berthollet published the *Essai de Statique Chimique*, in which he dealt with these problems by proposing that oxygen was not the exclusive acidifying principle. According to Berthollet, oxygen did not have to be present in all acids, which he defined simply as substances with affinities for the alkalis:

The distinguishing character of acids is to form combinations, by their union with alkalis, in which the properties of acidity and alkalinity can no longer be discovered, when the proportions of the acid and the alkali are such as to produce that degree of saturation called neutralisation. Acidity and alkalinity are therefore two co-relative terms of one species of combination.¹⁷

¹⁴ Le Grand, *ibid.*, conveniently summarizes Berthollet's objections in this way. It is important to note the difference between 1 and 2, which threatened the status of oxygen as the necessary condition for acidity, and 3 and 4, which left room to regard oxygen as a necessary (though insufficient) condition for acidity. Whilst Lavoisier always maintained that the presence of oxygen was a necessary condition for acidity, the decomposition of water caused him to question whether it was a sufficient condition.

¹⁵ However, Berthollet seemed to agree with Lavoisier that they probably did contain oxygen very tightly bound to their "radicals".

¹⁶ As Le Grand (1972, pp. 11–12) explains, Lavoisier himself was troubled by this fact, but only in the case of water, as he believed he could explain the non-acidity of the metallic oxides.

¹⁷ Berthollet (1804), vol. 1, p. 43.

Where oxygen *did* cause the acidity of a substance, it was not enough for it to be present, but it had to remain at least partially “unsaturated”. Berthollet claimed that “the acidity of an oxygenated substance shows that the oxygen has only experienced an incomplete saturation in it, since its properties remain predominant.”¹⁸ Saturation could cause affinities to disappear; therefore where oxygen *was* the cause of acidity, the properties it brought to each acid depended on the degree to which it was saturated.

Although he retained aspects of LOTA and granted that oxygen was important to the acidity of the majority of known acids, Berthollet developed a much more sophisticated explanation of acidity based upon his new ideas about complex chemical affinities. Berthollet’s explanations were chemically superior to LOTA: he was able to explain all of the phenomena explained by LOTA *and* to answer all of his own objections. Berthollet’s conception of acidity was also founded on a much more secure experimental basis than LOTA. Despite all that, it was largely ignored, partly because it was a consequence of the mechanistic, affinity-based approach to chemistry advanced by Berthollet in his *Essai de Statique Chimique*, which the chemical community largely rejected or ignored. Ironically, the general lack of interest in Berthollet’s explanation of acidity may have been compounded by the fact that, as Le Grand put it, “Berthollet, in advancing his own rival *theory*, undercut many of his earlier experiment-based objections to Lavoisier’s theory.”¹⁹

In the *Essai*, Berthollet withdrew his objection that oxygen seemed to deprive OMA of its acidity relative to MA (see point 3 above). He explained that he had previously “overlooked the state in which [the oxygen] exists. The oxygen is but feebly retained in oxymuriatic acid, so that it easily abandons the muriatic acid.”²⁰ This observation was based upon an experiment in which he had exposed a solution of OMA to light, and found that oxygen gas was disengaged, leaving MA behind in solution. Berthollet argued that if the oxygen in OMA was held so weakly in combination with the MA as to be expelled by the action of light alone,

¹⁸ Ibid., vol. 2, pp. 9–10.

¹⁹ Initially Berthollet’s ideas were criticized by some (often on the basis of misunderstandings) and ignored by many others, due to the difficulties associated with applying them in practice, and the poor clarity of expression in the *Essai*. Le Grand has suggested that so soon after the Chemical Revolution, chemists were reluctant to abandon once again their familiar framework in favour of Berthollet’s complicated and unfamiliar ideas. See Le Grand (1976), p. 229.

²⁰ Berthollet (1804), vol. 2, p. 8.

then the affinities of oxygen should not be expected to dominate the behaviour of the compound.

On the role of oxygen as the acidifying principle, Berthollet commented: “it appears to me that too much latitude has been given to the principle . . . while on my side, I have restricted it too much.”²¹ As Le Grand notes, such remarks may have been interpreted as signalling a return to Lavoisier’s views,²² but this was certainly not Berthollet’s intent. Despite the disappointing reception of the *Essai de Statique Chimique*, Berthollet did not bring his view of acidity back into line with Lavoisier’s at any point. However, his explanation of acidity may have been (wrongly) perceived by others as a modification of LOTA rather than the real alternative he meant it to be.

Whilst retaining oxygen as an acidifying principle in certain circumstances, Berthollet rejected the fundamental assertion of LOTA: that oxygen is the *unique* acidifying principle. In Berthollet’s theory of acidity, unlike in Lavoisier’s, oxygen was *not* a necessary component of all acids. In referring to his definition of acidity, Berthollet said: “this species of affinity for the alkalis may belong to substances which do not contain oxygen, we must not therefore always infer from the acidity of a substance that it contains oxygen.”²³ It is clear, then, that Berthollet’s objections to the proposal that OMA was an element were not motivated by a desire to defend LOTA; he rejected this theory definitively in 1803 and did not change his mind.

LOTA was not the cause of Berthollet’s objections to elementary chlorine, nor was chlorine the reason for Berthollet’s rejection of LOTA. But did elementary chlorine cause the rejection of LOTA by other chemists? It seems to us that LOTA did not maintain importance for chemists in general long enough for elementary chlorine to have a significant impact on it. By the time it was realized that MA did not contain oxygen, this was just one more entry in a long list of counter-examples to LOTA, a list that had already led several leading chemists to speak out against LOTA.

Berthollet was certainly not alone in doubting LOTA long before the elementary nature of chlorine was proposed. Another close colleague

²¹ Ibid.

²² Le Grand (1976), p. 236.

²³ Berthollet (1804), vol. 2, p. 9.

of Lavoisier's, Antoine-François de Fourcroy (1755–1809), rejected LOTA in 1802. Gay-Lussac also realized, well before chlorine, that oxygen was not the only substance capable of communicating acidity. There was also Thomas Thomson, perhaps the most influential British chemist of the period between the heydays of Joseph Black and Humphry Davy. Thomson is one of the five cases mentioned by Le Grand, along with Martin H. Klaproth (1743–1817), Frederick Accum (1769–1838), Richard Chenevix (1774–1830) and Samuel Parkes (1761–1825), all of whom concluded before 1807 that not all acids contained oxygen. Jean-Claude De La Métherie (1743–1817), editor of the *Journal de Physique* in Paris, may have been one of those unnamed “cranks” in Le Grand's list, as he was a staunch opponent of Lavoisierian chemistry in general, but that would not be a fair description.²⁴

The anti-LOTA arguments advanced by Chenevix, Thomson, and Gay-Lussac are worth noting briefly. In the same year as Fourcroy, Chenevix expressed his doubts over the validity of LOTA as follows:

