# From Lavoisier to Mendeleev : the identification of chemical elements in practice between 1770 and 1870

Sarah Hijmans

Université Paris Cité
**Ecole doctorale 623 – Savoirs, Sciences, Education**
***Laboratoire SPHERE (UMR 7219)***

# From Lavoisier to Mendeleev

## *The Identification of Chemical Elements in Practice between 1770 and 1870*

Par Sarah HIJMANS

Thèse de doctorat d'Histoire et de Philosophie des Sciences

Dirigée par Jean-Pierre LLORED

Présentée et soutenue publiquement le 27 février 2023

Devant un jury composé de :

José Ramon Bertomeu Sánchez, Senior Lecturer, Institut d'Història de la Medicina i de la Ciència "López Piñero" & Universitat de València, rapporteur
Ursula Klein, Professor, Max Planck Institut für Wissenschaftsgeschichte, rapporteuse
Hasok Chang, Professor, University of Cambridge, examinateur
Robin Findlay Hendry, Professor, Durham University, examinateur
Jean-Pierre Llored, Maître de conférences HDR, Ecole Centrale Casablanca & Ecole CentraleSupélec & Université Paris Cité, directeur de thèse
Karine Chemla, Directrice de recherche, CNRS & Université Paris Cité (UMR 7219), présidente du jury

# Résumé

Titre : De Lavoisier à Mendeleïev : l'identification d'éléments dans la pratique chimique entre 1770 et 1870

La définition de l'élément chimique en tant que substance simple, défendue par Antoine de Lavoisier dans son *Traité Elémentaire de Chimie* de 1789, est rapidement adoptée par les chimistes européens et reste dominante pendant la majeure partie du XIX$^{e}$ siècle. Malgré cela, les chimistes de l'époque admettent de nombreuses exceptions à cette définition lorsqu'ils tentent de déterminer si une substance est élémentaire ou non. La définition lavoisienne n'est, du reste, pas suffisante en elle-même pour identifier des substances élémentaires : la distinction entre substances simples et composées nécessite des connaissances préalables sur la composition des substances étudiées, sans lesquelles il est impossible d'interpréter les résultats expérimentaux.

Par conséquent, l'étude de l'évolution des définitions historiques ne permet pas à elle seule de comprendre les pratiques chimiques au cours de ce siècle. A partir d'une série d'études de cas, cette thèse étudie comment, entre 1770 et 1870, les chimistes ont concrètement identifié des substances spécifiques comme étant des éléments chimiques.

Les trois premiers chapitres traitent des travaux de Humphry Davy, Jöns Jacob Berzelius, Louis-Joseph Gay-Lussac et Louis Jacques Thenard au cours des deux premières décennies du XIX$^{e}$ siècle. Loin de fournir une méthode univoque pour l'isolement des substances élémentaires, leurs tentatives de décomposition chimique font partie d'une argumentation plus complexe intégrant des résultats expérimentaux, des inférences analogiques et des connaissances théoriques antérieures. S'appuyant sur l'idée selon laquelle les ressemblances de propriétés chimiques sont des signes d'une composition chimique similaire, ces chimistes se servent de l'analogie comme une forme de preuve dans l'étude de la composition.

La deuxième partie de la thèse traite de l'identification de nouveaux éléments par l'analyse chimique des minéraux à partir du débat autour de la nature du tantale, du niobium et d'autres « métaux du tantale » dont l'existence est débattue entre 1801 et 1866. Dans ce cas également, la simplicité expérimentale des substances en question ne joue qu'un rôle

secondaire dans l'identification des éléments : la pratique de l'analyse chimique inorganique vise à caractériser les éléments à partir de leurs composés, plutôt que de les étudier sous forme de substance simple. Ainsi, l'existence de nouveaux métaux est régulièrement démontrée à partir de l'identification de leurs oxydes métalliques sur la base d'un raisonnement analogique similaire qui repose sur le lien entre propriétés chimiques et composition. L'existence d'une tradition d'identification de diverses substances métalliques en lien avec leur intérêt économique permet aux chimistes analytiques de se fier aux méthodes établies sans avoir besoin de proposer des réflexions explicites sur leur usage de l'analogie.

A partir de ces études de cas, cette thèse montre qu'entre 1770 et 1870, les identifications d'éléments ne suivent que rarement la définition communément admise selon laquelle chaque substance indécomposable doit être provisoirement identifiée comme un élément chimique. Inversement, tous les éléments chimiques ne sont pas isolés sous forme de substances indécomposables. L'identification des éléments chimiques se fait uniquement sur la base d'une convergence pragmatique entre différents types de preuve provenant de résultats expérimentaux et raisonnements analogiques. Cette conclusion indique que certains aspects de la définition des éléments chimiques de Mendeleïev sont déjà implicitement présents dans la chimie (post)lavoisienne ; de plus, elle contredit la caractérisation du concept d'élément chimique comme une notion purement empirique pendant la période qui sépare les travaux de Lavoisier de ceux de Mendeleïev. En effet, le concept d'élément chimique se trouve à l'intersection des pratiques expérimentales et théoriques, dont l'imbrication est au coeur de l'histoire de la chimie.

Mots clefs : histoire et philosophie de la chimie – pratiques scientifiques – histoire de la chimie – élément chimique – raisonnement analogique

# Abstract

Title: From Lavoisier to Mendeleev: The Identification of Chemical Elements in Practice between 1770 and 1870

In his *Traité Elémentaire de Chimie* in 1789, Antoine de Lavoisier famously defined the element as a chemically indecomposable or 'simple' substance. This definition was quickly adopted by chemists throughout Europe and remained dominant at least until Dmitri Mendeleev advocated for a different definition in 1869. However, when determining whether a substance was elementary or not, chemists regularly made exceptions to this definition. In practice, Lavoisier's definition was not in itself sufficient for the identification of chemical elements: the distinction between simple and compound substances required prior knowledge of the composition of the substances under study, without which experimental results could not be interpreted.

Therefore, while the analysis of (changes in) historical definitions can provide the theoretical criteria for elementary nature, only a study of identification practices can show how such criteria were adapted to chemical practice. Focusing on 1770-1870, the period during which the element was defined as a simple substance, this thesis shows how chemists actually went about identifying chemical elements. It consists of a series of case studies analysing the arguments on the basis of which the elementary nature of specific substances was established and/or questioned.

The first three chapters focus on the work of Humphry Davy, Jöns Jacob Berzelius, Louis-Joseph Gay-Lussac and Louis Jacques Thenard in identifying the nature of aluminium, chlorine and ammonia between 1807 and 1820. I argue that far from providing an unambiguous method for the isolation of elementary substances, the results of their experimental decomposition attempts provided only part of a complex argumentation, in which empirical findings had to be made coherent with analogical inferences, chemical classification and existing theoretical knowledge. Relying on the idea that similarities in chemical properties indicated similarities in composition, chemists used chemical analogy as evidence in the study of chemical composition.

The second part of the thesis examines the field of mineral analysis, focusing on the repeated controversies on the nature of tantalum, niobium and a number of other potential "tantalum metals" between 1801 and 1866. I argue that the procedures of mineral analysis enabled the identification of metals using the chemical behaviour of their compounds without requiring their isolation in the form of simple substances. The existence of previously unknown metals was regularly inferred from the identification of their metallic oxides on the basis of a similar analogical inference that relied on the link between chemical properties and composition. In analytical chemistry, this use of analogy remained mostly implicit because practitioners could build on a longer tradition of identification of metals for their economic value and therefore did not need to reflect on their own methods.

The case studies that make up this thesis show that in practice, nineteenth-century chemists rarely followed the definition of chemical elements as simple substances. Not all indecomposable substances were viewed as elements, and not all elements were isolated in the form of indecomposable substances. Elementary nature could only be established on the basis of a pragmatic convergence between evidence from analogy and experiment. This conclusion suggests that aspects of Mendeleev's definition of chemical elements were already implicitly present in (post)Lavoisian chemistry, and contradicts a common view of the chemical element as a purely 'empirical' notion during the period between Lavoisier and Mendeleev. Rather, the concept of chemical element lay at the intersection of experimental and theoretical practices, the interweaving of which is at the heart of the history of chemistry.

Key words: history and philosophy of science – scientific practice – history of chemistry – chemical element – analogical reasoning

# Acknowledgements

I would like to express my gratitude to Ursula Klein and José Ramon Bertomeu Sánchez for their reports on this thesis and to Hasok Chang, Karine Chemla and Robin Hendry for accepting to act as my examiners. I admire their work and am honoured to have the occasion to discuss my own research with them. I likewise thank the members of my thesis committee, Hasok Chang, Nadine de Courtenay, Eric Scerri and Sacha Tomic, for their valuable feedback and for supporting me in a variety of other ways at different moments during my PhD.

Un grand merci à mon directeur de thèse, Jean-Pierre Llored, pour ses conseils et son soutien constant. Je le remercie de m'avoir encouragée à présenter mon travail et d'avoir partagé son réseau international avec moi, et cela dès mes années de master. Sa connaissance rigoureuse des sources et son ouverture vers différentes disciplines continuent d'être une inspiration pour moi.

Additionally, I am incredibly thankful to Hasok Chang for acting as sponsor during my three terms as a visiting student at the University of Cambridge. He took the time to read and discuss any draft with which I needed help and continued to work with me even during the periods that I was not officially affiliated with his university. He has gathered a wonderfully supportive and intellectually stimulating group of researchers around him and truly sets an example through his kindness and generosity.

A number of people took the time to read drafts that I wrote as part of this project: Ana Cazal, Antoine Duranton, James Frank, Jonathon Hricko, Thibault Jouis, Nicolas Michel, Janna Müller, Peter Ramberg, Klaus Ruthenberg, Marabel Riesmeier, Helene Scott-Fordsmand, Ruth Smith, Margo Stemmelin, the participants of the CHOSTM seminar at King's College and six anonymous reviewers. I am grateful for all of their comments, which significantly helped me in sharpening the argumentation of this thesis. Thank you as well to John Hedley Brooke, Catherine Jackson, Rune Nyrup and Friedrich Steinle who took the time to meet with me and discuss some aspects of my PhD.

Various institutions provided the funding that made it possible for me to carry out this research and I gratefully acknowledge their support: Ecole Doctorale 623 of the Université Paris Cité, the Royal Institution of Great Britain, Hendrik Muller Fonds and Région Ile de

France. I thank the staff of these institutions and the people who helped me prepare these and other funding applications: Nadine de Courtenay, Katy Duncan and Paul Sampson, among others. Thank you as well to the people who generously shared their home with me for anywhere between one and six months while I was working on this project: in England, Mike Albutt; en France, Alain Dénigot et sa famille ainsi que les colocataires de la rue des Annelets.

