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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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Back cover illustration: Chlorine gas, courtesy of the Department of Chemistry, University College London. Photo by Gretchen Siglar.

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The Discovery of Chlorine: A Window on the Chemical Revolution

Ruth Ashbee

1. Introduction

Chlorine is all around us, but hardly ever in its pure form. It is a highly reactive element that forms stable chemical combinations with many other substances. Common salt (sodium chloride) was known to all civilizations and there are many other chlorides lurking in all corners of nature, but from such familiar forms one would not be able to guess that elemental chlorine is a yellow-green gas, eerily beautiful and highly poisonous. Once isolated and let loose, chlorine creates chemical mayhem, pulling apart other molecules and attacking everything from germs to colours. That reactivity has much to do with chlorine's controversial life, which we will be tracing in this book. In this chapter we begin with the birth of chlorine, which was complicated enough in itself.

It was not until the late 18th century that chlorine in its elemental form was first isolated and studied. The discovery was the work of the Swedish chemist Carl Wilhelm Scheele (1742–1786). Mostly self-taught in chemistry, Scheele made his living as an apothecary. He was a prolific and ingenious experimenter, who made wide-ranging contributions in metallurgy, organic chemistry, and everything in between. There are a great number of substances that Scheele discovered and studied, including glycerol, lactic acid and prussic acid. Perhaps the most famous of those, along with chlorine, is oxygen, which Scheele called “fire air”. Although Scheele's publication was delayed and not widely circulated, he carried out his work on oxygen before Joseph Priestley or Antoine-Laurent Lavoisier.

When Scheele made chlorine in 1774 he called it “dephlogisticated muriatic acid”, and there were good reasons for that. For centuries alchemists and chemists had been familiar with “muriatic acid” (or, “marine acid”, or “the acid of salt”), so named because sea salt was a key ingredient in its manufacture. Today we call it hydrochloric acid (HCl) and, in modern terms, what Scheele did was to liberate the chlorine from this acid by removing the hydrogen with the help of manganese oxide. In Scheele’s own understanding, what he removed from the muriatic acid was not hydrogen but phlogiston, the substance of “fire” that made things combustible.

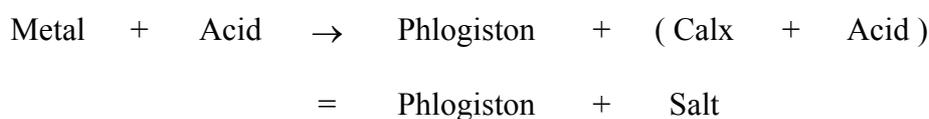
Scheele was a firm believer in the phlogiston theory, but the theory was under attack from followers of Lavoisier’s new chemistry of oxygen, who felt compelled to give a new theoretical interpretation of what Scheele had done. This task was taken up by Lavoisier’s close colleague Claude-Louis Berthollet (1748–1822), who would later pioneer the industrial process of bleaching with chlorine (see Chapter 5). As the Lavoisierians routinely interpreted the removal of phlogiston as the addition of oxygen, Berthollet saw chlorine as “oxygenated muriatic acid”, or “oxymuriatic acid”. Neither Scheele nor Berthollet regarded chlorine as an element; that conception only came in, with difficulty, through the work of Humphry Davy a few decades later (see Chapter 2). Interestingly, from a modern perspective Scheele’s account of chlorine might be taken to be closer to the mark than Berthollet’s, since Scheele’s term “phlogiston” has often been taken to refer to hydrogen, and Scheele saw chlorine as hydrochloric (muriatic) acid with its phlogiston removed.

The remainder of this chapter will give a careful account of this intriguing series of events, focusing on the comparison of Scheele’s and Berthollet’s differing perspectives. This episode gives a unique and informative window on the Chemical Revolution in which the phlogiston theory was overthrown by the oxygen theory. Section 2 explains Scheele’s experiments and the theoretical beliefs that led to his discovery and understanding of chlorine. Section 3 examines Berthollet’s re-interpretation of Scheele’s results. Section 4 takes a somewhat abstract view of the whole episode, analyzing it in terms of Thomas Kuhn’s notion of incommensurability, and addressing some historiographical issues about the legitimacy of using modern chemical concepts to aid our understanding of historical sources.

2. Scheele, phlogiston, and chlorine

2.1. Phlogistonism

For readers unfamiliar with the history of phlogiston theory, I will begin with a brief summary of its relevant aspects. Phlogiston was thought to be the matter of fire, given off in combustion and manifesting itself as heat and light. Highly combustible substances were thought to contain more phlogiston, as they burned more easily. The “calcination” of metals (which we would now call oxidation) also came to be regarded as a type of combustion, so metals were classed as combustibles. Through calcination the metal was turned into a “calx”,¹ the crumbly, rusty substance that was understood to be the part of the metal left over after phlogiston is removed from it. Thus, combustibles were compounds whose constituents were phlogiston and whatever remained after combustion, e.g., ash or calx. The chemist and historian of chemistry Albert Ladenburg says that Scheele, as well as Henry Cavendish and Richard Kirwan, identified phlogiston with hydrogen.² That makes sense, in light of the types of experiment schematized below:



In these reactions, a piece of metal dropped into an acid dissolved, forming a salt³ and releasing bubbles of a gas that was found to be combustible. This “inflammable air” was often seen as phlogiston itself (later identified as hydrogen). The salt was seen as a compound of the acid and the calx. This phlogistonist interpretation of metal–acid reactions made sense, as it was considered that all metals were rich in phlogiston, which was what gave them the common metallic properties of shininess, ductility, etc. If instead of the shiny metal its calx was made to react with the acid, the same salt was formed as before, but without the release of

¹ “Calx” was originally a phenomenalistic term meaning “any powder obtained by strongly heating a substance in air” (Eklund 1975, p. 23), which could include entities other than metal oxides. I thank Hasok Chang for pointing out this difference to me.

² Ladenburg (1905), p. 19.