Muriatic acid is for us a simple body; but it has acid properties of the strongest kind; therefore, from analogy we suppose it to contain oxygen. But may not this be too hasty a conclusion? . . . [W]e should begin by considering, whether the presence of oxygen in all bodies that have acid properties, has been rigidly demonstrated, and not determine by this law of the French chemistry, till we are well convinced it has not been too generally assumed.²⁵

Chenevix's concerns were echoed by Thomson. In the 1804 edition of his *System of Chemistry*, Thomson explicitly stated that “it is not true that oxygen is an essential ingredient in all acids, or that no body possesses the properties of an acid unless it contains oxygen. Sulphuretted hydrogen, for instance, possesses all the characters of an acid, yet it

²⁴ See Partington (1962), pp. 495, on De La Métherie's opposition to Lavoisier. Other chemists dissenting from LOTA included William Henry (1774–1836) and François R. Curaudau (1765–1813), as Le Grand (1974a, p. 219) himself documents. Jakob Joseph Winterl, a professor of chemistry in Budapest, also argued that not all acids contained oxygen, and presented substantial experimental evidence to back up his claims. However, according to Partington (1962, p. 599), he also had some rather odd ideas on the true causes of acidity (immaterial or spiritual principles that adhered to atoms). The German chemists Lorenz Crell and F. A. C. Gren, both of whom adopted some of Lavoisier's ideas whilst retaining aspects of phlogiston theory, concluded that there was no need to believe that oxygen was a constituent of all acids; see Partington (1962), pp. 634–635.

²⁵ Chenevix (1802), pp. 165–166.

contains no oxygen.”²⁶ He emphasized the need to reject LOTA, noting the serious problems it caused:

If we lay down as an axiom that oxygen is the acidifying principle we must either include among acids a great number of bodies which have not the smallest resemblance to those substances which are at present reckoned acids, or exclude from the class several bodies which have the properties of acids in perfection.²⁷

Gay-Lussac, the rising star of French chemistry, also supported Berthollet’s definition of an acid as “no more than a substance, whether it contains oxygen or not, which neutralises alkalinity.”²⁸ Therefore, while working with LOTA, Gay-Lussac disagreed with its fundamental tenet that all acids must contain oxygen.²⁹ In 1814, he presented a list of instances where acidity was caused without the presence of oxygen, all of which had been identified as such before the discovery that MA did not contain oxygen. It is important to note that Gay-Lussac realized that acidity could be communicated by substances other than oxygen even before he recognized chlorine as a candidate: “a substance can be acid or alkali without containing oxygen, and as a consequence acidity and alkalinity can be communicated by substances other than oxygen.”³⁰

Le Grand ends his survey in 1807, just before the emergence of another important piece of evidence against LOTA, which he discusses in another paper. Davy’s decomposition of the alkalis (soda and potash) provided clear evidence against LOTA and caused some of those previously uncritical of LOTA to begin to have doubts. Davy discovered that these *alkalis* contained oxygen, the supposed acidifying principle, and joked that oxygen might just as well be called the principle of alkalescence. The discovery that these alkalis contained oxygen should have given discomfort to followers of LOTA; however, according to Le Grand, British chemists William Nicholson (1753–1815) and Charles Sylvester (1774–1828) were the only new figures (albeit important ones)

²⁶ Thomson (1804), vol 2, p. 4.

²⁷ *Ibid.*, p. 5.

²⁸ Gay-Lussac (1814b), p. 145 (our translation). For the translation of chemical terms, we have referred to Patterson (1954).

²⁹ Crosland (1978), pp. 133–134.

³⁰ Gay-Lussac (1814b), p. 146 (our translation).

to doubt LOTA following Davy's discovery.³¹ Contrary to Le Grand's suggestion that few chemists appreciated the implications of the discovery, and that most therefore continued to use LOTA in its fullest form, the lack of reaction was probably an indication that LOTA was already perceived as a reasonable guide rather than a strict law.

The chemists who questioned LOTA or worked happily outside it, with or without alternative theories, were not working at the fringes of the scientific community: they were amongst the most influential chemists of their time, and included Berthollet and Fourcroy, two of the closest associates of Lavoisier. Overall, it seems that LOTA was regarded in the chemical community as more of a starting point for investigations than as an established theory vital to the chemical paradigm that had replaced phlogiston. Those chemists who appealed to LOTA "in an uncritical manner" did so because, in the absence of a better alternative,³² it still acted as a useful guide. The implications of elementary chlorine were entirely compatible with the only aspects of LOTA that had any real support: that oxygen was an important (though not the exclusive) acidifying principle. The reluctance displayed by Berthollet and others to accept that chlorine was an element therefore did not mean that they were fighting in LOTA's defence.

All of that is to say that the main body of the chemical community would not have been prevented from taking up the idea of elementary chlorine by an attachment to LOTA. In fact, it seems that mainstream opinion converted very rapidly to the idea of elementary chlorine. Still, some major chemists, including Berthollet, Murray and Berzelius, resisted elementary chlorine for a considerable time. Murray died in 1820 without accepting the elementary nature of chlorine, whilst Berzelius continued to write papers strongly opposed to elementary chlorine up until 1816, only including chlorine in a paper on the symbols and atomic weights of the elements in 1826. In order to reach a true understanding of the establishment of chlorine as a chemical element, we must learn the arguments advanced by these dissenters, and why those arguments were not successful. This is the task we undertake in the next three sections.

³¹ Le Grand (1974b), p. 63.

³² Berthollet's explanation was a better alternative but, as discussed earlier, it was neglected along with the whole framework of the complex affinity-based chemistry of the *Essai de Statique Chimique*.

4. The Murray–Davy debate

The Scottish chemist John Murray (1778?–1820) and Humphry Davy’s younger brother John Davy (1790–1868) conducted a lively debate on the nature of chlorine in the pages of *A Journal of Natural Philosophy, Chemistry, and the Arts* edited by William Nicholson (henceforth *Nicholson’s Journal*), running through seven volumes from 1811 to 1813.³³ This exchange illustrates contrasting personal styles as well as differing theoretical allegiances. Murray showed some adherence to LOTA, although it is not clear whether this was his reason for opposing the chlorine theory, or merely an additional weapon against it. In general, the points Murray made were of a somewhat philosophical nature, not made in an aggressive manner, but rather as an attempt to show an alternative to Davy’s views. That is, in this debate he seems to have been rather more interested in the philosophical question “How can we ever be sure what this is?” than the chemical question “What is this?”