Thank you to everyone who included me in their ongoing projects, whether it was by inviting me to contribute to an edited volume, to speak at a seminar or to help organise an event: Pierre Avenas, Geoffrey Blumenthal, Amélie Dessens, Elena Ghibaudi, Fabien Grégis, Annette Lykknes, Juan Camilo Martinez González, Alison McManus, Karoliina Pulkkinen, Eric Scerri, Brigitte van Tiggelen, Joachim Schummer, Vanessa Seifert and many more. I am likewise grateful to all the organisers of seminars and conferences where I had the opportunity to present my work.

Je voudrais également remercier les membres du laboratoire SPHERE, notamment Karine Chemla, Claude-Olivier Doron, Jean-Baptiste Grodwohl, Christine Proust et David Rabouin pour leurs conseils et aide sur divers points. Nadine de Courtenay m'a particulièrement aidée au cours de mon master, pendant la préparation de ma candidature et au début de ma thèse et je tiens à la remercier pour cela. Merci également à Virginie Maouchi, Patricia Philippe, Laurent Lemoine et Nad Fachard pour leur efficacité et leur aide précieuse au quotidien et à Sabine Rommevaux pour sa direction du laboratoire.

Ces années de doctorat n'auraient sans doute pas pu être aussi agréables sans le groupe de doctorant.e.s et ATER du laboratoire SPHERE, avec qui j'ai pu avoir des discussions passionnantes autant lors de nos pauses que dans le cadre du séminaire DISc. Merci à Caroline Angleraux, Clément Bonvoisin, Helmy Chekir, Jimmy Degroote, Gautier Depambour, Justin Gabriel, Edgar Lejeune, Nicolas Michel, Arilès Remaki, Adeline Reynaud, Miriam Rogasch, Flora Vachon, David Waszek, Liqiong Yang et tous.te.s les autres. J'aimerais adresser un remerciement plus particulier à Marie Lacomme pour les années que nous avons passées en tant que voisines de bureau et pour ses nombreuses contributions à la vie du laboratoire. Merci également à Mélanie Ephrème, ancienne étudiante du master LOPHISS, d'avoir partagé avec sa connaissance encyclopédique de la

chimie du XVIII$^{e}$ siècle avec moi. Je vous souhaite à toutes et tous de réussir dans vos projets.

Part of the research for this thesis was carried out while I was a visiting student at the department of History and Philosophy of Science at the University of Cambridge and I gratefully acknowledge that opportunity. I thank the members of this department for welcoming me, as well as Toby Bryant, Jack Dixon and other staff for helping me find my way. Katy Duncan, Grace Field, Céline Henne, Rory Kent, Ruward Mulder, Janna Müller, Miguel Ohnesorge, Marabel Riesmeier, Helene Scott-Fordsmand, Emilie Skulberg, Hannah Tomczyk, Bobby Vos, Oscar Westerblad and all the other participants of Hasok Chang's weekly reading group made me feel especially welcome and I thank them for all the stimulating exchanges we had. I look back fondly at a variety of online meetings which lightened up the pandemic days, particularly the 'integrated HPS' symposium which became the setting of some of the most fascinating discussions I have ever participated in.

I would like to thank my past teachers, most notably Alexandre Guilbaud, Thomas Pradeu, Jaïr Stranders and Carlien Moeljono, all of whom knowingly or unknowingly contributed to me following this path.

Plus personnellement, je souhaite remercier mes ami.e.s pour leur soutien précieux tout au long de mes années de doctorat. Graag bedank ik mijn vrienden, familie en bovenal mijn ouders, voor hun interesse en steun, dichtbij en op afstand. Samuel, Channa, Nynke, Margo et Antoine, pour tout ce que nous avons vécu ensemble et toutes les aventures à venir. Merci.

# Table of Contents

# INTRODUCTION

Aluminium, chlorine, nitrogen and tantalum are all examples of chemical elements. They are used daily in a variety of scientific and industrial processes, they each have their place in the periodic table and their nature may therefore seem completely self-evident. This is reinforced by chemical textbooks and lists of historical discoveries that often provide a discovery date and the name of the person who first isolated the chemical element in the form of a chemically indecomposable substance: for the examples cited above this happened during the late eighteenth and early nineteenth century. However, if we look at these historical cases in more detail, the story of their identification as elementary almost invariably turns out to be much more complicated. Rather than being a simple fact that was 'out there' for us to discover, knowledge of the elementary nature of each of these substances was the result of intricate processes of inquiry that involved puzzle-solving, collaborative efforts and, in many cases, controversies that animated chemists all over Europe.

During the time that these episodes took place, chemical elements were commonly defined as simple substances. This definition had most famously been defended by the French chemist Antoine-Laurent de Lavoisier (1743-1794), who argued that any substance that could not be decomposed in the laboratory should provisionally be seen as a chemical element (Lavoisier 1789). The Lavoisian definition characterized chemical elements according to a 'negative-empirical' criterion, as David Knight (1978, 23) has called it.[1] It is empirical in the sense that the definition only refers to the results of experimental operations, and negative because it defines chemical elements on the basis of the impossibility of decomposing them rather than by any positive criteria. The negative-empirical criterion could only lead to provisional identification, because no amount of failed decompositions can prove that the impossibility of decomposing a substance results from its actual simplicity rather than it being merely due to insufficient means of decomposition. Lavoisier was aware of this issue and advised his readers to stick as closely

[1] Others have taken on the term 'negative-empirical' to describe Lavoisier's definition, but this was the earliest occurrence of it that I could find.

as possible to the results of laboratory operations, and never to suppose that any simple substance might actually be composed until this was proven by experiment.

It thus seems as though Lavoisier established a simple and practical way for the identification of simple substances, while avoiding metaphysical questions regarding the ultimate nature of the elements. However, the actual identification of chemical elements rarely happened according to the negative-empirical criterion. Even Lavoisier himself did not strictly follow his own recommendations: for instance, he omitted the indecomposable substances potash and soda from his list of simple substances because they behaved like compounds.[2] Likewise, his followers predicted that hydrofluoric acid was a compound of hydrogen and the previously unknown element fluorine in the early nineteenth century (Banks 1986). The well-known debates on the elementary nature of palladium and chlorine moreover show that the isolation of chemical elements in the form of a simple substance did not necessarily suffice as proof of their elementary nature (Usselman 1978; Gray, Coates, and Åkesson 2007). In practice, the characterization of these elements was neither purely experimental, nor based only on the impossibility to decompose them.

Although they are generally treated as isolated examples, these cases are signs of an underlying issue: the negative-empirical criterion in itself could not suffice to identify chemical elements. Lavoisier's definition was circular: it defined a simple substance as a body that could not be decomposed, and decompositions as operations that break compounds down into simpler substances (see also Chang 2007; 2011a; 2012b, chap. 1). Depending on which substances were defined as simple to begin with, the same operations could be viewed as either combinations or decompositions. This made the interpretation of experimental results quite complicated. It may seem as though weighing the reagents and reaction products might solve this issue, but this only rarely provided an answer (see prologue chapter). Therefore, rather than providing a straight-forward and direct way to identify chemical elements by their isolation in the form of simple substances, the Lavoisian criterion for elementary nature could only form a part of a more complex argumentation. In addition to experimental indecomposability, positive arguments based on existing knowledge of chemical composition were required.

[2] This has been pointed out by many different authors, see for example Perrin (1973) or Klein and Lefèvre (2007).

This thesis will investigate the criteria that nineteenth-century chemists effectively used to determine which substances where chemical elements and which were not. So far, this question has not been answered in the literature. Many discoveries of elements have been studied for their own sake but broader perspectives that compare multiple cases are rare.[3] Although this thesis will build on these existing works, it will add a more systematic overview of the identification of elements between 1770 and 1870. Besides the inherent interest of the case studies discussed here, they will also improve our understanding of chemists' view of chemical elements beyond their theoretical descriptions. While (changes in) definitions can provide the theoretical criteria for elementary nature, only a study of identification practices can show us how such criteria were adapted to chemical practice.

## Methodology

I have chosen to limit this study to the time period between 1770 and 1870 in order to include the works of Lavoisier on the one hand and up until those of Dmitri Mendeleev (1834-1907) on the other. Lavoisier's definition of the chemical element was rapidly adopted throughout Europe and remained dominant at least until Mendeleev distinguished between the terms 'simple substance' and 'element' in 1869, reserving the latter for stable constituents that could only be detected via their atomic weight and not by any macroscopic properties (see Bensaude-Vincent 2019). An example that might illustrate this distinction is the element carbon and its simple substances diamond and graphite. Whereas graphite and diamond are each characterized by specific observable properties that are lost as they transform, carbon can be tracked as a stable quantity of matter as it combines to form a variety of different substances. Instead of characterizing them as empirically indecomposable substances, Mendeleev highlighted the role of elements as stable constituents by defining them only on the basis of their specific atomic weights.

[3] Examples of studies of discoveries of elements can be found in Weeks (1956), Partington (1962b), Siegfried (1963), Hirsh (1981), James (1984), Trofast (1996; 2011), Ashbee (2007), Klein (2014), Arabatzis and Gavroglu (2016) and Hricko (2021). Among the few authors that discuss the criteria for discovery of an element more generally are Rancke-Madsen (1976) and Kragh (2019).

Because of the historical significance of Lavoisier's and Mendeleev's definitions of the chemical element and the change between them, various works have focused on their respective views (see for example Paneth 1964a; Bensaude-Vincent 1986; Hendry 2005; Boyce 2019; Bensaude-Vincent 2020; Brooks 2020; Scerri 2020). Yet the period separating them is often overlooked, despite the fact that chemistry rapidly developed during this time.[4] One exception is Bernadette Bensaude-Vincent's (1981) study of the development of the concept of element from Lavoisier to Mendeleev from the point of view of its definitions and function in chemical theory. On the basis of a study of important textbooks of the time, she has argued that terminological and conceptual ambiguities persisted long after Lavoisier's definition, and these difficulties could only be solved by Mendeleev's redefinition of the concept and the development of the periodic table.

While it will provide an important background to this thesis, Bensaude-Vincent's results are only incomplete because her analysis relied on chemists' theoretical characterizations of the concept of element that cannot tell us how chemists used it in practice. Recent works in the history and philosophy of science have shown that concepts have to be studied as part of scientific practice in order to understand their development in ways that a focus on theories and results alone cannot achieve (see for example Steinle 2010; Chang 2011b; Feest and Steinle 2012; Chemla 2014). 'Scientific practice' is difficult to define exactly, but it can be characterized in opposition to a form of theoretical discourse: practice, then, is what scientists actually do, as opposed to what they say they do (Soler 2012).[5] This does not mean that practice is opposed to theory, because it can be theoretical as well as experimental. Rather, a study of scientific practice requires a focus on the processes of scientific inquiry instead of its products (see also Chang 2022). In line with this characterization of practice, I will study the processes by which chemists actually came to characterize specific substances as elementary.