³ “Salt” here refers to a whole class of chemical compounds that have some important similarities to common salt.

inflammable air, just as one would expect if calx was metal deprived of its phlogiston:



We can say that in this context the referent of the term “phlogiston” was indeed hydrogen.

But care is needed when asserting things like this.⁴ It is quite difficult to translate phlogistonist thinking into modern terms. As we do not recognize the existence of phlogiston, what are we to make of the phlogistonist notion that a metal was composed of calx and phlogiston? The phlogistonists believed the hydrogen to come from the metal, while we now say it comes from the water in the acid. I will address these questions more carefully in Section 4.

2.2. Scheele’s experiments with manganese

In 1774 Scheele made extensive investigations into pyrolusite, or impure manganese dioxide (MnO_2). Rather confusingly for the modern reader, Scheele called pyrolusite “manganese” (or “magnesia”).⁵ I will follow his usage, so in this chapter “manganese” refers to the oxide, not the pure metal. By reacting manganese with marine (muriatic) acid, he obtained chlorine. He saw the chlorine as muriatic acid with its phlogiston removed, on the basis of the properties of manganese which he had observed in other experiments.

From my examination of Scheele’s writings, I have identified six main properties he attributed to manganese, which supported his phlogistonist interpretation of his discovery of chlorine:

- 1) Ordinary manganese contains some phlogiston.⁶
- 2) Ordinary manganese has a strong attraction for (more) phlogiston.⁷

⁴ Ladenburg does note some of the difficulties implied.

⁵ Smeaton (1992), p. 128.

⁶ Scheele [1774] (1930), p. 23.

⁷ Ibid., p. 22.

3) Manganese attracts phlogiston more strongly when an acid is present.⁸

4) Manganese needs phlogiston to react with acid. When there is insufficient phlogiston, it will react only in part.⁹

5) Ordinary manganese does not contain enough phlogiston for all of it to react completely with a normal acid; some inner parts of the manganese will remain.¹⁰

6) Manganese in contact with acid can attract phlogiston from neighbouring manganese which is not in contact with the acid (i.e., the inner parts of the filings), and thereby dissolve in the acid.¹¹

Scheele believed item (4) for several reasons. In one experiment he put manganese in vitriolic acid (sulphuric acid), which partly dissolved it. Then he distilled the residue using heat, and obtained manganese again by driving off vitriolic acid gas. This residual manganese, however, did not dissolve in fresh acid as it had before this treatment. But *volatile* acid was able to dissolve this manganese. This proved to Scheele that the manganese needed phlogiston to dissolve, since he thought that the volatile acid contained more phlogiston. More phlogiston was needed to dissolve the treated manganese, because this manganese had given its phlogiston to the acid it was first dissolved in, which was consequently made gaseous. Before the treatment, the manganese had contained sufficient phlogiston to dissolve. This experiment, then, also proved to

⁸ Ibid.

⁹ Scheele (ibid., p. 22) actually says that when insufficient phlogiston is present, the mixture will form a blue or red solution, as opposed to the colourless one formed when sufficient phlogiston is present. However, in all his experiments on manganese, there are no references to a mixture of manganese and acid becoming blue or red! Rather, when insufficient phlogiston is present, the manganese simply does not react.

¹⁰ Ibid., p. 24.

¹¹ Ibid.

Scheele the truth of property (1).¹² He repeated the same experiment using acid of nitre (nitric acid), and obtained the same results.¹³

An additional detail from that experiment partly explains Scheele's belief in property (6). In the first treatment of the manganese with acid (both sulphuric and nitric), not all of the manganese dissolved: the outer parts of the filings dissolved, but the inner parts remained. Scheele explained this phenomenon by referring to property (3): the outer parts of the filings acquired a stronger attraction for phlogiston by being in contact with the acid, and so took additional phlogiston from the inner parts of the filings (which were not in contact with the acid).¹⁴ This, then, gives us property (5). The outer parts can then react with the acid, since they have sufficient phlogiston, but the inner parts are now dephlogisticated, and so cannot react with the acid, just as the treated manganese retrieved from the union with the acid, did not dissolve, since it too had been dephlogisticated.

As we can see, Scheele's belief in (6) depended on his belief in (3), and for a better understanding of this we must turn to another experiment. Scheele tried, and failed, to react manganese with sugar, honey, gum arabic or hartshorn jelly (all highly combustible, and therefore high-phlogiston substances). But he found that by mixing these substances with manganese in the presence of an acid, he could elicit a reaction. What was more, the whole of the manganese dissolved; the inner parts of the filings, which remained undissolved when the manganese was mixed with acid alone, dissolved when a high-phlogiston substance such as sugar was present. Scheele saw this as happening because the high-phlogiston substance had given phlogiston to the dephlogisticated inner bits of manganese, enabling them to react with the acid. This experiment was consonant with (3) and (4).¹⁵

In another experiment, Scheele found a further confirmation of (4): manganese would dissolve completely in concentrated vitriolic acid; in this case no inner parts of the manganese filings remained, even without the help from sugar, etc. Scheele thought that this was because the concentrated acid contained more phlogiston than ordinary acid, since

¹² To understand this in modern chemical terms would require a specialist chemist's opinion, and perhaps repeating the experiment.

¹³ *Ibid.*, p. 23.

¹⁴ *Ibid.*, p.24.