In the first paper in the series Murray was very measured, simply laying out all the observations presented as proof of the elementary nature of OMA/chlorine. He then explained in each case how the experiment could be interpreted if the substance in question were considered elementary (as chlorine) and if it were considered a compound of oxygen and MA, identifying which observations were problematic for each theory. For example, in the case already mentioned, white-hot carbon should, according to the compound theory, be able to remove oxygen from OMA to form carbonic oxide and MA, whereas in fact no reaction occurred. But Murray also noted a significant problem for the element theory of chlorine, as follows:

Oxymuriatic acid is considered by [this theory] as a principle belonging to the same class as oxigen [sic], which like it exerts powerful attractions to inflammable substances, and which is not inferior in energy of action, why therefore should it not like oxigen combine with charcoal?³⁴

John Davy’s response to Murray’s paper was very different in tone. From the outset the piece was aggressive, and Davy suggested that his

³³ For a different angle on the Murray–Davy controversy, see Golinski (1992), pp. 225–230.

³⁴ Murray (1811a), p. 137. In fact, Davy’s July 1810 paper to the Royal Society suggested that chlorine could be classified with oxygen as tending to combine with inflammable matter.

brother's conclusions constituted a proper "theory" while Murray's were mere "hypothesis": "Theory is a history of generalisations and facts, hypothesis is a series of suppositions."³⁵ He continued to make clear his opinion of LOTA:

To avoid all verbal controversy I candidly acknowledge, that I consider the acidifying principle as a mere arbitrary term. Oxygen strictly speaking can with no more propriety be said to be the cause of the acidity of sulphuric acid, than sulphur.³⁶

These extracts from the two men's papers are typical of their contrasting styles. Throughout the debate, Murray's arguments were longer and more considered, whilst Davy's were aggressive, pithy, and often personal. He not only disagreed with Murray's interpretation of experiments and accused him of relying on *ad hoc* hypotheses, but also questioned Murray's skills as an experimenter. Using the Baconian quotation, "What a man wants to be true, he believes easily",³⁷ Davy implied that Murray was not following the scientific method, and insisted that the chlorine theory was superior in all respects. Murray, meanwhile, merely tried to make clear that the chlorine theory had many problems of its own, and was not superior in all respects to the OMA theory. Murray's writings in *Nicholson's Journal* were full of philosophical insight, and it seems probable that he was more interested in a philosophical debate than the application of theory, as this response to Davy in 1811 suggests:

The two opinions are perfectly alike with regard to the evidence on which they rest derived from the above facts; and to select in one of them that part where the induction appears direct, and take it for granted that is true, the hypothetical assumptions, which must be farther made, necessarily follow: but to pursue the reverse method with regard to the other, to represent it as an hypothesis, by bringing forward the parts which require the assumption of hypothesis, and neglect or reject the more direct induction, is a mere sophism.³⁸

One might say that John Davy was more dogmatic than Murray, and hence rhetorically more convincing.

³⁵ Davy, J. (1811a), p. 194.

³⁶ *Ibid.*, p. 197.

³⁷ Davy, J. (1811b), p. 31.

³⁸ Murray (1811b), p. 298.

Murray's argument was not aided by his uncertain status as a chemist. Although he lectured on chemistry in Edinburgh and authored a well-known textbook of chemistry, he does not seem to have been highly respected by other chemists of the time. Murray's compatriot Thomas Thomson, in correspondence with Berzelius in 1816 said, "I am sorry you have been so severe upon Murray in your paper on chlorine. I entertained the same opinion of his papers that you do."³⁹ In his summary of the "Improvements in Physical Science during the year 1815", Thomson stated: "Chlorine is now pretty generally admitted to be a simple supporter of combustion. Almost the only chemist of eminence who adheres to the old opinion is Berzelius."⁴⁰ Clearly Thomson did not consider Murray a "chemist of eminence"! Even William Henderson, who wrote a paper in defence of the compound OMA theory, added a footnote stating: "I would not be understood as having reference here to Mr. Murray's view on the nature of potassium, but merely as arguing against its being a hydruret of potash".⁴¹ A rather poor opinion of Murray's science seems to have been widespread.

The debate between Murray and Davy trailed off somewhat in 1812. Murray became ill during this period, and it is possible to see marks of this in his writings, which showed an ever-increasing exasperation with Davy's unrelenting attacks. Whatever the others' opinions were, Murray seems to have gone to his grave unconvinced about the elementary nature of chlorine.

5. The conversion of Berthollet⁴²

Berthollet also recognized the same kind of empirical equivalence between the two theories of chlorine/OMA as identified by Murray. As mentioned at the end of Section 2, Berthollet had urged Gay-Lussac and Thenard against interpreting the failure of carbon to decompose OMA as support for elementary chlorine, proposing that the inability of MA to exist without water provided an equally satisfactory explanation of the

³⁹ Soderbaum (1918020), vol. 3 (I), p. 44.

⁴⁰ Thomson (1816), p. 27.

⁴¹ Henderson (1813), p. 18.

⁴² For a more comprehensive treatment of the French side of the story, especially the work of Curaudau, see Chabot (2006), a paper that we have only discovered as this book was going to press.

observed experimental results. In another experiment, Gay-Lussac and Thenard showed that hydrogen gas reacted with OMA to make MA, no water being produced. This suggested, as Gay-Lussac and Thenard appreciated, that MA was a compound of OMA and hydrogen (and therefore that OMA was elementary). If OMA contained oxygen then some water should be produced when this oxygen abandoned MA to combine with the hydrogen gas. In Berthollet's interpretation water *was* produced but remained unseen because it was held in combination by the MA gas, which could not exist without it.⁴³ It was therefore impossible to distinguish between the two proposed hypotheses for the composition of OMA/chlorine using these experiments.⁴⁴

In his 1811 paper Berthollet explained why, despite the apparent equivalence of the two hypotheses, he still believed chlorine to be a compound. He argued that whilst both hypotheses could explain the results of the experiments, the compound hypothesis was much more convincing because, unlike the elementary hypothesis, it did not over-complicate the situation, especially by supposing that water was being decomposed in some of the reactions under consideration. It is not that Berthollet did not grant the possibility that water could be decomposed in chemical reactions, but he also emphasized that water was often "necessary for . . . decompositions to take place, without influencing events by its own decomposition".⁴⁵ In the case of the reactions involving OMA, "we find no indication of the composition or decomposition of water, but we suppose it because it is required by the new hypothesis. At the same time we must suppose the de-oxidation of metals, which is more difficult to admit, and in other cases the oxidation of metals, without any sign of its occurrence."⁴⁶ (See Chapter 1, Section 3.3 for further details on Berthollet's complex handling of water in chemical reactions.)

Berthollet's arguments can be further illustrated by comparing the competing explanations of the oxidation of metals in the presence of OMA/chlorine. In quasi-modern chemical equations, we can express the situation as follows. According to the hypothesis of elementary chlorine:

⁴³ Berthollet et al. (1811), p. 128.