[4] The only other chemists who is sometimes mentioned is John Dalton, because of the importance of his atomic theory (Siegfried 2002; Banchetti-Robino 2020).

[5] For a summary of the aims and arguments that are shared by most works of the practice turn, see Soler et al. (2014).

This also provides a solution to the issue of terminology: what exactly was a 'chemical element' for chemists of the late eighteenth and nineteenth centuries? As Bensaude-Vincent (1981) has shown, chemists of the period used 'principle', 'simple substance,' 'undecompounded substance', 'element' and similar terms seemingly interchangeably, without clearly and explicitly explaining the differences between those terms. This makes the concept difficult to trace and disambiguate in chemical texts without projecting a retrospective view of what chemical elements are today. In this thesis, I will solve that issue by approaching chemical elements as a certain kind of substance. Independently of the terms they used, chemists of the time clearly identified a separate class of substances characterized by their relative simplicity, which they saw as the constituents of compounds. They produced lists and classifications of these entities, for which I will use the term 'chemical elements' for the sake of clarity.[6] Without getting into the nature of the concept of element itself, I will therefore simply study the arguments on the basis of which specific chemical elements were added to, or deleted from, such lists and classifications.

The focus on chemical elements as a class of substances will also enable me to take into account their materiality, following a recommendation made by Ursula Klein (2008a). By materiality, Klein does not only mean the sensory qualities of material substances but also the possibilities of transforming them through chemical operations, including the various difficulties that might influence their characterization, classification and identification. Whereas chemists could reflect on the general concept in theoretical discourse, they only encountered these kinds of difficulties when dealing with the identification of specific chemical elements. Even if they wanted to follow their own theoretical criteria for elementary nature, the behaviour of material substances did not necessarily align with their ideas. The study of the processes by which they came to identify

[6] I will use the terms 'undecompounded' and 'indecomposable' interchangeably, to refer to any substances that could not be decomposed using the available means at a specific moment in time. By 'indecomposable' I therefore do not mean bodies that were absolutely impossible to decompose using any imaginable methods but rather substances that had never been effectively decomposed. Both of these terms are different from (provisional) simplicity, which is a more complex judgement explaining why a body is indecomposable.

specific substances as elementary will therefore show how chemists went about making their ideas work in practice.

The period between 1770 and 1870 was an incredibly productive time during which many new chemical elements were identified, isolated or otherwise studied (see Weeks 1956, 889–94 for a chronological list). Each of these elements has a discovery story, but my aim is not to provide a retrospective summary of these stories, as can be found for example in Mary Weeks' *Discovery of the Elements* (1956). The idea of discovery is intrinsically linked with the attribution of credit, as it is first and foremost a label of achievement that research communities use to retrospectively celebrate certain practices as examples of good research (see Schaffer 1986; 1994). This label is reserved for scientific endeavours that are retrospectively deemed successful, whereas my study will also include more controversial claims. Furthermore, the idea of discovery bears the connotation of bringing to light some pre-existing fact, which highlights the final result rather than the process by which it was established. Historical priority disputes and discovery claims will be useful to this study as they provide information about the criteria for elementary nature, but the outcome in terms of results or attribution of credit will not be my main focus. Instead I will investigate the argumentation used to establish the elementary nature of that which was claimed to be discovered.

Furthermore, rather than providing an exhaustive overview of all discoveries that took place during this time, I will focus on the in-depth analysis of a relatively small number of identifications of elementary nature. The cases studied in this thesis have been selected because they were controversial or exceptional in such a way that chemists had to explicitly argue in favour or against the elementary nature of specific substances. Thus, the elementary nature of chlorine was the subject of a debate between 1810 and 1816. Likewise, the elementary nature of vanadium and niobium was questioned in the early nineteenth century before they were rediscovered in a different source. During the middle of the century, a number of so-called 'tantalum metals' were claimed to exist in the tantalum-niobium family and their existence was debated. The investigations of the composition of ammonia between 1807 and 1812 were quite controversial as well and motivated chemists to question the elementary nature of nitrogen and hydrogen. The possible existence of a metal called 'ammonium', the metallic constituent of ammonia,

occupied chemists for years before it was finally abandoned as a curious exception. Lastly, while it was not a matter of controversy, the metal aluminium was commonly accepted as an element more than fifteen years before it was isolated in the form of a simple substance and chemists therefore had to justify this exception.

Most of these episodes have not been described in detail elsewhere. Rather than as perfect exemplifications of a general theory of the identification of elementary nature, I will approach them as "phenomena in their own right", as John Law and Annemarie Mol (2002, 15) would say. While these cases will point towards a more general lesson, they are each instructive in their own peculiar way. The newly emerging discipline of chemistry was by no means uniform during this time and each investigation took place within a specific historical context. I do not wish to reduce this complexity and will describe the specific actors and their views, their methods and institutional settings, their rivalries and collaborations. Instead of presenting a comprehensive map of the nineteenth-century study of chemical composition from a bird's-eye view, seeing cases in this way enables us to explore them by foot, so to speak, and see a variety of things along the way.

The stories of these (supposed) elements involve a community of mainly French, German, British and Swedish chemists, many of whom were in contact with each other because they studied together, worked together, corresponded about their discoveries and/or published in the same journals.[7] The main primary sources for these case studies will be the publications in scientific journals that contained discovery claims or other contributions on the nature of the elements in question. Within these sources, I will focus on what Jutta Schickore (2017) has called 'methods discourse': the parts of historical scientific publications that describe (experimental) method, ranging from the description of specific protocols all the way to broad commitments to experimentation as a means of acquiring knowledge. More specifically, I will focus on the step-by-step experimental

[7] For the early development and history of scientific journals up to 1790, see Kornick (1962). For the history of scientific publications and their readership in nineteenth-century Britain, see Topham (2000) and Dawson, Lightman, Shuttleworth and Topham (2020). For the history of scientific journals in France, see Tesnière (2021). Crosland (1992, chap. 8) discusses on the historical development of publications at the French Academy of Sciences; Fyfe, Moxham, McDougall-Waters and Mørk Røstvik (2022) focus on scientific publishing at the Royal Society.

procedures and the interpretation of specific results, in order to identify the arguments that chemists relied on for the establishment (or refusal) of elementary nature. In order to contextualise these publications and evaluate their reception by the broader chemical community I will rely on dictionaries, textbooks and yearly reports on the advancement of science. Lastly, correspondences will provide more details on the tentative hypotheses and perceived failures that were left out of publications.

Despite the variations between them, each of these examples of identifications of elementary nature will reveal some aspects of the ways in which chemical elements were characterized during the eighteenth and nineteenth centuries. Following a methodology of integrated history and philosophy of science outlined by Hasok Chang (2012a), I will rely on a philosophical analysis to articulate the ideas that are implicitly present within the historical episodes. Specifically, I will identify the role of different types of evidence in the identification of chemical composition. Generalizing from these episodes, I will argue that the negative-empirical criterion was only part of a more complex argumentation regarding the nature of elementary substances. In addition to indecomposability, another factor was invariably of key importance in the establishment of elementary nature: chemical analogy. Clarifying the structure of chemists' argumentation will not only help in understanding these episodes themselves, but also point to broader implications for the philosophical literature on analogy in science and the nature of the concept of chemical element. Ultimately, such philosophical analyses can help improve our understanding of the historical development of chemical knowledge. In that sense, my approach will be more closely aligned with philosophical history of science than with historical philosophy of science (Arabatzis 2017).

## Chemical analogies as evidence of chemical composition

Analogy is a type of comparison that highlights similarities between what is generally called a *source* and a *target* system (see Bartha 2019). More specifically, analogies establish a certain similarity as being relevant in such a way that it can serve as an explanation or to warrant further reasoning. One might highlight, for instance, the many similarities between dolphins and sharks, but these similarities are not relevant to the question of why dolphins need to come up to the surface to breathe. Here, a comparison with humans might provide a more fruitful analogy, because humans and dolphins both

have lungs: like humans, dolphins therefore cannot breathe underwater. In other words, it is not the number of similarities that makes for a good analogy, but rather the relevance of the similarities that are pointed out. Once such relevant similarities are identified, they can form the basis of analogical arguments in order to infer that the target will plausibly share further features with the source system.

Recently, a number of case studies have shown various roles for analogical reasoning in science, for example in conceptual development in synthetic biology (Knuuttila and Loettgers 2014) and in providing reasons to pursue a theory or model in physics (Nyrup 2020). Using historical examples from chemistry, Amy Fisher (2018) has proposed an interpretation of analogical reasoning as a methodological principle. She has found that scientists rely on analogy as an 'experimental stratagem': analogy thus facilitates research by helping scientists identify patterns in their experimental results, formulate working hypotheses and design further experiments in order to test those hypotheses. The chemists described in this thesis indeed relied on analogy as an experimental stratagem, but this was not the only role that analogy played. The most relevant use of analogies for this study was their role in producing evidence for the study of composition, similar to what Adrian Currie (2018, chap. 7) has described when it comes to the historical sciences (such palaeontology and archaeology).

In order to understand how analogy could function as a type of evidence in the identification of chemical elements, it is important to distinguish between analogical reasoning in general and what nineteenth-century chemists called 'chemical analogy'. As a way to establish patterns in chemical behaviour among different types of substances, chemical analogy primarily functioned principle of classification. From the mid-eighteenth century onwards, the arrangement of chemical classifications was dictated by two principles: analogy and composition (see Klein and Lefèvre 2007). Simple substances were distinguished from compounds, which in turn were separated according to complexity of composition. Within each level of composition, classes of chemical substances were established on the basis of relevant similarities in their chemical properties: when two or more substances exhibited patterns of significant similarities in solubility, combustibility, reaction with certain reagents and the formation of a specific kind of oxide, acid or salt, they were seen as chemically analogous.

Chemical practitioners commonly admitted that chemically analogous substances were composed in a similar way: earlier in the nineteenth century this meant that classes of substances all contained the same or similar elements and later this also became a matter of analogous chemical formulae. This link between properties and composition enabled the inference of chemical composition on the basis of analogy. If a body behaved similarly to substances that were seen as chemical elements, it was likely to be a chemical element itself. On the other hand, if it behaved like a certain type of compound, it probably contained similar constituents. Such inferences not only guided further experiments but could also be used to interpret and even contradict experimental results. Thus, rather than strictly on the basis of the negative-empirical criterion, the provisional simplicity of chemical elements was established on the basis of a more complex argumentation that integrated existing knowledge of chemical composition, chemical analogies and new experimental results.