¹⁵ *Ibid.*, pp. 24–25.

heat was necessary in the production of concentrated acid.¹⁶ This is similar to the point above, where volatile acid is considered to have more phlogiston than ordinary acid. Property (4) was further demonstrated to Scheele by the fact that manganese did not dissolve in tartaric acid in the cold, but on the addition of heat (which, for Scheele, also meant additional phlogiston), it did dissolve.¹⁷

2.3. Scheele's discovery of chlorine

When Scheele mixed his sample of “manganese” with muriatic acid (hydrochloric acid), he found that the manganese dissolved first to give a brown solution, which then became colourless, producing a gas as it changed colour. This gas was what is known today as chlorine. All this happened without additional phlogiston supplied in the form of heat, sugar, etc. Now, since Scheele knew from previous experiments that manganese did not contain enough phlogiston to react completely with muriatic acid (recall property 5), some explanation was required. Scheele concluded that muriatic acid contained phlogiston, and that the manganese attracted this phlogiston to itself in order to react with the acid. This left “dephlogisticated muriatic acid”, which was given off as the gas Scheele collected. The changing colour of the solution was explained as follows. Scheele thought that manganese had insufficient phlogiston to be dissolved properly in muriatic acid, and that the solution formed without insufficient phlogiston had a red colour.¹⁸ The mixture of this red solution with the black particles of undissolved manganese floating in it created the appearance of brown. And then, when the manganese took additional phlogiston from the muriatic acid, the solution was rendered colourless while some of the muriatic acid became dephlogisticated. When Scheele repeated the experiment but added a high-phlogiston substance (sugar, turpentine, or linseed), he found that the manganese reacted, but that no gas was produced. In his view, this was because the manganese could get the requisite phlogiston from the added substance, rather than taking it from the muriatic acid.¹⁹

¹⁶ Ibid., p. 24.

¹⁷ Ibid., p. 21.

¹⁸ Ibid., p. 22.

¹⁹ Again, from a modern perspective it is not clear how this would have happened. It is possible that the sugar reacted with the nascent chlorine and prevented it from being given off as a gas.

As mentioned earlier, a charitable modern interpretation of Scheele might assert that he had an essentially correct description of chlorine when he called it “dephlogisticated muriatic acid”, since chlorine is what remains when hydrochloric acid has its hydrogen removed, and phlogiston was often identified with hydrogen. But such an assertion would be false. Scheele thought that the manganese had taken the phlogiston from the muriatic acid because of his previous experiments with manganese, in which phlogiston was identified with heat and combustibility. If Scheele had combined pure hydrogen with chlorine and reproduced hydrochloric acid, or if he had saturated manganese with hydrogen and then shown it to be incapable of producing chlorine, then we could say that “phlogiston” referring to hydrogen was the explanation for him identifying chlorine as dephlogisticated muriatic acid. But in fact he arrived at his conception of “dephlogisticated muriatic acid” on the basis of his previous experiments, in which the term “phlogiston” frequently did not refer to hydrogen. Still, we could say that Scheele was being rational, producing good reasoning from his experiments even though his theory was mistaken. His experiments and reasoning were largely consistent, and he found several confirmations of his ideas. The only questionable part is his assertion regarding the red colour of the manganese solution with insufficient phlogiston, which does not seem to have independent support from other experiments.

Scheele noted many of the properties of the new gas: it was very reactive, destroying vegetable colours, attacking metals, killing insects and extinguishing flames. He said that it produced all these effects by removing phlogiston from other substances in contact with it.²⁰ He reported that when dephlogisticated muriatic acid came into contact with a combustible (a phlogiston-rich substance), it took up phlogiston from it, and thereby turned back into muriatic acid.²¹ Today we can see that this cannot have been true: to return to hydrochloric acid, chlorine must combine with hydrogen, which it could not have obtained from a metal, which Scheele counted as combustible. James McAllister has noted that evaluation in the history of science produced the historical discovery that many of Galileo’s “experiments” were in fact thought experiments.²²

²⁰ Ibid., pp. 31–32.

²¹ See, for example, *ibid.*, p. 30.

²² McAllister (1986), p. 329.

Here, evaluation of Scheele's work shows that one of three things must have happened.

The first possibility is that he invented data to support his theory. This is unlikely, given the meticulous and dedicated nature of Scheele's empirical work. Or he may have rather hastily extrapolated his findings from sugar, etc., to all combustibles including metals. It is also easily possible that water was present in his experiments and provided the source of hydrogen, unbeknownst to Scheele, since he considered water to be an element.²³ Water in chemical experiments was a very common source of error around and during the Chemical Revolution;²⁴ since it was considered elemental, it was often present in experiments without causing concern to the experimenters. It could furnish hydrogen or oxygen unnoticed, whose origin the experimenters would then attribute to another of the substances in the experiment. Conversely, it could disguise the production of new water from hydrogen and oxygen combining in the experiment. Water will appear several more times as we trace chlorine through the Chemical Revolution. The composition of water, and the realization that it could produce errors by virtue of its compound nature, was a decisive factor in Lavoisier's defeat of the phlogiston theory, and the conversion of previously phlogistonist chemists such as Berthollet to the anti-phlogistonist doctrine. Berthollet's first anti-phlogistic paper was on chlorine. However, even the newly converted Berthollet continued to be led astray by the presence of water in his experiments on chlorine, as we shall see later.

3. Berthollet, chlorine and the Chemical Revolution

3.1. Lavoisier's anti-phlogistonism

In 1783 Antoine-Laurent Lavoisier began an "aggressive assault" on the phlogiston doctrine,²⁵ proposing his own chemistry which held, among other things, that something (oxygen) was absorbed in combustion rather than being released. However, he had difficulty recruiting chemists to his anti-phlogistonist doctrine, for several reasons. Although the weight gain in combustion seemed to support him, the phlogistonists

²³ See, for example, Scheele [1785] (1930), p. 286.

²⁴ I thank Hasok Chang for pointing this out to me.

²⁵ McCann (1978), p. 31.

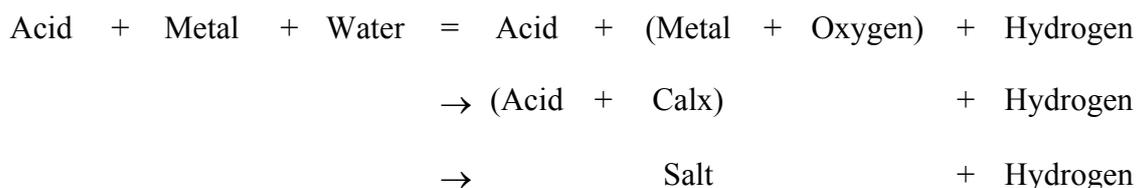
could accommodate this; in fact, several different phlogistonist explanations were put forward, including an exchange of phlogiston for oxygen in combustion, an exchange of phlogiston for fixed air (carbon dioxide), or negative weight for phlogiston. Lavoisier's quantitative thinking was not yet generally regarded as important in chemistry; qualitative explanation was seen as more important, and the phlogiston theory was better than Lavoisier's at this, explaining the similarities among the metals, why certain things were combustible,²⁶ and several important reactions, some of which are considered below. Furthermore, the idea of fire as an element was persistent in chemists' minds, and combustion by fire does look very much as if something is being released. Lavoisier contended, as part of his antiphlogistic theory, that all acids contained oxygen, and there were experimental doubts about this, some of them expressed by Berthollet (see Chapter 2, Section 3 for further details).