⁴⁴ Ibid., pp. 126, 128.

⁴⁵ Ibid., p. 127 (our translation).

⁴⁶ Ibid., pp. 133–134 (our translation).



Some of the water present at the start is decomposed during the reaction; hydrogen from the decomposed water combines with the chlorine to produce hydrochloric acid, whilst oxygen combines with the metal to form the oxide. Some water is left over. In contrast, according to the hypothesis of compound OMA:



Here the metal takes oxygen from the OMA, leaving the MA to take some water from the surroundings, which it requires in order to exist in independent form. Again, there is less water at the end than we started with, but none of it has been decomposed.

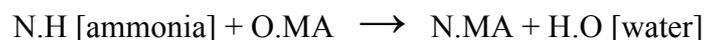
As well as claiming that it was unnecessary to complicate matters by introducing the decomposition of water, Berthollet argued that explanations based on the hypothesis of elementary chlorine contradicted one another in certain cases. According to Davy, when lime was heated with hydrochloric acid (HCl), water was formed by the hydrogen from the hydrochloric acid combining with the oxygen from the lime. In this case water was synthesized by the action of heat. On the other hand, if chlorine was exposed to light in the presence of water, or passed through a heated, moistened tube, oxygen was given off as result of water being decomposed. How could it be, Berthollet asked, that in one case heat caused the composition of water, whilst in other cases it was supposed to cause its decomposition?⁴⁷ Berthollet stressed how simple and natural the explanations based on compound OMA appeared, compared to the contradictory and contrived explanations provided by the elementary hypothesis, and he noted that the behavior of muriatic acid appeared much more analogous to that of other acids when considered within the compound hypothesis.⁴⁸ The arguments Berthollet put forward in defence of his long established view of the compound nature of OMA were detailed and convincing. But he changed his mind eventually. Why?

⁴⁷ Ibid., p. 133.

⁴⁸ Ibid., p. 129. For example, according to the compound hypothesis, when OMA combines with metals, it forms muriates analogous to sulphates.

It was in 1816 that Berthollet conceded for the first time that he considered OMA to be the element chlorine.⁴⁹ Berthollet's 1816 paper is very intriguing, and deserves some detailed examination. Interestingly, Berthollet claimed that he was guided towards the conclusion that chlorine should be considered an element, by Lavoisier's "great principle" that all substances for which composition cannot be proved by analysis, should be considered simple.⁵⁰ But this is not convincing. Already in 1809, Gay-Lussac and Thenard's exhaustive attempts to decompose pure OMA in 1809 had made it clear that the composition of OMA could not be proved by analysis. Had Lavoisier's principle really been a significant influence, then Berthollet would have considered OMA as an elementary substance in 1809; instead, he restrained Gay-Lussac and Thenard from jumping to the hypothesis of elementary chlorine. As we have seen at the start of Section 2, even Lavoisier himself did not adhere strictly to his own operational definition of element, and Berthollet certainly did not.

Perhaps more important was Berthollet's recognition of an error in an earlier experiment by Fourcroy, which Berthollet had regarded as a decisive piece of evidence for the compound nature of OMA. This experiment was the reaction of ammonia gas and OMA.⁵¹ When Fourcroy originally made the experiment, some water had been produced.⁵² The production of water was expected according to the interpretation of OMA as a compound, but could not be explained if OMA was an element: Berthollet argued that the water must have been formed from oxygen from OMA and hydrogen from ammonia. Again, in the form of a quasi-modern chemical equation:



⁴⁹ Berthollet (1816), p. 605. As a member of the Senate, Berthollet's scientific activities were interrupted during 1814 and 1815 by the fall of his patron and friend, Napoleon Bonaparte, and the restoration of the monarchy. It may be that he changed his mind about chlorine as early as 1814, but did not have the chance to publish until 1816.

⁵⁰ Ibid.

⁵¹ Fourcroy himself interpreted this experiment as proof of the composition of ammonia rather than that of OMA. In fact the experiment was published in the same volume in which Fourcroy expressed doubts that OMA contained any oxygen, so he cannot have attached the same significance to them as Berthollet, who had a somewhat different agenda.

⁵² Fourcroy (1802), p. 243.

If there was no oxygen in OMA/chlorine, how would water be formed in this reaction? In 1811, however, John Davy repeated Fourcroy's experiment and showed that in fact *no* water was produced when carefully dried ammonia and chlorine gases reacted.⁵³ Now the chlorine-based explanation of the reaction was quite straightforward, and Berthollet realized that elementary chlorine *was* a viable alternative to compound OMA.

Once more, we find Berthollet's account slightly disingenuous. If John Davy's repudiation of Fourcroy's ammonia experiment had been the key moment, Berthollet would have changed his mind about chlorine in 1811! We know he didn't. Back then he simply changed his interpretation, to say that when ammonia gas reacted with OMA, the expected water was not collected simply because the water was held in combination by the muriate of ammonia produced in the reaction. This way of thinking was quite similar to the idea (mentioned in Section 2) that MA gas could only exist in combination with water, and would not have posed a serious anomaly in Berthollet's system. In 1811 he did not think he was twisting the facts to fit his favourite theory; on the contrary, earlier he had declared: "I shall be the most vigilant among scientists to discover the causes of error which [theory] may have imposed upon me."⁵⁴ So, Davy's 1811 ammonia experiment will not do as the explanation of Berthollet's conversion.

What is the explanation, then? Further experimental evidence did play a part. In his 1816 memoir, Berthollet declared: "within the currently known facts we can find proofs, in the light of which we are obliged to consider chlorine as an element."⁵⁵ As an example of an observation which could only be made sense of by considering chlorine to be an element, Berthollet gave details of the various methods used to determine the proportion of water in potassium hydroxide (*hydrate de potasse*). He explained that Jean d'Arcet (1725–1801) had reacted potassium hydroxide with sulphuric acid, and used the products of the reaction to calculate that potassium hydroxide contained 27% of its weight in water. Berthollet himself, using the more indirect method of reacting potassium hydroxide with MA, and then heating the muriate of potassium formed to create a new product, calculated a water content of 13.64%, just half of d'Arcet's

⁵³ Berthollet (1816), p. 604.

⁵⁴ Berthollet (1804), vol. 2, p. 451.

⁵⁵ Berthollet (1816), p. 605 (our translation).

value.⁵⁶ Berthollet proposed that these apparently contradictory results could be reconciled if chlorine were considered to be an element, although he did not explain exactly how.⁵⁷

It is likely that Berthollet was also influenced by the discovery of the element iodine, which displayed clearly analogous properties to chlorine and was immediately classed alongside it (see Section 7). Much of the work on iodine was carried out by Gay-Lussac at Arcueil, so Berthollet would immediately have been aware of the implications of the new discoveries. Following the discovery of iodine and also the plausible conjectures regarding fluorine, it would have seemed increasingly unreasonable for Berthollet to continue resisting the elementary nature of chlorine, and we believe it was this general shift in chemistry, more than the aforementioned experiments, that really made Berthollet change his mind.