The role of analogy in the identification of chemical elements has not been studied, despite the fact that multiple historians have remarked its importance. For example, without elaborating on this statement, David Knight (1978, 23–24) has noted that

> "chemists did not adhere rigidly to Lavoisier's recommendations; all - including even Lavoisier himself - seem to have been open to arguments from analogy, and tended not to regard as elementary a substance which closely resembled known compounds, even though it had not itself been decomposed."

Others have likewise remarked in passing that analogy played the role of a "heuristic" (Gray, Coates, and Åkesson 2007, 43) or a "guiding principle" (Ruston 2019, 130) in resolving questions about the elementary nature of substances in the early nineteenth century, but dedicated no more than one sentence to this use of analogy. Robert Siegfried (1963) is the only one to have investigated the importance of analogy in the assessment of the elementary nature in more detail. He has shown how the early nineteenth-century chemist Humphry Davy (1778-1829) argued in favour of the characterization of potassium and sodium as elements, not because they were indecomposable substances but rather because they were chemically analogous to metals. Since metals were commonly accepted to be elements, the identification of potassium and sodium as metals also meant they would also be seen as elementary. Siegfried's work on this topic is very valuable but it is limited

to a single example. In this thesis I will provide many more examples and describe the role of analogy in the identification of elementary substances in the early-to-mid nineteenth century in more detail.

## Outline

The main body of this thesis is divided into two parts. The first part will focus on a group of early nineteenth-century chemists including Humphry Davy and some of his collaborators and rivals. One of the shared interests of this group of chemists was a new instrument called the voltaic pile, which was invented in 1800 and could be used to study chemical composition. The three chapters that make up the first part focus on three substances that they studied using this instrument and other experimental methods that were mainly aimed at decomposing and recomposing substances. Far from providing an unambiguous method for the isolation of elementary substances, I argue their decomposition attempts provided only part of a more complex argumentation, in which new experimental findings had to be made coherent with analogical inferences, chemical classification and broader theories of chemical composition.

The first chapter describes the acceptance of aluminium following Davy's isolation of the alkaline and alkaline earth metals and shows that analogical inference functioned as complementary evidence for the composition of substances. By examining investigations into the composition of ammonia and its relation to the problematic nature of nitrogen and ammonium (the supposed metallic constituent of ammonia), chapter two will show the iterative relation between experimental results and analogical inference. Chapter three focuses on the debate on the nature of chlorine between 1810 and 1816, and will show that conclusions regarding elementary nature depended on chemists' individual views on the importance of analogy, simplicity and regularity in choosing between hypotheses.

The second part of the thesis studies the identification of chemical elements using mineral analysis, which was the most common source of the discovery of new elements during the eighteenth and nineteenth centuries. I will focus on the controversy surrounding the 'tantalum metals' between 1801 and 1866. Of these metals, only tantalum and niobium are still recognised as elements today; the discovery claims of columbium, pelopium, ilmenium and dianium were all retracted or refuted. Despite the theoretical and institutional changes that chemistry underwent during this time, the debates on the tantalum metals

point towards a continuity in the identification of metals. For most of the nineteenth century, chemists continued to use the same types of analytical procedures as their mid-eighteenth-century predecessors. Chapter four describes these methods and their origins. Chapter five shows how these analytical procedures were used during the first decade of the nineteenth century to identify metals by the chemical behaviour of their compounds without requiring their isolation in the form of simple substances. In chapter six I will analyse the debates on the tantalum metals during the middle of the century, and argue that the central issues were the correct identification of the properties of compounds and the elimination of impurities, rather than the simplicity of the new metals. Underlying these identifications was a similar, though implicit, use of chemical analogy as that described in the first three chapters of the thesis.

Before I can turn to any of these historical episodes, I will need to discuss Lavoisier's view of chemical elements in more detail, as well as the broader ideas of chemical composition on which it was based. Moreover, my claim that the negative-empirical criterion itself was insufficient for the identification of chemical elements needs more support: what were the difficulties of Lavoisier's definition and why could the emergence of chemical atomism not solve them? Why did chemists resort to the use of chemical analogy? These questions will be answered in a prologue chapter.

# PROLOGUE – Chemical Elements and Simple Substances: Eighteenth-Century Views of Composition

This thesis investigates the way in which elementary nature was established during the period when chemical elements were defined as simple substances. After it was defended by Lavoisier in his *Traité Elémentaire de Chimie* in 1789, this definition remained commonly accepted for most of the nineteenth century.[8] In order to understand the characterization of chemical elements during this period, it is therefore important to understand what this definition was and where it came from. What were the different influences that shaped early nineteenth-century views of composition? What was Lavoisier's characterization of chemical elements, in theory and in practice, and in which context did it arise? Lastly, did the development of chemical atomism in the beginning of the nineteenth century change these views, or could we still characterize them as Lavoisian? This chapter will reply to these questions and thereby function as a prologue to the historical episodes treated in the rest of the thesis.

The definition chemical elements as simple substances logically required the distinction between substances that are simple, or composed only of themselves, and compounds that contain multiple components. While this may seem perfectly intuitive to anyone who has studied modern chemistry, it is not the only possible view of composition. During the seventeenth and eighteenth centuries, substances became increasingly characterized in terms of their chemical composition. This view differed from earlier views according to which all chemical substances were homogeneous mixts and their properties were caused by active principles. Furthermore, chemists started to identify groups of substances on the basis of their tendencies to combine rather than the kinds of active

[8] Lavoisier was a relatively atypical chemist; whereas most chemists of the time were trained as physicians or apothecaries, he was a lawyer and 'fermier général', responsible for collecting various kinds of taxes under the French 'Ancien Régime'. For biographical information on Lavoisier, see Guerlac (1973) and Beretta (2008) and the various references cited therein. See also *Panopticon Lavoisier*, a database of thousands of works by and about Lavoisier, edited by Marco Beretta and accessible at http://moro.imss.fi.it/Lavoisier.

principles they contained. The result was a characterization of chemical substances according to chemical behaviour and composition that would remain central throughout the nineteenth century. Lavoisier's new system of chemistry can be seen as the culmination of a gradual shift towards this view of composition.

Lavoisier's work is often seen as the final refutation of the four elements with a list of experimentally identified chemical elements. From then on, elementary nature became a question that could be answered through the study of composition. However, identifying chemical elements was more complicated than simply attempting to decompose substances. In practice, he did not strictly follow his own definition, as he did not view all indecomposable substances as chemical elements and likewise accepted chemical elements that had not been isolated in the form of indecomposable substances. He also speculated on the true nature of chemical elements and characterized some of them as capable of causing properties such as acidity and expandability. While his metaphysical speculations may have been a remnant from earlier chemistry, his exceptions were also a way to get around some of the difficulties caused by the definition itself. The negative-empirical criterion left a number of questions unanswered, both regarding the true nature of the simple substances and the practical ways to identify them. Chemical atomism and the use of weight has been said to provide a solution to these difficulties, but I will argue that they could not provide all the additional evidence needed in order to identify composition.

The aim of this chapter is therefore two-fold: on the one hand, I will provide the necessary background to understand the origins and content of nineteenth-century views of composition, and show what it meant to characterize chemical elements as simple substances. On the other hand, I will also further justify the need to study the identifications of chemical elements in practice. Although chemical elements were defined according to the negative-empirical criterion for most of the nineteenth century, their actual identification was neither strictly negative nor strictly empirical.

# Changing views of chemical composition in the eighteenth-century

During the chemical revolution in the second half of the eighteenth century, the theoretical structure of chemistry underwent significant reforms.[9] Although Lavoisier's contributions were of central importance to the establishment of a new theoretical structure for chemistry, various aspects of eighteenth-century chemistry remained unchanged by his reforms.[10] In this section I will describe how a view of chemical substances as characterized by composition and analogy developed in eighteenth-century chemistry and argue that this had a key influence on Lavoisian chemistry. It is important to take these earlier influences into account, not only because the chemical revolution can be seen as part of a broader development, but also because, in Holmes' words, eighteenth century chemical practices "laid the conceptual and operational foundations on which much of the chemistry of the nineteenth century developed" (F. L. Holmes 1989, 55).

## The ontological shift from principles to compounds

Until the seventeenth century, composed substances were seen as completely homogeneous according to various versions of the Aristotelian concept of mixt.[11] Although the constituent elements can be reproduced from Aristotelian mixts, they do not continue to exist within the composed bodies. Instead, when two substances combine, they are seen as disappearing and giving rise to a new one with entirely new properties. These ideas

[9] There is some debate in the literature on whether or not this transformation truly constituted a revolution(see for example Klein 2015; Chang 2015); here I simply use this term because it is how this period in the history of chemistry is commonly known.

[10] One of the areas where Lavoisier's reforms had little effect is plant chemistry – although it was an important part of chemistry, this subject will be very little discussed here as it did not lead to the identification of new elements. For a discussion of the changing views of composition in plant (and later organic) chemistry, see Klein (2005; 2008a).

[11] On the philosophical problem of the mixt/mixis see Earley (2005) and Bensaude-Vincent (2008, 51–64). The terms 'mixt' or 'mixis' are used in order to distinguish from 'mixture' which is the opposite of a chemical combination.

remained very influential in the history of alchemy and chymistry.[12] In the beginning of the sixteenth century, a modification of the Aristotelian theory was made by Theophrastus von Hohenheim (1493-1541), better known as Paracelsus. He saw natural bodies as mixts consisting both of the four elements and of three principles (salt, mercury and sulphur).

Rather than as material constituents of substances, principles were seen as the cause of properties of substances. Early modern chymists saw natural bodies as consisting of both material and spiritual substances, and Paracelsus' principles were likewise metaphysical as well as material (Klein and Lefèvre 2007, 40–44). For example, Paracelsus compared the elements to the matrix or womb, and three principles to the 'semina' carrying different types of qualities with them that they could give to the resulting mixt. Over the course of the seventeenth century, two extra principles (earth and water) were added and by the beginning of the eighteenth century it was standard to have five principles (Siegfried 2002, chap. 1). Principles were useful tools for chemical transformations because they were active substances that could be used to transform the mixts into which they entered.