A key problem for Lavoisier was the metal–acid reaction referred to earlier, which resulted in the production of inflammable air (which he later called hydrogen). Initially he could not explain where the hydrogen came from in this experiment, since he rejected the phlogistonist doctrine that hydrogen was a constituent of metals. The breakthrough for Lavoisier came when it occurred to him that water must contain hydrogen, rather than being an element, because water was present in these reactions in the dilute acids. He set out to devise an experiment to show that hydrogen was a constituent of water, so as to convince chemists of the tenability of his theory.²⁷ In 1783, with the help of Pierre-Simon Laplace, he burned hydrogen and oxygen together and obtained water, satisfying himself about the composition of water.²⁸ The nature of water as a compound of hydrogen and oxygen saved Lavoisier's theory, and the metal–acid reaction could now be understood as follows:

²⁶ Salzberg (1991), p. 198.

²⁷ Donovan (1993), p. 134.

²⁸ *Ibid.*, p.154. This actually produced an anomaly for Lavoisier, because oxygen should have turned hydrogen into an acid under his theory. However, Lavoisier's theory of acids was not necessary to his antiphlogistic theory, a point which I will return to later when Berthollet is considered.



Lavoisier re-interpreted most of the basic substances involved in this reaction: metal was a simple substance, water was a compound of inflammable air (hydrogen) and oxygen, and calx was a metal oxide. Note that in the phlogistonist interpretation of this experiment, the water present in the dilute acids was not thought to have any effect.

Lavoisier could explain why the phlogiston theory had been able to account for this experiment; moreover, he could explain an anomaly which the phlogiston theory had faced: when metals were dissolved in undiluted acids, no inflammable air was produced; the phlogiston theory could not explain this. Because Lavoisier said the inflammable air (hydrogen) came from the water and not the metal, he *predicted* that undiluted acid would not produce hydrogen, since it did not contain water. Lavoisier's idea on composition of water also negated the problematic prediction by the phlogistonist Richard Kirwan and his supporters that the product of phlogiston (hydrogen) and dephlogisticated air (oxygen) would be fixed air (carbon dioxide).²⁹

However, Lavoisier's synthesis of water did not mean the end of the phlogiston theory. Many chemists remained unconvinced that he had actually shown water to be composed of hydrogen and oxygen. So Lavoisier proceeded to analyze water into its constituent hydrogen and oxygen, to provide further evidence for its composition. In 1785 he demonstrated both the analysis and a dramatic large-scale synthesis of water to the *Académie Royale des Sciences* in Paris, and in that year he also read the "*Réflexions sur la Phlogistique*", his "rhetorical masterpiece", to the *Académie*.³⁰ And it was in 1785, too, that Berthollet read his memoir on dephlogisticated muriatic acid to the *Académie*, his first paper to be based on the antiphlogistic doctrine.

²⁹ Le Grand (1975), p. 67.

³⁰ Donovan (1993), p. 135.

3.2. *Berthollet on chlorine*

To understand Berthollet's conception of chlorine, it is useful to consider his reasons for adopting Lavoisier's anti-phlogistonism. J. R. Partington writes that "it was the supposed composition of muriatic and oxymuriatic acids which convinced Berthollet of the correctness of the antiphlogiston theory",³¹ but I can find little support for this claim: Berthollet did claim that he had begun investigating dephlogisticated muriatic acid so as to verify his new idea that the phlogiston hypothesis had become useless,³² but his reasoning in this paper rather leads me to suppose that Berthollet had already decided on the truth of the antiphlogiston theory *before* he considered these substances. This will be demonstrated later. H. Gilman McCann holds that it was the composition of water that convinced Berthollet to side with Lavoisier,³³ and this is much more plausible: Berthollet himself stated this at the very start of his paper of 1785 on chlorine, published in 1788:

The important experiments by which the nature of water had just been determined . . . threw great light on the whole of chemistry; phlogiston . . . appeared to me to have at last become a useless hypothesis, whereupon I believed it incumbent on me to subject dephlogisticated marine acid to new experiments, as its properties might destroy or confirm the position I had adopted.³⁴

The composition of water removed an important anomaly for Lavoisier, explained previous successes of the phlogiston theory, and refuted an important prediction of the phlogiston theory.³⁵ Also, as Homer Le Grand emphasizes, it is somewhat misleading to think of Berthollet as being "converted" since there was much more continuity in his thought than this term implies. Before 1785 Berthollet had agreed with much of Lavoisier's experimental findings, and admitted that there were problems with the phlogiston theory, though he still adhered to it. After 1785, he

³¹ Partington (1962), p. 504.

³² Berthollet [1788] (1897), p. 11.

³³ McCann (1978), p. 33.

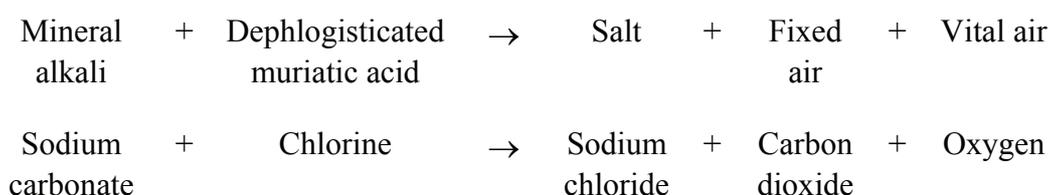
³⁴ Berthollet [1788] (1897), p. 11.