6. Berzelius and theory-choice

If Berthollet only responded to accumulated evidence concerning the group of elements known as the halogens, rather than the first indications that OMA might be elementary, Jöns Jakob Berzelius (1779–1848) opposed the elementary theory of chlorine for even longer. The case of Berzelius is quite puzzling, and we have relied on his personal correspondence as well as his publications in order to arrive at a plausible interpretation of his thinking.

It is important to note that Berzelius's thinking was framed in terms of his own highly developed electrochemical theory. His correspondence with Alexandre Marcet (1770–1822), a mutual friend of Davy and Berzelius, indicates that he saw the chlorine theory as a dead-end. His own research programme, on the other hand, which required OMA to be compound in nature, seemed full of promise. In January 1813 Berzelius wrote in humorous vein: "How is Davy's health? — What does he

⁵⁶ *Ibid.*, p. 606, provides only some details of these reactions.

⁵⁷ *Ibid.*, p. 607. He was further convinced of the case for elementary chlorine as d'Arcet's figure had been confirmed by Gay-Lussac and Thenard using two different experimental methods.

say of my arguments against his daughter Chlorine, who will die of her jaundice (yellowness)?”⁵⁸ In April 1813 he wrote:

I have waited for a long time for him to take the pain to refute the arguments against his hypothesis on muriatic acid, or else to return to the old idea.— This new hypothesis is nothing but a trifle, contributing a considerable holding back of the progress of science, because it does not harmonize with the chemical system and because a number of chemists who need to rely on other people’s authority will surely look to Davy’s authority.⁵⁹

One main source of Berzelius’s opposition to the idea of elementary chlorine was its conflict with his understanding of oxidation.⁶⁰ When Humphry Davy announced the existence of “euchlorine”,⁶¹ Berzelius welcomed it as evidence for his own peculiar theory of multiple degrees of oxidation, which was inspired by his study of the work of Jeremias Richter. In an excited letter, Berzelius expressed the hope that Davy, too, would soon come around to this idea:

You have seen, therefore, that I do not share your opinion on the nature of muriatic acid and its different degrees of oxidation, and I have some hope that you also abandon them soon. The saline combinations of this acid prove that it contains oxygen, and it is not difficult to determine how much it contains, the moment we know two other of its degrees of oxidation. But I have found that, if we are to apply to the muriatic acid radical the same law of progression in relation to its different degrees of oxidation, we are missing one of these degrees. The ordinary progression of the oxidation being 1, 1.5, 2 and 4, muriatic acid offers 1 (muriatic acid), 1.5 (a. oxym.) [sic] and 4 (a. oxymuriatic) [sic]; in short, the degree 2 is missing. I have made vain searches for this, an account which I have given in my treatise on this matter. So imagine, Sir, how agreeable I found the communication of your discovery of a gas composed of two volumes of oxymuriatic gas

⁵⁸ Berzelius to Marcet, 29 January 1813, in Soderbaum (1912–14), vol. 1 (III), p. 24. Berzelius also mentioned in a letter to Davy at around the same time that he did not approve of the nomenclature “chlorine” for exactly the reason that Davy had chosen it: it merely described the observables (green/yellow), not any theoretically useful information, unlike “oxymuriatic acid”. It was this lack of theoretical content that he believed would be chlorine’s downfall. See *Ibid.*, p. 37.

⁵⁹ Berzelius to Marcet, 22 April 1813, in *Ibid.*, p. 36.

⁶⁰ See Melhado (1992), p. 150.

⁶¹ Euchlorine was considered by Davy and his followers to be ClO. Carmen Giunta suggests that it must actually have been a mixture of Cl₂ and ClO₂. (See <http://web.lemoyne.edu/~giunta/archema.html#euchlorine>; most recently accessed on 14 May 2007.)

and one volume of oxygen gas, which is exactly the degree of oxidation that I predicted the existence of by calculation, but whose discovery was missed by an experimenter less skilled than you.⁶²

Unfortunately for Berzelius, this degrees-of-oxidation theory ran into some difficulties, the most significant of which concerned the nature of ammonia. Berzelius (and Davy, for a time) believed ammonia to be a higher oxide of azote (nitrogen), with azote in turn an oxide of hydrogen. This was the only way to make ammonia fit into the degree-of-oxidation scheme, but the oxygen presumed to be a constituent of ammonia (or nitrogen) was not to be found. It is possible, therefore, that Berzelius would have gradually decided that this area of research was not progressive and therefore this argument against elementary chlorine would also have been weakened in his mind.

Another of Berzelius's objections to elementary chlorine was, however, much harder to dismiss, and in fact more fundamental. In 1812, a new compound of chlorine and azote (nitrogen) was synthesized in France. News quickly spread to England. After carrying out some experiments, which nearly blinded him, Davy presented a detailed account of this dangerous detonating oil to the Royal Society in 1813. Davy's initial experiments led him to believe that azote and chlorine were produced on the detonation of this compound, and subsequent studies indicated that this was indeed so. Davy remarked in this paper that "the heat and light produced during its expansion into gaseous matter, supposing it to be composed of azote and chlorine, is without parallel instance, in our present collection of chemical facts."⁶³

Berzelius used this highly unusual compound in an extensive critique of the chlorine theory. The piece, which was originally published in Gilbert's *Annalen* and then translated and published in Thomson's *Annals of Philosophy*, was extremely long and detailed.⁶⁴ It covered all known objections to the OMA theory and objections to the chlorine theory, in each case using the terminology of both doctrines. Many of the

⁶² Berzelius to Davy, 10 June 1811, in Soderbaum (1912–14), vol. 1 (III), p. 28. Berzelius and Davy corresponded frequently and on friendly terms between 1809 and 1813. Davy had been the first to sign the recommendation of Berzelius for a fellowship of the Royal Society in 1813. After Davy's first major trip to the Continent in 1813, however, there was an interval of eight years during which they did not correspond.

⁶³ Davy, H. (1813), p. 6.

⁶⁴ Berzelius (1816).

arguments had already been covered by other opponents to the chlorine theory, including Murray and Henderson. The section on the muriate of azote (nitrogen trichloride in modern terminology) was buried amongst the usual arguments and spread over two different volumes, a fact which may have prevented all but the most dedicated followers of the debate (of whom there were few by 1816) from realizing its importance.