Early modern chemical arts and crafts dealt with various commodities that could be isolated from natural bodies. Iatrochemistry (early modern medicinal chemistry) and metallurgy produced pure chemical substances that could each be distinguished and characterized by specific properties and chemical behaviours. Initially, such substances were thought of as artefacts, productions of the laboratory that did not exist in nature. However, Ursula Klein (1994) has explained that pure substances gradually came to be seen as the most important objects of chemistry, by which chemists indirectly studied nature.[13] When isolating and recombining these pure substances, chymists observed that

[12] On the philosophies of matter in Greek and Arabic alchemy, see Viano (2005). For a detailed overview of the historical development of the concept of element from Aristotle to Lavoisier see Hooijkaas (1933). The term 'chymistry' is often used to describe the early modern practice that was a mix of alchemy and chemistry, see Newman and Principe (1998).

[13] This notion of pure substance is still of central importance today. According to Joachim Schummer (2010, sec. 2) the choice of pure substances as the object of chemistry is chemists' method to adjust the material world to their conceptual needs. As Van Brakel (2008, 157) points out, the distinction between pure substances and mixtures always relies on some pragmatic definition depending on what one wants to do with the substance.

there were regularities and perhaps even laws governing their combinations because certain substances always tended to combine with certain others in the same ways. They interpreted these regularities in terms of chemical affinity, a kind of attraction between substances that caused them to specifically combine with certain others. The idea of pure substances combining and recombining according to regular patterns was key in the emergence of the notion of chemical compound.

Klein has identified the establishment of the concept of compound with the publication of the "Table des différents rapports observés en chimie entre différentes substances" by Etienne François Geoffroy (1672-1731) in 1718. Geoffroy's table consisted of sixteen columns, each headed by a different substance, followed by the substances with which it combined in order of decreasing affinity such that a substance would displace any other that was listed below it. Geoffroy's table visually represented the regularities in the (re)combination of pure chemical substances, mostly the components of salts and various metals. According to Klein, the most significant feature of Geoffroy's concept as distinct from the views of his Paracelsian predecessors was the idea of stable components that remained unchanged throughout the reversible operations of composition and decomposition. The reversibility of the operations that chemists carried out gave them reason to think that the components of substances were preserved, and that chemical transformations were nothing more than the rearrangements of components that retained their chemical identity. On the other hand, the fact that such stable components were held together by forces of mutual affinity set the chemical compound apart from mere juxtapositions and mixtures.

Hasok Chang (2011a; 2012b) has interpreted the idea of chemical compound as part of a system of practice he calls 'compositionism'.[14] In his view, the most important epistemic activities of compositionist chemistry were the composition and decomposition of compounds and the identification and tracking of components through these operations. Chang (2012b, 35–42) opposed compositionism to another system of practice he has called 'principlism' based on the fact that each of these systems incorporate a different

[14] In Chang's terminology, a 'system of practice' corresponds to a set of epistemic (knowledge-related) activities that function together coherently towards the achievement of a number of aims. See Chang (2022, chap. 1).

"metaphysical doctrine about the fundamental ontology of substances" (Chang 2012b, 37). In the case of principlism, this ontology is hierarchical because some substances are passive and others active: the latter can act upon the former and modify their properties. Compositionism on the other hand can be characterized by a flat ontology because all substances are material bodies that can be handled in the laboratory, they are all placed on the same level.[15] Besides their ontology, Chang has also distinguished between the two systems on the basis of their epistemic activities. Instead of (de)composition, principlism was occupied with transformation, using principles to impart properties to other substances; it could also explain the properties of chemical substances by the presence of such principles.

Certain aspects of compositionism were already present in early modern alchemy and chymistry, such as the use of reversible reactions to show the stability of corpuscles in compounds. Seventeenth- and eighteenth-century chemistry built on these experimental observations but it gradually excluded explanations that relied on any spiritual entities. Fors (2015) has linked this to a shift in focus from transmutation towards useful manufacturing, which required only the existence of substances that could be manipulated. Eighteenth century chemists limited themselves to explanations that referred only to substances that can be handled in the laboratory. Klein and Lefèvre (2007, 37) call this 'the chemical approach': instead of (partially) relying on philosophical ideas, this approach explains chemical composition *purely* as the rearrangement of stable chemical building blocks. This focus on the ways in which components could be separated and recombined was characteristic of the practices of salt chemistry and affinity tables.

## Composition and analogy in affinity tables and salt chemistry

The view of chemical composition that was central to Lavoisier's chemistry originated within the combined tradition of salt chemistry and the study of affinity tables. Besides the distinction into different levels of composition, another important aspect that emerged in these practices was the distinction between different types of substances within each level of composition.

[15] The term 'flat ontology' was coined by Klein (2015), who agreed with this aspect of Chang's analysis.

Salt chemistry gained in importance in the early eighteenth century in France. Around 1700, chemists started to increasingly focus on reversible reactions involving salt formation, acids, alkalis, earths, metals and their alloys. They noticed that similar patterns of chemical transformation happened under normal circumstances, forming reversible cycles of composition and decomposition: for example, it was possible to produce an acid from a salt and combine it with a so-called 'salifiable base' to restore the salt. This type of reversible reactions gave chemists the idea that salts were composed of stable components that were present within them even when their properties could not be observed. The first generalization of this view can be found in a classification of salts published by Wilhelm Homberg (1652-1715) in 1702 (F. L. Holmes 1989, chap. 2). Besides the traditional simple salts, he introduced there a new kind of 'middle' salt, which was composed of an acid and alkali.[16]

It was this practice which produced the results ordered in Geoffroy's table. Geoffroy's table provided a useful overview of the patterns according to which the components of salts (as well as some other pure substances) combined. Over the course of the eighteenth century, many other tables like that of Geoffroy were published.[17] They were all initially inspired by Geoffroy's table, but a distinct tradition emerged thanks to significant modifications by Gellert and Torbern Bergman. The latter practice was more focused on metallurgy whereas the followers of Geoffroy in France were more concerned with theoretical and methodological questions. In both cases, improvements were made either by expanding the tables through the inclusion of more substances or by simplifying them. Later in the century it was sometimes also considered that affinity depended at least in part on the circumstances of the reaction. The practice of making affinity tables did not last into the nineteenth century, but the accompanying characterization of chemical substances did.

Affinity tables served chemists in their needs of establishing orderly patterns in the results of various reactions. This was generally done purely as a classification of empirical

[16] Homberg was living in Paris where he was one of the most productive chemists in terms of publications in the newly founded *Mémoires de l'Académie Royale des Sciences*. On Homberg's work at the Académie, where chemistry was included from 1666, see Principe (2020).

[17] On the history of affinity tables, see Duncan (1996) and Kim (2003). Duncan provides a list of all tables that were published (1996, 112-4) as well as a genealogy (*ibid*., 153-6).

results and distinct from any reflection regarding the forces and mechanisms that explained affinity itself. The main purposes of the tables were to help students memorize the numerous facts of chemistry, to help predict the outcome of reactions (although this did not always work). In some cases, chemists hoped to use the tables to establish some universal pattern of affinity, ideally according to a Newtonian law of attraction (Duncan 1996, 156–59). There were various Newtonian interpretations, generally revolving around the idea that affinity consisted in forces of attraction and repulsion among particles. The consensus around 1730 in Britain, which arrived a generation later in France, was that these powers were intrinsic properties of the particles. For example, Guyton de Morveau and Macquer interpreted affinity as a force they likened to gravity (*ibid*., chap. 3). In some cases, chemists also attempted to quantify affinity (*ibid*., chap. 5). However, the general attitude was one of cautious empiricism, taking affinity simply as a tendency to combine according to a certain pattern.

The transformations that were visually represented in affinity tables required the distinction between simple (or relatively simple) substances and compounds, the latter being represented as composed of the former. According to Duncan (1996), the affinity tables gradually established an implicit notion of simple substance because they ordered substances according to their level of composition.[18] This notion was implicit, because (relatively) simple substances that headed the columns of the affinity tables were completely distinct from the views of composition that chemists provided in their introductory textbooks; only the former had practical utility in the laboratory. This was a view of composition centred on the possibility of producing substances in the laboratory or workshop, not on any deeper theories of matter. The simplicity of these components was only relative, depending on the kinds of operations that were possible rather than a question of the ultimate composition of compounds.

In other words, although affinity tables implied a distinction between different levels of composition, their ontology was flat. The relatively simple building blocks were

[18] Classifying substances according to their level of composition may seem completely intuitive today but is only one choice among many, as Ursula Klein and Wolfgang Lefèvre (2007, 109) have noted: one might instead classify substances according to their origins, applications or perceptible properties such as taste, smell or colour, as was the case in various domains of chemistry well into the eighteenth century.

chemical substances, ontologically not different from the compounds since all of these substances were also chemical commodities (Klein and Lefèvre 2007). For example, vitriolic acid was one of the simple building blocks even though most chemists of the middle of the eighteenth century agreed that it was not a true element. They deliberately left the question of elementarity open and only focused on the economically useful fact that substances such as vitriolic acid could be produced from compounds and used again to reproduce compounds. As components, the simple substances were very different from the ultimate elements/principles in two crucial ways: principles were only recognizable indirectly through the properties of the mixt in which they entered, and principles could not be isolated as distinct chemical substances (*ibid*., 123). Components and compounds had exactly the same status as they were both observable substances that could be handled in the laboratory. Principles/elements and mixts however were not part of such a flat ontology and could not be classed according to chemical composition.

The separation according to level of composition was not the only organization of substances in affinity tables. In addition, within each level of composition, substances were ordered according to their properties and the idea of certain types of classes of substances started to emerge. Klein and Lefèvre have identified implicit groupings of acids, earths, alkalis and metals in the sequence of the columns of Geoffroy's table (Klein and Lefèvre 2007, chap. 9.1). The salifiable bases were all arranged together and separated from the acids (representing the fact that the acids react with the bases). In Bergman's table, Duncan (1996, 166) has identified five classes: acids (both organic and mineral, including carbonic acid); salifiable bases (alkalis and earths); water and air; a miscellaneous group (phlogiston, sulphur, liver of Sulphur, spirit of wine and oil); and metals. Throughout the century, much of these groupings remained stable, but their members increased in number as new earths, airs, salts, acids and alkalis continued to be identified. Nevertheless, these groupings remained mostly implicit arrangements, unlike classifications in which classes were explicitly separated from one another.

The link between the implicit groupings of affinity tables and the practice of salt chemistry is quite clear. Crucially, Klein and Lefèvre (2007, 128) have pointed out that many of these groups were primarily characterized as "potential components of compounds" because they were identified and classified by the way they reacted with other

constituents. The clearest example is the group of alkalis, which was defined by the fact that they neutralized acids, often with the production of effervescence. Together with the earths, they formed the larger class of salifiable substances on the basis of their shared tendency to combine with acids in order to form neutral salts (see Klein and Lefèvre 2007 chap. 9.2 for the history of each of these types of substance).