³⁵ Other factors must have played a part, too, in Berthollet's "conversion" to Lavoisier's theory. Berthollet was in a good deal of personal contact with the charismatic Lavoisier, and witnessed his impressive live experiments and his delivery of "Reflexions sur la Phlogistique". See Le Grand (1975, p. 63) and McCann (1978, p. 34) on these points.

still rejected some important points of Lavoisier's chemistry, notably his oxygen theory of acidity and the caloric theory.

Re-visiting Scheele's original report on chlorine, Berthollet re-interpreted chlorine as muriatic acid with added oxygen taken from "manganese". We can see this as an example of the oxygen theory being an inversion of the phlogiston theory:³⁶ where Scheele saw phlogiston being removed by the manganese, Berthollet saw oxygen being added. In support of his own interpretation, Berthollet reported several experiments as proof that phlogiston was unnecessary in explaining the production of "dephlogisticated muriatic acid", and that this substance was in fact oxygenated muriatic acid.³⁷

The first experiment is most usefully viewed schematically, with translation into today's terms, so that we may understand more easily what is going on:



Berthollet said the fixed air came from the alkali, and the vital air from the dephlogisticated muriatic acid, which he re-conceptualized as oxygenated muriatic acid.³⁸ From a modern chemical standpoint we can see that Berthollet was mistaken; the vital air (oxygen), as well as the fixed air (carbon dioxide), must have come from the sodium carbonate. Scheele's view was that the dephlogisticated muriatic acid took phlogiston from the mineral alkali, which then released the vital air and fixed air that it had contained.³⁹ This interpretation too, was incorrect by today's standards. According to the modern interpretation, the chlorine rather removes the sodium from the sodium carbonate, leaving the other components free to manifest themselves as the product gases.

³⁶ Siegfried (1989) has developed this idea.

³⁷ Berthollet often used the term "marine acid", but to save the reader unnecessary confusion I have tried to use "muriatic acid" throughout, except in direct quotations.

³⁸ Berthollet [1788] (1897), p. 15.

³⁹ *Ibid.*, p. 16.

In another experiment, Berthollet extracted a large quantity of oxygen by heating “manganese”, reducing the manganese by an eighth of its original weight. He then mixed this treated manganese with muriatic acid, and obtained much less chlorine than with ordinary manganese. He took this to prove that vital air was a constituent of chlorine,⁴⁰ and said that it should be called “oxygenated marine acid”. However, we can guess at an explanation Scheele could have offered in response. He regarded oxygen as having a strong affinity for phlogiston.⁴¹ Remove the oxygen from manganese, and it cannot attract phlogiston; therefore, less phlogiston would be removed from the muriatic acid. This is in accord with the modern chemical explanation of Berthollet’s experiment, if Scheele’s phlogiston is identified with hydrogen. But again, this is not a simple case of identity. The idea that oxygen had such a strong affinity for phlogiston came from the phlogistonist account of combustion, and combustion in modern chemistry does not involve hydrogen necessarily. If we were to seek to identify phlogiston with something in the isolated context of combustion today, it would have to be “negative oxygen”, rather than hydrogen.⁴²

Another phlogistonist interpretation could have come from the identification of phlogiston with heat, which Scheele often made.⁴³ By heating the manganese Berthollet could be seen to be adding phlogiston, so that the manganese could become saturated with it, and would not need to take any from the muriatic acid before reacting with it to form a colourless solution straight away, without the intermediate stage of brown solution. This predicts a different empirical result from Scheele’s original experiment, in which he thought that a brown solution was produced because the manganese was incapable of attracting the phlogiston it needed to form a colourless solution. Berthollet did not say what colour the solution took in his experiment.⁴⁴

From this we can see the confusing and complicated nature of the phlogiston theory, which contributed to its downfall: it was capable sometimes even of offering several incompatible interpretations of the same experiment, depending on which aspect of the theory was empha-

⁴⁰ Ibid.

⁴¹ Scheele [1785] (1930), p. 286.

⁴² Siegfried (1989), p. 31.

⁴³ For example, see Scheele [1774] (1930), pp. 25, 28.

⁴⁴ Here again, a re-creation of the experiment could give us a greater understanding.

sized. These different aspects could even all be held by one chemist, as in the case of Scheele, since they seemed to be mutually compatible and supported by experiment. It was only when the phlogiston theory was extended to explain new phenomena that its complicated and self-contradictory nature became more obvious. It wasn't that the phlogiston theory could not explain these phenomena; rather, it could do so in too many and too complicated ways, and it was too confusing to choose which way was correct. So even when talking about the phlogiston theory alone, we must remember its incommensurability within itself, as it were, in order to understand it correctly.

Berthollet also dissolved iron and zinc in a solution of chlorine, and did not detect any hydrogen being produced. He took this to prove that dephlogisticated muriatic acid was in fact oxygenated muriatic acid: the metals must have taken the oxygen they needed to react, from the oxymuriatic acid; if they had taken it from the water of the solution then hydrogen would have been produced.⁴⁵ A chemist's opinion will help on this point: was hydrogen actually produced, and Berthollet failed to detect it? Or do metals not react with oxygen when they dissolve in solution of chlorine? In this case Berthollet would have been correct in his observation, but his reasoning would have been flawed: he said that Lavoisier had shown that metals always combined with oxygen when they dissolved in acids, so the metals must take their oxygen from the oxymuriatic acid. But Berthollet had already noted, earlier in the same paper, that oxymuriatic acid was "almost entirely deprived of acidity".⁴⁶ So he was not warranted in his assumption that metals should dissolve in oxymuriatic acid in the same way as they did in acids.