Berzelius had devised an electrochemical theory to explain the production of heat in chemical reactions, and of cooling in the solution of substances. Berzelius's sophisticated theory not only exhibited impressive reasoning, but also showed evidence of careful and precise experiments. Berzelius introduced the theory in his 1813 paper in *Nicholson's Journal*:

When a combination already formed, as, for instance, between *A* and *B*, is decomposed by the more powerful affinity of a third body *C*, so that this last separates *A* from the combination *AB*, and forms *CB* — such a decomposition is usually accompanied with an elevation of temperature, or even with fire; and this elevation is greater the more considerable the difference may be between the affinities of *A* and of *C* to *B*. We may form a notion that this effect is owing to a more perfect neutralization of the electro-chemical properties of the constituent parts in the new, than in the old combination. If, on this occasion, *B* were oxygen [sic], and *A* and *C* two combustible bodies, the electro-chemical nature of *B* must be admitted as more perfectly neutralized by *C* than by *A*; and at the instant when *A* is reduced to its original combustible state, it receives from *C*, which loses its like state, a quantity of positive electricity, equal to what it had lost when it entered into combination with *B*.⁶⁵

This passage may sound long-winded, but it gives a clear generalized description of why heating accompanied such reactions, which Berzelius developed further in his paper in *Annals of Philosophy*:

[A]n explosion cannot take place unless when [sic] a compound . . . can arrange its constituents in other proportions, by means of which their opposite electro-chemical properties can be much more completely neutralized than before. . . . [D]o we know of any example of two combined bodies, whose simplicity is undisputed, that separate from each other with an increase of temperature produced by the

⁶⁵ Berzelius (1813), p. 159.

separation itself, and which assumes a state of complete disunion? For my part, I am acquainted with no such example. . . . [I]n chemical decomposition, heat is rather absorbed than evolved.⁶⁶

This was a beautiful piece of reasoning, more advanced than any of the proto-electrochemical theories entertained by other chemists such as Henderson. Berzelius proposed that the reaction in which muriate of azote decomposed into azote and OMA could not occur with a bang, which it did, because heat and light could only be produced when the electrochemical properties of bodies were neutralized. In the case of free-standing elements the electrochemical properties are not neutralised at all, so there could not be any heat and light in a reaction whose products are elements. So Berzelius proposed an alternative interpretation in which oxygen was closely associated with the azote in the muriate of azote. In the decomposition of the muriate of azote, the oxygen migrated to MA because it had a significantly greater affinity for oxygen than azote did, and this led to a more complete neutralization of the electrochemical properties of both bodies, which in turn caused the observed heat and light. Therefore, Berzelius was able to produce a powerful explanation of new phenomena that confirmed the compound nature of OMA.

Why was Berzelius's electrochemical argument against chlorine neither picked up on by other opponents to the chlorine theory, nor criticized by its proponents? One simple reason could be that nobody really understood the argument. Berzelius's argument only worked on the basis of the explanation of heat in chemical reactions derived from his own electrochemical theory. His explanation of why compound OMA fitted the electrochemical description of these heating processes, whilst elementary chlorine did not, also required some kind of atomic theory, at least to the extent of being able to visualize particles of each component rearranging themselves at the smallest molecular level. These ideas, although they were becoming more widely accepted, did not form part of the "normal science" of the day, and Berzelius was unusual in having adopted Daltonian chemical atomism at such an early date. As Alan Rocke puts it, by June 1809 Berzelius had begun "to move aggressively in this new direction."⁶⁷

⁶⁶ Berzelius (1816), pp. 431–432.

⁶⁷ Rocke (1992), p. 122.

Berzelius's chemistry was very different from that of chemists in Britain and mainland Europe, and this raises two interesting questions. First, what caused this difference, and second, why was Berzelius so respected? The distance in chemical thought can be largely attributed to physical distance. Although Berzelius corresponded with eminent chemists in many countries including Berthollet, Davy, Marcet, and Thomson, his letters contain repeated pleas for papers to be sent to Sweden, and for his friends to translate his work and arrange for its publication. His correspondents were keen to oblige, but the transmission of the latest information to and from Sweden must still have been fairly inconsistent and unreliable. As a result, Berzelius had not read the same papers as his peers, and may also have focused on texts that they had not read or did not consider to be of major significance.⁶⁸ He was probably unaware of what some of them were doing. By the same token, the chemical community was largely privy only to Berzelius's completed works, which were long and challenging pieces. If these are compared with Humphry Davy's short and frequent bulletins in the *Philosophical Transactions* and the *Quarterly Journal of Science*,⁶⁹ we can see that even a casually interested reader could follow the progress of Davy's thinking on a particular problem, while Berzelius's readers were obliged to tackle his ideas in their final and fully general state. This required considerable effort and would have been quite a feat for the average reader.

Yet, even without understanding the details of the chemistry Berzelius described, his readers would have got a picture of clear reasoning and detailed, thorough, and extensive experimentation. Very few chemists of the day were prepared to launch into serious debate with such a chemist, and those who engaged seriously with his work could not have failed to be impressed by its quality. We could say that Berzelius was working in a different research programme or paradigm from the other major chemists of the day, and that this was in part due to his physical distance from his peers. The theory of electrochemistry in its advanced

⁶⁸ Melhado (1992, pp. 146–147) mentions Berzelius's use of Richter's work, which was not widely read at the time. Berzelius also referred to the experiments of Mrs. Fulhame published in 1794 in England and 1798 in Germany as if these would have been on every chemist's reading list. In fact her works were not very well known, and unlikely to be fresh in the minds of the readers of the *Annals of Philosophy* in 1815.

⁶⁹ Volume 1 of the *Quarterly Journal of Science* contained four papers by Davy, of a few pages each. Berzelius's papers almost always spanned two volumes of *Annals of Philosophy* or *Nicholson's Journal*.

state was central to the progress of Berzelius's chemistry. The chlorine theory not only failed to square with Berzelius's electrochemistry, but also did not come with a new, competing research programme to replace it. It was, therefore, quite rational (as Imre Lakatos would have put it) for Berzelius to continue his opposition to the chlorine theory until such time as a competing research programme capable of incorporating elementary chlorine could be developed.⁷⁰

Between 1817 and 1820 Berzelius's correspondence and papers avoided the subject of the nature of OMA altogether. By the 1820s any references Berzelius made to chlorine suggested that it was elementary rather than compound, and in an 1826 investigation into the relative atomic weights of the elements, Berzelius listed chlorine as one of the elements. He devised a symbol for it, established its atomic weight, and even used to it establish the atomic weight of other elements.⁷¹ What happened? Berzelius seems to have simply given in to the tide of prevailing opinion. In the introduction to his 1816 paper in *Annals of Philosophy* he had said: "I am aware that the obstinacy with which many philosophers adhere to old opinions is owing to their incapacity of perceiving the force of arguments which are urged against them."⁷² Berzelius was apparently aware of the danger of clinging to a theory which no one else adhered to. In 1815, he was still hopeful that his arguments might convince some members of the chemical community of the error of the chlorine theory, but by the 1820s it must have been clear that the term OMA was outdated and increasingly meaningless for young chemists. It would have been foolish and self-defeating to persist in rallying against the chlorine theory, and Berzelius was not a foolish man.