Thus already during the middle of the eighteenth century, chemical classification happened not only on the basis of composition but also on the basis of patterns of similarities in chemical behaviour. Without pointing out the significance of this change, Duncan (1996, passim) describes a shift in view of chemical similarities resulting from the use of affinity tables. Whereas at the beginning of the century, substances were classed together according to similarities in 'essence' (mainly linked to the principles they contained), components increasingly came to be characterized according to similarities in the way they combined with other components. This identification by 'chemical properties' or 'chemical behaviour' in terms of tendencies to combine remained crucial to the identification of simple substances for much of the nineteenth century, as I will argue in later chapters of this thesis.

## From phlogiston to oxygen: the chemical revolution

During the last decades of the eighteenth century, Lavoisier and his colleagues proposed a general reform of chemical theory. This transformation has been treated from various angles by historians, but one of the key aspects is generally accepted to be the overthrow of the idea of phlogiston and its replacement by an oxygen-centred theory, with an accompanying new view of chemical composition (see also Siegfried and Dobbs 1968). Lavoisier's new system of chemistry was often characterized as 'antiphlogistic' because it attacked older theories that relied on the principle phlogiston to explain various chemical transformations (F. L. Holmes 1989, 45–49; Brock 1992, 78–84).

During the first decades of the eighteenth century, the Bavarian chemist Georg Ernst Stahl (1659-1734) first developed the idea of phlogiston as an adaptation of a theory by Johann Joachim Becher (1635-1682). Stahl explained the properties of substances on the basis of a small number of principles, of which phlogiston was one. For instance, the shine of metals could be explained by the phlogiston they contained. Stahl's theory was especially fruitful because it could explain so many different types of chemical

reactions using a single coherent system. He established an analogy between the processes of combustion and calcination, which he both saw as emissions of phlogiston. This enabled him to explain, for example, why combustion stopped at a certain moment: either the air was saturated with phlogiston, or all the phlogiston had been eliminated from the combustible body. Phlogiston could also explain acidity and alkalinity, as well as various processes in plant chemistry.

Various European chemists adopted Stahl's ideas. In France, Stahl's ideas were mostly transmitted through the open-air lectures of Guillaume François Rouelle (1703-1770) at the *jardin du roi* in Paris (Bensaude-Vincent and Stengers 1992, 82–85; Lehman 2011). Rouelle slightly modified Stahl's ideas and viewed the four elements both as instruments and as constituents. For example, fire was the chemists' main instrument in procedures such as fire analysis, and phlogiston was the constituent associated to this element in Rouelle's theory. In other words, phlogiston could be seen as fire that was contained in certain bodies and endowed them with properties such as shininess or elasticity.

Meanwhile, chemical practice during the eighteenth century did not only consist of theoretical explanations of matter and its transformations, since these theories were also closely linked to experimental and industrial endeavours. By the middle of the century, chemistry had grown into a very successful 'investigative enterprise' and the number of chemical substances and operations known continued to grow (F. L. Holmes 1989). While Stahl's chemistry circulated in France, the practice of salt chemistry spread from France to the German lands and together with the investigations of metallurgy this enabled the identification of various types of 'earthy' substances. In other words, it gradually became clear to chemists that there was not just one element Earth, but multiple types of chemically distinct earths.

In parallel, the development of pneumatic chemistry in Great Britain enabled the identification of various types of air (Brock 1992, 96–111). In 1727, Stephen Hales (1677-1761) developed a method to capture the vapours produced by chemical reactions using his pneumatic trough, which made it possible to study them. Although Hales still saw air as a single element, further works using modified versions of his instrument led to the identification of multiple chemically distinct airs. Henry Cavendish (1731-1810), Joseph Priestley (1733-1804), Joseph Black (1728-1799) and

others continued to work with Hales' apparatus and developed it into a way for studying the fixation and release of airs from solids. In 1756, Black distinguished the 'fixed air' (carbon dioxide) released by carbonates from atmospheric air, because it turned lime water milky and nothing could burn in it. Similarly, Cavendish produced inflammable air (hydrogen) by reacting together sulphuric acid and iron. Priestley was the most productive pneumatic chemist: he identified around twenty new airs during the last three decades of the eighteenth century (on the work of Priestley, see also Golinski 1992; Chang 2012b).

Thus, when Lavosier started his work on pneumatic chemistry in the early 1770s, it was already known that there were multiple types of air, and that atmospheric air was possibly a mixture or a compound. In 1773, Lavoisier published the observation that the reduction of metals produced air, whereas sulphur and phosphorus gained in weight when burned. The fact that substances (sometimes) gained in weight when burned had already been known, but was not really seen as significant by chemists that adhered to Stahl and Rouell's ideas. For Lavoisier, however, it was significant: he saw these results as an indication that some type of air might be involved in the phenomena of combustion and calcination, and he declared that this finding would cause a 'revolution' in chemistry.

When it came to identifying which portion of the air might be important for calcination, Lavoisier's attention was initially drawn to fixed air because the reduction of various metals produced this substance. However, in 1774 he was made aware that when mercury calx (HgO) was heated, it reduced without the presence of charcoal (which had been thought until then to provide the necessary phlogiston for the reduction of metals) and produced so-called dephlogisticated or vital air.[19] During the next few years, Lavoisier's interpretation continued to shift, involving some constituent of air, 'pure' air, and sometimes phlogiston (see F. L. Holmes 1988). By 1777, Lavoisier generalized from these different partial explanations and concluded that the phenomena of combustion, calcination and respiration all proceeded in the same way.

During this time, Lavoisier was also working on the question of acidity (Crosland 1973). The fact that fixed air and various of the other recently discovered airs were acidic

[19] Priestley and Scheele had already been working on this reaction and were studying dephlogisticated/vital air – the substance that would later come to be known as oxygen. The discovery of oxygen is a well-known case of multiple discovery, see for example Kuhn (1962), Schaffer (1986) or Partington (1962b).

had already pointed towards a link between air and acidity, and Lavoisier starting investigating this in the early 1770s. In his 1773 paper he had already noted that phosphorous became acidic after combination with air, and he suggested that all acidification might proceed in this way. By 1776, Lavoisier had realized that his 'pure air' might play a role in causing acidity, and he became certain of it in 1779: he therefore named this new air "oxygen", which in Greek means 'acid generator'. The acids he analysed (nitric, sulphuric, phosphoric, carbonic) all contained oxygen and he therefore suggested that all acids contained this 'principle of acidity' combined with a different base. He was also able to explain the fact that higher oxides of metals were often acidic by correlating the acidity of a substance to the amount of oxygen it contained.

By the end of the 1770s, Lavoisier had therefore formulated a theory that explained combustion, calcination, respiration and acidity as a combination with oxygen. Lavoisier's new chemistry was incompatible not only with phlogiston but with all of the four elements. Multiple earths and airs had already been known, and Lavoisier argued that fire was a process rather than a substance. Lastly, he argued that water was a compound rather than a simple element. Priestley and Cavendish had already been aware that inflammable air (hydrogen) produced water when it was sparked in air. In February 1785, Lavoisier performed large scale experiments in front of academicians during which he decomposed and recomposed water and measured its composition (see Golinski 1994 on this experiment and the role of instruments in demonstrating the new chemistry). Multiple interpretations of this observation were possible, but for Lavoisier this consisted in proof that water was composed of oxygen and hydrogen (see Chang 2012 chap. 1). This demonstration convinced many of his contemporaries.

In 1785, Lavoisier considered he had gathered enough evidence and launched his explicit attacks on the notion of phlogiston (Brock 1992, 111–24). He did this together with a group of colleagues that could be seen as the ancestor to nineteenth-century research schools (Crosland 2003). His large-scale experiments had convinced Claude-Louis Berthollet (1748-1822) (see Grand 1975), who was soon followed by Antoine François Fourcroy (1755-1809) and other academicians. In 1786-7, the Dijon chemist Louis Bernard Guyton de Morveau (1737-1816) came to Paris where he also became convinced of Lavoisier's new chemistry. Marie-Anne Paulze (Madame de

Lavoisier; 1758-1836) was also an important part of the research group that started to form around Lavoisier: she helped in the laboratory, drew the illustrations of experimental setups, and provided translations of foreign works (Kawashima 2013).[20] In 1789, Lavoisier and his colleagues moreover founded the *Annales de Chimie* as a journal in which they could publish their new ideas (see Crosland 1994). Besides this journal, an important avenue for the diffusion of the new chemistry was the publication of textbooks (see Bensaude-Vincent 1990a). In 1789, Lavoisier published his own *Traité élémentaire de chimie*. In it Lavoisier exposed many of his discoveries (and those of his colleagues) and introduced his readers to the new system of chemistry.

## The lasting influence of salt and affinity chemistry in Lavoisian chemistry

Lavoisier's oxygen theory implied a new view of the composition of various substances: metals became simple (whereas they had previously been thought of as compounds of phlogiston) and acids (which had previously been seen as simple) became compounds of oxygen. Klein and Lefèvre (2007, 185) have shown that this was a symmetrical change within a classificatory structure that otherwise remained stable: Lavoisier's new classification of substances inversed the view of the composition of two pairs of classes of substances (acids and metals calces became compounds, whereas salifiable bases and metals became simple) but it did not affect the structure of chemical classifications itself. The new chemistry adopted a fundamental ontology of chemical composition that was already present in phlogistic chemistry.

The 'conversion' of Guyton de Morveau to the new chemistry was especially important for the influence of salt chemistry on the Lavoisian view of composition. In 1782, de Morveau had proposed to reform the nomenclature of salts. During the seventeenth and most of the eighteenth century, substances were often named after their properties or origin but there was no systematic approach. De Morveau's nomenclature provided a more systematic approach: he proposed to name salts in a way that reflected their composition,

[20] Madame de Lavoisier's translation of two pamphlets written by Richard Kirwan (1733-1812) especially contributed to the acceptance of oxygen over phlogiston by the European chemical community, as they included arguments in favour of the oxygen theory (Bret and Kawashima 2019).

by naming them after the acids and bases used to produce them. Because this was a mostly empirical nomenclature that was not based on any deeper theoretical conception of composition, de Morveau could directly integrate his system with Lavoisier's chemistry. In 1787, de Morveau, Berthollet, Lavoisier and Fourcroy defended such an integrated nomenclature in the *Méthode de nomenclature chimique* that promoted a complete restructuration of chemical language around Lavoisier's ideas (see Crosland 1962, pt. 3).