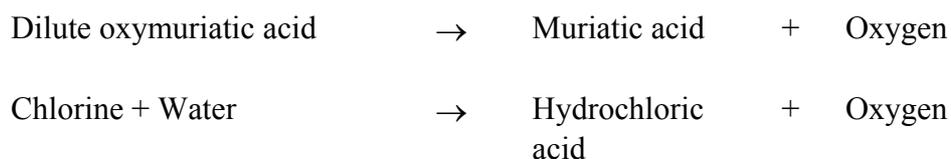
3.3. Water strikes again

Berthollet saw further support for his theory in yet another experiment: when he saturated distilled water with chlorine, he found that the action of sunlight caused oxygen bubbles to be released from the solution, and that by this process the solution turned back into ordinary muriatic acid. Berthollet saw this as the removal of oxygen from the oxygenated muriatic acid (which was in solution with the water), turning it back into muriatic acid.⁴⁷

⁴⁵ Berthollet [1788] (1897), p. 20.

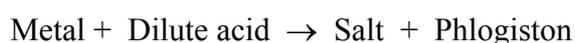
⁴⁶ *Ibid.*, p. 15.

⁴⁷ *Ibid.*, p. 18.

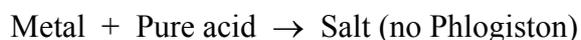


This experiment was, however, linked to a significant problem for Berthollet's interpretation of chlorine as oxygenated muriatic acid. Pure chlorine, undiluted with water, could not be induced by any experimental means to give up oxygen.⁴⁸ This seemed to be an experimental refutation of Berthollet's theory, especially since he had asserted that, in the experiment above, "the vital air adheres so feebly to the marine acid that the action of light suffices to disengage it promptly."⁴⁹ To understand the significance of this problem for Berthollet, we might again evaluate the experiment against today's account. The reason that oxygen was produced from the diluted chlorine was not, as Berthollet supposed, that it was given off by the chlorine, since chlorine is an element and does not contain oxygen. Rather, it was because the chlorine combined with the hydrogen in the water, thereby leaving the oxygen free to manifest itself as the bubbles that Berthollet observed.

Now, Berthollet had already seen chemical reasoning with exactly the same structure as he used here; the difference was that this argument had been used by the phlogistonist chemists to support their theory! The phlogistonists, as we have seen, took this reaction as an indication that metals contained phlogiston:



The phlogistonists had faced an anomaly here, however, identical in form to that which Berthollet faced with chlorine:



Compare this with Berthollet's problem that the apparent liberation of oxygen from oxymuriatic acid only took place when there was water present. The phlogistonist argument had been attacked by Lavoisier, Berthollet and their colleagues by reference to the composition of water: the hydrogen in the metal-acid reaction came from the water not the metal, so when there was no water, no hydrogen was produced. This

⁴⁸ Lowry (1936), p. 214.

⁴⁹ Berthollet [1788] (1897), p. 17.

proved the anti-phlogistonist thesis that metals were simpler substances than calxes, and calxes were oxidized metals. Similarly, in Berthollet's experiment the oxygen must have come from the water, and the fact that no oxygen could be produced from undiluted chlorine is seen today as proof that chlorine is simpler than hydrochloric acid, rather than being a compound of the latter and oxygen.

It is strange that Berthollet did not recognize the similarity of his anomaly with what the phlogistonists had faced, and continued to view chlorine as a compound of muriatic acid and oxygen (one of water's constituents), just as some phlogistonists had viewed metals as a compound of calx and hydrogen (water's other constituent). It is all the more amazing because while the phlogistonists had thought water to be an element when they made this mistake, Berthollet knew that water was a compound of hydrogen and oxygen. Moreover, as we saw in Section 3.2, the composition of water had been a key factor in Berthollet's rejection of phlogiston, because it exposed the phlogistonist mistake in the interpretation of the experiment just considered! In other words, the possibility of water decomposing in a chemical reaction was not something Berthollet would have easily forgotten.

Berthollet's handling of water is puzzling, and quite possibly inconsistent. Sometimes he was clearly aware of the composite nature of water, and its importance in experiments. He criticized Scheele and Bergman for failing to recognize the non-acidity of dephlogisticated muriatic acid because they had water in their experiments, and then detailed an experiment in which he was very careful to keep water out, so as not to corrupt the results.⁵⁰ In his 1785 paper on aqua regia (a mixture of hydrochloric acid and nitric acid), which directly followed his paper on chlorine, Berthollet said that his findings showed that metals decomposed water by uniting with its vital air (oxygen) and so releasing the inflammable air (hydrogen).⁵¹ Another interesting case is his discussion of the reaction of chlorine with metals:

Dephlogisticated marine acid dissolves⁵² iron and zinc without any gas being disengaged . . .; for that these metals should dissolve in an acid it is only necessary that they should unite with a portion of vital air, as M. LAVOISIER has proved; and as dephlogisticated marine acid can

⁵⁰ Ibid., p. 15.

⁵¹ Berthollet (1788).

⁵² The term "dissolves" here is closer to today's "reacts with" than "dissolves".

furnish them with the portion of vital air necessary when it dissolves them, there is no decomposition of water and no inflammable air is produced.⁵³

Today's chemistry shows that no oxygen is involved, but the important point here is that Berthollet explicitly ruled out the possibility of the oxygen coming from the water, using the fact that no hydrogen was released as evidence. Shortly after this point, Berthollet reiterated the point about metals in acids which was used against the phlogiston theory:

[C]hemists agree that the metals are reduced to calces when they are dissolved by means of marine acid, and consequently that they are combined with vital air; but it is not the marine acid which has been able to communicate the vital air to them, for it is not decomposed in these dissolutions; it must necessarily be the water which furnishes it to them, as it must be it which gives the inflammable gas.⁵⁴

In experimenting with mercury and chlorine, however, Berthollet appears to have forgotten his knowledge of the composition of water and its ability to provide hydrogen or oxygen to reactants. He mixed chlorine-water with mercury and observed that mercury calx (oxide) was formed, and also that the liquid became an acid, concluding that "the metal begins by removing the vital air from the [dephlogisticated] marine acid."⁵⁵ In fact, this oxygen must have come from the water in which the chlorine was in solution. Similarly, in the reaction between phosphorus and chlorine-water, Berthollet found that if the two were combined and exposed to heat or light then "the colour of the [dephlogisticated marine] acid is dissipated, its odour disappears, the liquid reddens blue vegetable colours . . . ; so [one can infer] that phosphorus combines with the vital air of dephlogisticated marine acid, and becomes phosphoric acid."⁵⁶ Berthollet, again, does not seem to have considered that water could be providing the oxygen in this reaction.