The case of Berzelius is especially interesting because there does not appear to have been any conversion to the hypothesis of elementary chlorine. He gave no explanation for his sudden use of the new terminology (by then not so new), and there was no new experimental evidence to sway him. When he resumed his correspondence with Davy by congratulating him on his Presidency of the Royal Society in 1821 he said: "Our epistolary correspondence has been interrupted since your first journey to the continent, but our mutual friend, Mr. Marcet, has often told

⁷⁰ For example, a concept of entropy and enthalpy neatly removes the problems which Berzelius identified with the detonating oil, nitrogen trichloride (NCl₃).

⁷¹ Berzelius (1826).

⁷² Berzelius (1816), p. 273.

me your news.”⁷³ This could be seen as an attempt (in some ways successful) to draw a line under the disputes of the past and return to something of their former closeness. There was no mention of the elementary nature of chlorine in any of the subsequent correspondence between the two men, which suggests that Berzelius had not converted to the new theory.

How could Berzelius have continued to be convinced that OMA was compound in nature, while at the same time using elementary chlorine in his chemistry, and contributing to controversial discussions?⁷⁴ Davy’s behaviour during the same debate gives some clues about the ability of chemists at that time to make use of more than one interpretation of experimental results. Davy was able to concede to Berzelius in the midst of their disagreement over chlorine in 1813:

I think it very probable that azote, chlorine, and the metals and inflammable bodies are compounds. I think it probable that the first two contain oxygen and the last contains hydrogen; but it is absolutely necessary to distinguish between what is very probable and what is known.⁷⁵

This shows that Davy was able to approach chemistry on two levels. On one level, he acted as a fact-led Enlightenment empiricist, dismissing compound chlorine and azote because they had not been decomposed. On the other level, he had an underlying Romanticist *belief* that these substances were probably compound. This juxtaposition of attitudes gives us some insight as to how this man was such a prolific element-discoverer, while on philosophical grounds he objected to the proliferation of fundamental bodies. Both Berzelius and Davy were perceptive chemists, with qualities of creativity and rationality that marked them out from their more one-sided and less eminent peers. Berzelius and Davy seemed to have understood that much work in chemistry dealt with hypotheses and models, and that explanatory power was much more relevant than the question of reality. What things really *are* could be of passing interest, but what *happens* was the really important question in chemistry.

⁷³ Soderbaum (1912–14), vol. 1, p. 65.

⁷⁴ See Crosland (1980), p. 102. These included the debate over Prout’s hypothesis, which will be discussed in detail in Chapter 3.

⁷⁵ Soderbaum (1912–14), vol. 1 (II), p. 59.

7. Elementary chlorine and Lavoisierian chemistry

For many chemists, it was iodine that finally tipped the balance of evidence in favour of elementary chlorine, as can be seen in Thomson's summaries of chemistry in the years before and after the discovery of iodine. Summing up chemists' opinions in 1813, prior to the discovery of iodine, Thomson concluded: "The two opposite hypotheses of chlorine and oxymuriatic acid are liable each to objections, which, in our present state of knowledge it is almost impossible to obviate."⁷⁶ Two years later, with iodine and also fluorine grouped together with chlorine to make up the halogens, Thomson made it clear that the leading chemists had accepted chlorine once and for all.⁷⁷

The discovery of chlorine therefore made a significant impact on chemistry at the time. Alongside the other halogens (iodine and fluorine), chlorine played an important part in removing oxygen from the central place that it had been given in Lavoisier's chemistry, though it would be misleading to view the exception elementary chlorine provided against Lavoisier's oxygen theory of acidity as the principal catalyst for the upset it caused. As Thomson explained:

The modern discoveries in chemistry have deprived oxygen of a good deal of its dignity. Davy has shown that it forms alkalis as well as acids, and that many acids exist which contain no oxygen. It is not therefore the acidifying principle. This indeed is a doctrine which was all along maintained by Berthollet, whose sagacity in many points of chemical theory deserves the highest admiration. Oxygen has lost likewise the property of being the only simple supporter of combustion. For chlorine possesses that property perhaps in a greater degree than oxygen. . .⁷⁸

Thomson mentioned chlorine in conjunction with combustion, rather than acidity in this passage (although MA was one of the acids without oxygen, which he mentioned in general terms). The oxygen theory of combustion was indeed a more fundamental part of Lavoisier's chemistry than the oxygen theory of acidity had ever been. Combustion had been the major point of conflict with phlogiston theory, and had suffered much less criticism than the theory of acids before chlorine. Elementary chlorine's greatest legacy was the proof that oxygen was not the unique

⁷⁶ Thomson (1814), p. 13.

⁷⁷ Thomson (1816), p. 27.

⁷⁸ *Ibid.*, p. 26.

supporter of combustion, refuting a fundamental tenet of Lavoisier's chemistry which had not been seriously questioned previously.

Bibliography

Berthollet, Claude-Louis. 1804. *Essay of Chemical Statics*, translated by B. Lambert. London: J. Mawman. Originally published as *Essai de Statique Chimique* in Paris in 1803.

———. 1816. “Note sur la décomposition de l'acide oxymuriatique.” *Mémoires de la Société d'Arcueil* 3: 603–612.

Berthollet, Claude-Louis, Jean-Antoine Chaptal and Louis-Nicolas Vauquelin. 1811. “Rapport sur un mémoire de M. Curaudau.” *Annales de Chimie* 80: 54–80, 121–139.

Berzelius, Jöns Jakob. 1813. “An Explanatory Statement of the Notions or Principles upon which the Systematic Arrangement is Founded, which was Adopted as the Basis of an Essay on Chemical Nomenclature.” *A Journal of Natural Philosophy, Chemistry, and the Arts (Nicholson's Journal)*, second series, 34: 142–146, 156–166, 240–246, 313–319.

———. 1816. “A Comparison of the Old and New Theories Respecting the Nature of Oxymuriatic Acid, to Enable us to Judge which of the Two Deserves the Preference.” *Annals of Philosophy* 7: 272–280, 429–441, and 8: 200–209, 256–264, and 470 (correction).

———. 1826. “Ueber die Bestimmung der relativen Anzahl von einfachen Atomen in chemischen Verbindungen.” (*Poggendorff's Annalen der Physik* 8: 1–24, 177–179, 191.