De Morveau's classificatory ambitions were influences by the work of Torbern Bergman (1735-1784)., the most productive author of affinity tables. Via the works of Bergman, the binomial nomenclature of salts was indirectly inspired by Linnaeus' *Species Plantarum* which introduced a binomial nomenclature of plants in 1753 (Crosland 2009). Moreover, the idea of classifying bodies in terms of their level of composition was anticipated in the works of Bergman and his mineralogist colleagues (see Oldroyd 1975; T. M. Porter 1981; Fors 2014). During the middle of the eighteenth century, this community adopted a mineral classification on the basis of chemical composition, which required the identification of multiple levels of composition and the presence of constituents within compounds. The idea of simple substance was implicit in this practice. It is possible that Lavoisier inherited the term 'simple body' ("corps simple") from Guyton de Morveau who used it in 1777:

> "By simple bodies here must be understood only the last products of the decompositions which nature operates under our eyes, & this explanation prevents any difficulty. Whether or not the elements are themselves of a single matter differently modified, it is still true to say that what we here call simple bodies are very surely compounds, & even in an order already more or less advanced; but they are for us the units of chymical decomposition, & in this sense, acids, alkalis, earths, [and] phlogiston, will obviously be simple bodies, until we have succeeded in changing their essential characters, otherwise than by a new combination, that is to say, by taking away rather than adding to them" (Guyton de Morveau 1777b).[21]

[21] "Il ne faut entendre ici par corps simples que les derniers produits des décompositions que la nature opère sous nos yeux, & cette explication prévient toute difficulté. Que les élémens soient eux-mêmes ou non d'une seule matière différemment modifiée, toujours est-il vrai de dire que ce que nous nommons ici corps simples, sont très-sûrement des composés, & même dans un ordre déjà plus ou moins avancé ; mais ils sont pour nous

Lavoisier definition of chemical elements used a very similar phrasing to De Morveau's characterization of simple bodies.

Besides this distinction of multiple levels of composition, the different types classes of substances that appear in the Lavoisian classifications can also in part be explained by the influence of salt and affinity chemistry via De Morveau. Klein and Lefèvre (2007, chap. 7.2, 8 and 9) have shown how the classification of substances from the *Méthode* was structured around the ideas of neutral salts, different types of air and alloys. By the end of the eighteenth century, these groups of substances were well established. The operations linked to these groups of substances were of three types: the decomposition and composition of salts in solution, the calcination and reduction of metals and the combination of metals into alloys (see also *ibid*., chap. 6.1). Despite its seemingly revolutionary character, the classification of substances in the *Méthode de Nomenclature* therefore reflected the main fields of chemical inquiry and their development during the eighteenth century.

Likewise, the "tableau des substances simples" in Lavoisier's *Traité* (Lavoisier 1789, 192) classed the simple substances into separate groups that were clearly influenced by salt chemistry (see Figure 1). These groups consisted of substances that shared the same tendencies to combine, more specifically the same tendencies to form acids or bases which can then combine to form salts. The pre-existing groups of salifiable earths and metals also appear. Siegfried (1982) has argued that this structure of Lavoisier's table can be explained by the association between de Morveau's system of salt chemistry and Lavoisier's oxygen theory.[22] This association explains why groups such as earths and salifiable bases remained important in chemistry even after Lavoisier's restructuring of chemical theory.

l'unité de la décomposition chymique, & dans ce sens, les acides, les alkalis, les terres, le phlogistique, seront évidemment des corps simples, jusqu'à ce qu'on soit parvenu à changer leurs caractères essentiels, autrement que par une nouvelle combinaison, c'est-à-dire, en leur ôtant plutôt qu'en leur ajoutant."

[22] On the influence of affinity tables on the structure of Lavoisier's table of simple substance, see also Duncan (1970).

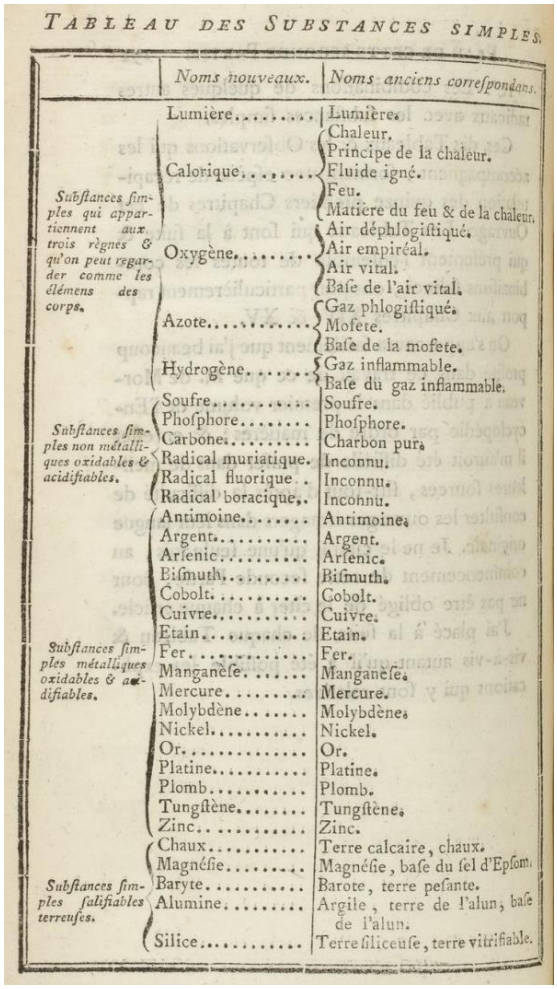


TABLEAU DES SUBSTANCES SIMPLES.

| | Noms nouveaux. | Noms anciens correſpondans. |
|---|---|---|
| Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps. | Lumière | Lumière. |
| | Calorique | Chaleur.<br>Principe de la chaleur.<br>Fluide igné. |
| | Oxygène | Feu.<br>Matière du feu & de la chaleur.<br>Air déphlogiſtiqué.<br>Air empiréal.<br>Air vital.<br>Baſe de l'air vital. |
| | Azote | Gaz phlogiſtiqué.<br>Mofete.<br>Baſe de la mofete. |
| | Hydrogène | Gaz inflammable.<br>Baſe du gaz inflammable. |
| Subſtances ſimples non métalliques oxidables & acidifiables. | Soufre | Soufre. |
| | Phoſphore | Phoſphore. |
| | Carbone | Charbon pur. |
| | Radical muriatique | Inconnu. |
| | Radical fluorique | Inconnu. |
| | Radical boracique | Inconnu. |
| Subſtances ſimples métalliques oxidables & acidifiables. | Antimoine | Antimoine. |
| | Argent | Argent. |
| | Arſenic | Arſenic. |
| | Biſmuth | Biſmuth. |
| | Cobolt | Cobolt. |
| | Cuivre | Cuivre. |
| | Etain | Etain. |
| | Fer | Fer. |
| | Manganèſe | Manganèſe. |
| | Mercure | Mercure. |
| | Molybdène | Molybdène. |
| | Nickel | Nickel. |
| | Or | Or. |
| | Platine | Platine. |
| | Plomb | Plomb. |
| | Tungſtène | Tungſtène. |
| | Zinc | Zinc. |
| Subſtances ſimples ſalifiables terreuſes. | Chaux | Terre calcaire, chaux. |
| | Magnéſie | Magnéſie, baſe du ſel d'Epſom. |
| | Baryte | Barote, terre peſante. |
| | Alumine | Argile, terre de l'alun, baſe de l'alun. |
| | Silice | Terre ſiliceuſe, terre vitrifiable. |

*FIGURE 1 - The table of simple substances (from Lavoisier 1789, 192). Source: Bibliothèque nationale de France.*

## Lavoisier's characterization of chemical elements

Although he was not the first to define chemical elements on the basis of the impossibility to decompose them, Lavoiser was the first to effectively establish a list of simple bodies that should be seen as the constituents of all other chemical substances. In this section, I will describe Lavoisier's theoretical characterization of elements and compare it to his actual list of chemical elements. I will argue that in practice, Lavoisier distinguished between indecomposable substances, chemical elements and absolute elements. These distinctions were reactions to the logical insufficiencies of his definition,

rather than to influences from his predecessors. Since the negative-empirical criterion could not suffice to show which substances were simple, he relied on analogical inferences and metaphysical speculations to complement the results of decomposition experiments.

## Lavoisier's definition of the chemical element

Lavoisier's definition of the chemical element can be found in his introduction to the *Traité Elémentaire de Chimie* (1789). He opened his section on the chemical elements by criticizing the classical notion of element:

> "All that can be said upon the number and nature of elements is, in my opinion, confined to discussions entirely of a metaphysical nature. The subject only furnishes us with indefinite problems, which may be solved in a thousand different ways, not one of which, in all probabilities, is consistent with nature. I shall therefore only add upon this subject, that if, by the term elements, we mean to express those simple and indivisible atoms of which matter is composed, it is extremely probable we know nothing at all about them; (…)" (Lavoisier 1790, xxiv).[23]

He dismissed the question of the ultimate composition of matter as a metaphysical question, arguing that it was impossible to know the true elements as chemical experiments could never prove their existence.

Instead of speculating on questions that could not be answered, Lavoisier argued that chemists should concentrate on questions that could be studied in the laboratory. He therefore wanted to do away with the idea of absolute elements and focus instead on a more direct way of characterizing composition. The starting point for such a view of composition were the indecomposable chemical substances that chemists were used to manipulating:

[23] "Tout ce qu'on peut dire sur le nombre & sur la nature des élémens se borne suivant moi à des discussions purement métaphysiques: ce sont des problèmes indéterminés qu'on se propose de résoudre, qui sont susceptibles d'une infinité de solutions, mais dont il est très-probable qu'aucune en particulier n'est d'accord avec la nature. Je me contenterai donc de dire que si par le nom d'élémens, nous entendons désigner, les molécules simples & indivisibles qui composent, les corps, il est probable que nous ne les connoissons pas (…)" (Lavoisier 1789, xxij).