One of the last points which Berthollet makes in relation to the composition of water in his paper on chlorine is extremely interesting:

⁵³ Ibid., p. 20.

⁵⁴ Ibid., p. 21.

⁵⁵ Ibid., p. 22. Although Berthollet wrote "removing the vital air from the marine acid" here, since it was "dephlogisticated marine acid" and its reaction with mercury that he described in the sentence directly before this, we may conclude that it was actually dephlogisticated (or oxygenated) marine acid that he meant, which became simple marine acid by this removal of oxygen.

⁵⁶ Ibid., p. 25.

The oil which enters into the composition of vegetable matters certainly contains much of the inflammable gas obtainable from water, so that it is very probable that water is decomposed in vegetation, that the vital air which it contained is in part exhaled if the light favours its disengagement, as it does for dephlogisticated marine acid and for nitrous acid . . . ; but when the decomposition of water is not favoured by light it takes place probably to a much less extent, vegetation languishes, the plants have much less oily and resinous matter, and thereby are even deprived of colouring matters: M. SENEBIER also observed that the sickly plants were much less inflammable.⁵⁷

The similarity, at least on the face of it, with today's understanding of photosynthesis, is striking. Berthollet thought that light helped to break up water in plants into hydrogen and oxygen, and he likened this process to how light breaks up oxymuriatic acid into muriatic acid and oxygen. In fact both are processes of light breaking up water! Again, his approach to water seems inconsistent.

What can we make of Berthollet's interpretation of chlorine? His arguments against the phlogistonist interpretation are quite circular, assuming first that the phenomena are best explained by supposing that chlorine is oxygenated muriatic acid, and then proceeding to explain the phenomena thus, without properly refuting any competing phlogistonist interpretations of the same experiments.⁵⁸ Many of Berthollet's experiments could have been explained equally well under the phlogiston theory, as I have shown. Indeed, in his 1785 paper Berthollet goes into little detail about the experiments, and therefore his paper does not seem very convincing in refuting the phlogistonist account of chlorine. It would be fair to say that Berthollet only managed to fit chlorine into Lavoisier's chemistry, rather than using it as clear evidence against the phlogiston theory. (In Chapter 2, especially Section 5, we will see how Berthollet's view of chlorine evolved further, in response to the arguments that it is an element.)

⁵⁷ *Ibid.*, p. 29.

⁵⁸ Kapoor (1970, p. 76) expresses a similar judgement.

4. Incommensurability, translation, and historiography

4.1. Translation in aid of historical understanding

Some interesting philosophical issues emerge from our study of the discovery of chlorine. Both Scheele and Berthollet conceived of chlorine as an entity which modern science declares to be impossible. There is no phlogiston, modern chemistry says, so that Scheele's designation of "dephlogisticated muriatic acid" is meaningless. As for Berthollet, we know there is no chemical compound made up of hydrochloric acid and oxygen, so "oxygenated muriatic acid" is not a cogent concept. Given this kind of difficulty, how can we even hope to understand what these 18th-century authors were really saying?

I do not advocate any extreme forms of constructivism or anti-realism. I take it for granted that the substances that populate the world today are the same as those in the late 18th century, that they exist independently of humans and how we understand them, and that any laws governing chemical reactions have always been the same. I have often translated the experimental reports in the work of Scheele and Berthollet into the terms of our modern chemistry.⁵⁹ Translation helps us understand what was going on in the experiments: I was mystified by Scheele's papers until I laboriously translated all the old terms into modern ones. We can understand phlogistonism better if we learn why and how phlogistonist chemists thought they were dealing with phlogiston in specific experiments. We can confirm if the results really would have been as they were recorded, and if there is an apparent discrepancy, we can ask why. This actually opens up useful avenues of historiographical inquiry; it is only in the hands of an uninquisitive historian that translation will simply lead to the distortion of the historical record.

Translation also helps us evaluate the past scientists' reasoning. The story of the Chemical Revolution is a story of theory-choice: in order to understand it fully, we need to understand and evaluate the complexity and self-consistency of the competing theories and the particular arguments and experiments borne of them. Where our evaluation shows the scientists' reasoning to be poor or flawed from our perspective, we may ask what caused this behaviour: perhaps it is even possible that scientists can have a dogmatic addiction to a theory, as Ladenburg has suggested of

⁵⁹ Eklund (1975) has been invaluable for this.

Scheele.⁶⁰ One of the mistakes I have found in Berthollet's reasoning may be understood as a result of his newly found enthusiasm for rejecting the phlogiston theory. But an evaluation of Scheele's reasoning and of the state of the phlogiston theory in 1785 will show that it is too naïve to say that Berthollet wrongly rejected Scheele's correct interpretation of chlorine.

Berthollet was motivated to reject Scheele's interpretation of chlorine and offer his own because he thought the whole phlogistonist system of chemistry was incorrect and that Lavoisier's new system should supersede it. But within the Lavoisierian system, why didn't Berthollet simply maintain that chlorine was muriatic acid with its inflammable air removed? This would have given an interpretation correct by today's standards, since the term "(light) inflammable air" consistently and only refers to hydrogen. Scheele's experiments would have given Berthollet little support for this view, however, since Scheele's reasoning depended on experiments he performed on manganese in which phlogiston could not be identified with inflammable air: the historical explanation of Scheele's term "dephlogisticated muriatic acid" does not involve "phlogiston" referring to hydrogen. Moreover, claiming that dephlogisticated muriatic acid was in fact oxygenated muriatic acid was in good accord with the general strategy of attack on phlogistonism: Lavoisier had turned the loss of phlogiston into the gain of oxygen in combustion, and now Berthollet had done the same for the production of chlorine, by claiming that instead of the manganese taking phlogiston from the muriatic acid, it gave oxygen to it.