Brock, William H. 1992. *The Fontana History of Chemistry*. London: Fontana Press.

Brooke, John Hedley. 1980. “Davy's Chemical Outlook: The Acid Test.” In Forgan 1980, pp. 121–176.

Chabot, Hugues. 2006. “Les origines d'un nouvel élément chimique: l'affaire du chlore.” *Du nouveau dans les sciences (Recueil issu du séminaire Lyon–Grenoble d'histoire et de philosophie des sciences)*, no. 24: 121–169.

Chenevix, Richard. 1802. “Observations and Experiments upon Oxygenised and Hyperoxygenised Muriatic Acid; and upon some Combinations of the Muriatic Acid in its Three States.”

- Philosophical Transactions of the Royal Society of London* 92: 126–167.
- Crosland, Maurice. 1973. “Lavoisier’s Theory of Acidity.” *Isis* 64: 306–325.
- . 1978. *Gay-Lussac: Scientist and Bourgeois*. Cambridge: Cambridge University Press.
- . 1980. “Davy and Gay-Lussac: Competition and Contrast.” In Forgan 1980, pp. 95–120.
- Davy, Humphry. 1810a. “The Bakerian lecture for 1809. On Some New Electrochemical Researches, on Various Objects, Particularly the Metallic Bodies, from the Alkalies, and Earths, and on Some Combinations of Hydrogene.” *Philosophical Transactions of the Royal Society of London* 100: 16–74.
- . 1810b. “Researches on the Oxymuriatic Acid, its Nature and Combinations; and on the Elements of the Muriatic Acid. With some Experiments on Sulphur and Phosphorous, made in the Laboratory of the Royal Institution.” *Philosophical Transactions of the Royal Society of London* 100: 231–257.
- . 1813. “On a New Detonating Compound.” *Philosophical Transactions of the Royal Society of London* 103: 1–7.
- Davy, John. 1811a. “Some Remarks on the Observations and Experiments of Mr. Murray on the Nature of Oximuriatic Acid, and its Relations to Muriatic Acid.” *A Journal of Natural Philosophy, Chemistry, and the Arts (Nicholson’s Journal)*, second series, 28: 193–206.
- . 1811b. “An account of a New Gas, with a Reply to Mr. Murray’s last observations on Oximuriatic Gas.” *A Journal of Natural Philosophy, Chemistry, and the Arts (Nicholson’s Journal)*, second series, 30: 28–33.
- Forgan, Sophie, ed. 1980. *Science and the Sons of Genius: Studies on Humphry Davy*. London: Science Reviews Ltd.
- Fourcroy, Antoine de. 1802. *Système des Connaissances Chimiques*, vol. 2. Paris.
- Gay-Lussac, Joseph-Louis. 1814a. “Mémoire sur l’iode.” *Annales de Chimie* 91: 96–121.
- . 1814b. “Sur l’acidité et l’alcalinité.” *Annales de Chimie* 91: 130–152.

- Gay-Lussac, Joseph-Louis, and Louis-Jacques Thenard. [1809] 1897. "De la nature et des propriétés de l'acide muriatique et de l'acide muriatique oxygéné." In Scheele et al. 1897, pp. 34–48. Originally published in *Mémoires de Physique et de Chimie, de la Société d'Arcueil* 2: 339–358.
- Golinski, Jan. 1992. *Science as Public Culture: Chemistry and Enlightenment in Britain, 1760–1820*. Cambridge: Cambridge University Press.
- Henderson, William. 1813. "On Sir Humphry Davy's Theory of Chlorine and its Compounds." *Annals of Philosophy* 2: 13–18, 122–123.
- Knight, David. 1992. *Humphry Davy: Science and Power*. Oxford: Blackwell.
- Lavoisier, Antoine-Laurent. [1790] 1965. *Elements of Chemistry*, trans. by Richard Kerr. New York: Dover. Originally published in Paris in 1789; original English translation published in 1790.
- Le Grand, Homer E. 1972. "Lavoisier's Oxygen Theory of Acidity." *Annals of Science* 29: 1–18.
- . 1974a. "Ideas on the Composition of Muriatic Acid and Their Relevance to the Oxygen Theory of Acidity." *Annals of Science* 31: 213–226.
- . 1974b. "Determination of the Composition of the Fixed Alkalis 1789–1810." *Isis* 65: 59–65.
- . 1976. "Berthollet's *Essai de Statique Chimique* and Acidity." *Isis* 67: 229–238.
- McKie, Douglas. 1952. *Antoine Lavoisier: Scientist, Economist, Social Reformer*. London: Constable.
- Melhado, Evan M. 1992. "Novelty and Tradition in the Chemistry of Berzelius (1803–1819)." In Melhado and Frängsmyr 1992, pp. 132–170.
- Melhado, Evan M., and Tore Frängsmyr, eds. 1992. *Enlightenment Science in the Romantic Era: the Chemistry of Berzelius in its Cultural Setting*. Cambridge: Cambridge University Press.
- Murray, John. 1811a. "Observations and Experiments on the Nature of Oximuriatic Acid, and its Relation to Muriatic Acid." *A Journal of Natural Philosophy, Chemistry, and the Arts (Nicholson's Journal)* 28: 132–152.

- . 1811b. “On the Nature of Oximuriatic Acid, in Reply to John Davy.” *A Journal of Natural Philosophy, Chemistry, and the Arts (Nicholson’s Journal)* 28: 294–310.
- Partington, James R. 1962. *A History of Chemistry*, vol. 3. London: Macmillan.
- Patterson, Austin M. 1954. *French Dictionary for Chemists*, 2nd ed. London: Chapman & Hall.
- Rocke, Alan J. 1992. “Berzelius’s Animal Chemistry: From Physiology to Organic Chemistry (1805–1814).” In Melhado and Frängsmyr 1992, pp. 107–131.
- Scheele, Carl Wilhelm, et al. 1897. *The Early History of Chlorine*, Alembic Club Reprint No. 13. Edinburgh: William F. Clay.
- Soderbaum, H. G., ed. 1912–14. *Jac. Berzelius Bref*, vol. 1 of 6. Uppsala: Almquist and Wiksells.
- . 1918–20. *Jac. Berzelius Bref*, vol. 3 of 6. Uppsala: Almquist and Wiksells.
- Thomson, Thomas. 1804. *A System of Chemistry*, 2nd ed. Edinburgh: Ball & Bradfute.
- . 1814. “Sketch of the Improvements in Science made during the year 1813.” *Annals of Philosophy* 3: 1–32.
- . 1816. “Account of the Improvements in Physical Science during the year 1815.” *Annals of Philosophy* 7: 1–71.
- Zucker, Arthur. 1988. “Davy Refuted Lavoisier not Lakatos.” *British Journal for the Philosophy of Science* 39: 537–540.