Berthollet was not irrational to reject Scheele's interpretation of chlorine. Indeed, we could say that he was behaving rationally by leaving the degenerating phlogiston research programme, and attacking it under the banner of the progressive anti-phlogistonist research programme.⁶¹ What then can we say about his mistake regarding the role of water in chlorine-water? It seems almost unforgivable, since this mistake was so clearly paralleled in the phlogistonist programme he was rejecting. I think the explanation for this may lie in the excitement and persuasiveness of Lavoisier's increasingly successful anti-phlogistonism. Either Berthollet realized the mistake and ignored it because he was convinced

⁶⁰ Ladenburg (1905), p. 19.

⁶¹ See Musgrave (1976) for a discussion of the Chemical Revolution as an example of Lakatos's methodology of scientific research programmes.

of the falsity of phlogistonism and therefore of the importance of his attack on it, or he really was so caught up in the righteousness of his cause that he did not realize the mistake. So perhaps “conversion” is after all an appropriate term for his behaviour, despite Le Grand’s qualifications mentioned in Section 3.2. Blinded by the bright light of anti-phlogistonist rationality, Berthollet did not see an anomaly that should have been obvious to a man of his particular expertise.

4.2. *Incommensurability*

Although I have argued for the historiographical benefits of conceptual translations, there are still clear difficulties in translating and evaluating past chemistry due to the problems of incommensurability, most notably discussed by Thomas Kuhn and Paul Feyerabend.⁶² Although a term in a scientific theory may refer successfully in a particular given context, when we deal with a whole theory we must remember that a term may be used in many different contexts, and those contexts are not isolated from each other. The historical origin of the term may extend back further; in our case the phlogiston concept extends into the early 18th-century theories of combustion. The term “phlogiston” does not *generally* map onto any term we have today, although phlogistonist reasoning about each individual experiment can be translated into modern terms. Since phlogiston was originally conceived of as the material released from combustibles when they burned, it fails to refer, since no such substance is in fact released from the combustible substance. Some later chemists used the term “phlogiston” to refer to hydrogen, although the word was still entangled in the old non-referring theory of combustion.

An interesting case illustrating the pitfalls of *global* translation is found in the discussion of Scheele by the chemist and historian of chemistry T. M. Lowry. According to Lowry, Scheele would have interpreted the release of oxygen from chlorine-water as the water being robbed of its phlogiston by the dephlogisticated muriatic acid, so that the water’s oxygen is set free.⁶³ This agrees with the modern chemical account of this experiment, if phlogiston is identified with hydrogen.

⁶² See, for example, Feyerabend [1963] (1998) and Kuhn (1962).

⁶³ Lowry (1936), p. 214.

However, that is in fact not what Scheele would have said. In his 1785 response to Lavoisier's and Cavendish's experiments on the composition of water, he lists his own experiments and thoughts on the matter: he thought of fire air (oxygen) as containing water as one of its constituents, and did experiments which he saw as proving this, and concluded: "I am therefore wholly disinclined to believe that water consists of the fundamental principle of fire air, and of phlogiston."⁶⁴ Lowry was misled by an assumption of commensurability. Scheele's phlogiston did *not* map straightforwardly onto today's hydrogen, in its supposed presence in metals and in "mineral alkali" (sodium carbonate), in its strong affinity for oxygen, and, as I have shown, in its role in Scheele's explanation of the production of chlorine.

When we are translating and evaluating, we need to know what the term "phlogiston" refers to in particular circumstances. Translation is necessary, but not sufficient for understanding. It is only the first step. The next step is trying to make sense of the relationships between the terms, the grammar of the theory. Translation does not even have to be between terms which refer to something believed to exist in each context, such as "phlogiston" and "hydrogen". It can also be between something previously believed to exist, like phlogiston, and a phrase in our language produced to help make sense of what it used to mean even though we believe it has absolutely no reference now, like "the substance released in combustion". In these cases, it is attempts at translation that will lead us to the recognition of incommensurability.

"Incommensurability" is a word that has generated a great deal of philosophical excitement. In the case at hand, what incommensurability consists in is straightforward, and in keeping with Kuhn's later formulations of the concept: Berthollet's and Scheele's theories do not map simply on to each other, in terms of the reference-classes of the basic terms they used.⁶⁵ Nor does our modern theory map straightforwardly onto either of theirs. This may have implications about the status of scientific ideas or language that are perhaps worrying to some. But it is possible to set aside such worries for the moment, and admit the obviously complicated relationships between different systems of thought. Chemistry was a murky subject at the time of Scheele and

⁶⁴ Scheele [1785] (1930), p. 286.

⁶⁵ See, for example, Kuhn (1977).

Berthollet, and it was very difficult to see what was going on. If one group thinks that substance *A* is elementary and substance *B* is compound, and another group thinks the opposite, then of course the various ways of understanding chemical phenomena are not going to have a translation that is straightforward in any way. Incommensurability goes beyond the differences in the meaning of words; subtler and more complicated are the differences in the grammar and the relationships between words. Before chemists arrived at the stable and vastly successful system of chemistry that we have today, they had to make experiments and use theories to interpret their findings while those theories were themselves being shaped.

Incommensurability should not inspire despair. It is still possible to attain a deep understanding of past scientists' ideas — by reading them, translating specific parts to get a handle on them, and getting used to seeing the world on their basis (until we close the book and get on with our modern lives). The historian's mind can be trained. Despite incommensurability we can learn by *doing*. Incommensurability can actually help us to make sense of the process and to know that we can be confident in what we have learned. As Kuhn argued, it is only by admitting incommensurability that we can properly begin the process of understanding past science. Attempts at history of science which assume commensurability will fail as they can only understand past ideas that map onto today's, and a perfect mapping is not a realistic expectation. It may seem contradictory to argue for incommensurability at the same time as giving translations of past scientific work. This chapter demonstrates that it is not. Struggling with incommensurability is the only way we can come to an understanding of past scientific work.

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