> "(…) if we apply the term elements, or principles of bodies, to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition. (*ibid*.)[24]

In other words, he proposed to replace the four elements (or any a priori fixed number of elements) with a list of substances that chemists were not able to decompose any further. For Lavoisier, the products of successive decompositions should thus be seen as the constituents of matter, even if it could not be known whether they were truly simple:

> "Not that we are entitled to affirm, that these substances we consider as simple may not be compounded of two, or even of a greater number of principles; but, since these principles cannot be separated, or rather since we have not hitherto discovered the means of separating them, they act with regard to us as simple substances, and we ought never to suppose them compounded until experiment and observation has proved them to be so" (Lavoisier 1790, xxiv).[25]

For Lavoisier, substances should provisionally be seen as simple as long as they could not be decomposed, even if there was no way to know whether they were truly simple or merely indecomposable using the available means. Lavoisier argued that this provisional identification should happened strictly on the basis of laboratory operations, and that these provisionally simple substances should be the admitted as the only constituents of matter. Such a list could only ever be provisional, because no amount of failed decompositions could guarantee that the simple substances could not be decomposed in the future. Nevertheless, Lavoisier proposed not to speculate on these questions: it was impossible to

[24] "(…) si au contraire nous attachons au nom d'élémens ou de principes des corps l'idée du dernier terme auquel parvient l'analyse, toutes les substances que nous n'avons encore pu décomposer par aucun moyen, font pour nous des élémens" (*ibid*.).

[25] "(…) non pas que nous puissions assurer que ces corps que nous regardons comme simples, ne soient pas eux-mêmes composés de deux ou même d'un plus grand nombre de principes; mais puisque ces principes ne se séparent jamais, ou plutôt puisque nous n'avons aucun moyen de les séparer, ils agissent à notre égard à la manière des corps simples, & nous ne devons les supposer composés qu'au moment où l'expérience & l'observation nous en auront fourni la preuve" (Lavoisier 1789, xvij–xviij).

know for sure where decomposition would one day end, and he advised against reflecting on questions that could not be answered.

Lavoisier's definition of the chemical element was central to his new theories of chemical composition, but many aspects of it were directly influenced by his colleagues. Likewise, various chemists had already defined the elements by their resistance to chemical decomposition, including Macquer for instance:[26]

> "But this analysis, & this decomposition of bodies is limited: we can only push it to a certain point, beyond which all our efforts are useless. In whichever way we proceed, we are always stopped by substances which we find unalterable, which we can no longer decompose, and which serve us as barriers beyond which we cannot go. It is to these substances that we must, I think, give the name of principles or elements, at least they are really so in relation to us; such are principally Earth and Water, to which we may add Air and Fire. For although there is reason to believe that these substances are not actually the primordial parts of matter, & the simplest elements; since experience has taught us that it is impossible for us to recognise by our senses of which principles they are themselves composed, I think it is more reasonable to leave it at that, and to consider them as simple bodies, homogeneous & principles of the others, than to strain ourselves to guess what parts or elements they may be composed of, having no means of assuring ourselves whether we have met with the right idea, or whether our ideas are only chimeras" (Macquer 1749, 2–3).[27]

[26] The definition of elements as indecomposable substances had been around long before Lavoisier's work (Davis 1931; according to Newman 2011, 318–20 the negative-empirical principle existed since the middle ages). Nevertheless, they generally differed from Lavoisier's ideas. It is sometimes thought that Robert Boyle provided similar reflections on the chemical elements, but he was rather providing a reflection on the explanatory function that elements held at the time. See Brocke (1992, 68–69) and Bensaude-Vincent and Stengers (1992, 49–53).

[27] "Mais cette analyse, & cette decomposition des corps est bornée : nous ne pouvons la pousser que jusqu'à un certain point, au-delà duquel tous nos efforts sont inutiles. De quelque manière que nous nous y prenions, nous sommes toujours arrêtés par des substances que nous trouvons inaltérables, que nous ne pouvons plus decomposer, & qui nous servent comme de barriers au-delà desquelles nous ne pouvons aller. C'est à ces substances que nous devons, je crois, donner le nom de principes ou d'élémens, au moins le sont-elles véritablement par rapport à nous ; telles sont principalement la Terre & l'Eau, auxquelles on peut ajouter l'Air & le Feu. Car quoiqu'il y ait lieu de croire que ces substances ne sont pas effectivement les parties

The difference between Lavoisier and his predecessors was therefore not the idea that chemical elements were indecomposable substances, but rather that his predecessors combined this view with the traditional four elements. In 1749, when Macquer's definition was published, water and earth were still effectively indecomposable substances. Nevertheless, Macquer continued to identify the four elements as simple bodies in the 1778 edition of his *Dictionnaire de Chimie* where he defined the elements both by their indecomposability and the fact that they were the constituents of compound bodies (Macquer 1778, 376). Likewise, in 1777, de Morveau distinguished between the "natural elements" (earth, fire, air, and water) and the "chemical elements", the latter of which were the simple bodies of chemistry.[28] Lavoisier, on the other hand, argued that there should be no elements beyond the simple substances. This list of simple substances became the foundation for his chemical system.

As Bernadette Bensaude-Vincent (1981, 48–56, 78–87) has explained, in Lavoisier's view of chemistry, the idea of the simple body became at once the ideal end point and starting point for chemistry: simple substances were both supposed to be the end product of series of decompositions and the foundation for chemical theories that were meant to proceed from simple to complex. This new order in Lavoisier's chemistry was centred on a vision of analysis inspired by the enlightenment philosopher Etienne Bonnot de Condillac (1714-1780). Lavoisier had read Condillac's *Logique* (1780) and was convinced by the link between language and thought that was highlighted in this work (see Bensaude-Vincent 2010). He relied on this idea to motivate both the reform in nomenclature and the publication of his own textbook: the perfection of chemistry could only happen through a perfection of its language. Likewise, Condillac had a specific vision

primordiales de la matière, & les élémens les plus simples ; comme l'expérience nous a appris qu'il nous est impossible de reconnoître par nos sens quels sont les principes dont elles sont elles-mêmes composées, je crois qu'il est plus raisonnable de nous en tenir là, & de les considerer comme des corps simples, homogènes & principes des autres, que de nous fatigue à devenir de quelles parties ou élémens elles peuvent être composes, n'ayant aucun moyen de nous assurer si nous avons rencontré juste, ou si nos idée ne sont que des chimères."

[28] "Il faut en dire autant de bien d'autres substances, qui, sans être, comme l'eau, des élémens naturels, sont néanmoins des corps simples pour la Chymie, & à qui nous donnerons en conséquence le nom d'Elémens Chymiques" (Guyton de Morveau 1777a, 11).

of learning as proceeding from the simplest to the more complex ideas. Accordingly, Lavoisier structured his textbook to proceed from the simple to the complex and from the known to the unknown.[29] For Lavoisier, the central goal of chemistry was analysis, by which he meant both the analytical way of thinking and the chemical procedure of decomposition.

## Principles, indecomposable substances and chemical elements

As stated above, Lavoisier's list of simple substances was by definition provisional. He repeated this view later in his *Traité*:

> "Thus, as chemistry advances towards perfection, by dividing and subdividing, it is impossible to say where it is to end; and these things we at present suppose simple may soon be found quite otherwise. All we dare venture to affirm of any substance is, that it must be considered as simple in the present state of our knowledge, and so far as chemical analysis has hitherto been able to show" (Lavoisier 1790, 177).[30]

Because of the impossibility to know whether a substance was truly simple, Lavoisier argued that any substance which behaved as simple should be provisionally seen as such. Accordingly, his list of simple substances was not meant as a list of absolutely simple substances, but only as substances that could not (yet) be decomposed: Lavoisier himself referred to it as a "table of simple substances, or at least those that the current state of our knowledge forces us to see as such" ("tableau des substances simples, ou du moins de celles que l'état actuel de nos conoissances nous oblige à considerer comme telles") (Lavoisier 1789, 193). This echoes the earlier remarks in which Lavoisier urges his readers to follow the results of decomposition attempts as closely as possible. Yet, looking at the

[29] At least, this is what he announced in the introduction: in reality, only the second part of the Traité proceeds along this order.

[30] "La chimie marche donc vers son but & vers la perfection, en divisant, subdivisant, & resubdivisant encore, & nous ignorons quel sera le terme de ses succès. Nous ne pouvons donc pas assurer que ce que nous regardons comme simple aujourd'hui le soit en effet : tout ce que nous pouvons dire, c'est que telle substance est le terme actuel auquel arrive l'analyse chimique, & qu'elle ne peut plus se subdiviser au-delà dans l'état actuel de nos connaissances" (Lavoisier 1789, 194).

actual contents of his list, it becomes clear that his table of simple substances contradicted these statements.

Lavoisier's first contradiction to his advice against speculation was his choice to include what appear to be principles in the first group of his table of simple substances (see Perrin 1973). The most important and most obvious principle in Lavoisier's chemistry was of course oxygen, the "acidifying principle common to all [acids]" (Lavoisier 1790, 176). Lavoisier's characterization of oxygen clearly echoed the ideas of his principlist predecessors, because oxygen was not just a component but also capable of conferring properties to the substances it entered into. Similarly, caloric could be seen as the principle of heat and expandability. According to Lavoisier's theory, all gases contained caloric: for example, oxygen gas was seen as a compound of oxygen and caloric, and when it combined with phosphorous, the gas was decomposed and the oxygen combined with the phosphorous to produce phosphoric acid, releasing free caloric (Lavoisier 1790, 52-53, 57). Neither caloric nor oxygen had been isolated in the form of a simple substance.

The interpretation of Lavoisier's first group as principles also provides us with an explanation for its title of "simple substances that belong to the three kingdoms and that can be seen as the elements of bodies" ("substances simples qui appartiennent aux trois règnes et qu'on peut regarder comme les élémens des corps*"*).[31] Henry Guerlac (1973, 82) has cited Lavoisier's explanation:

> "The principal justification is revealed in a note Lavoisier set down in 1792 where he writes: 'It is not enough for a substance to be simple, indivisible, or at least undecomposed for us to call it an element. It is also necessary for it to be abundantly distributed in nature and to enter as an essential and constituent principle in the composition of a great number of bodies.'"

This note implies that Lavoisier did not just use his terms in an ambiguous way: his designation of principles was based on a precise idea of a distinction between elements and simple substances. Besides being abundant in nature, his elements functioned as principles in conferring specific properties to compound substances.

[31] Siegfried has suggested that the first group of simple substances was just a miscellaneous class of "taxonomic garbage" or "leftovers" (Siegfried 1982, 37,44). However, its title suggests that it was more than that.

The distinction between true elements and simple substances contradicts Lavoisier's own definition of chemical elements. Despite his defence of the negative-empirical criterion, Lavoisier admitted elements that were identified using different crtieria. For Guerlac, this citation shows that Lavoisier could not completely let go of speculations regarding the constituent principles of bodies. According to this interpretation of the exceptions to his own rules as a mere remnant of older chemistry, Lavoisier's violations of his own rules could be seen as independent from his view of the elements. Eric Scerri (2006), for example, has insisted that Lavoisier intended to rid chemistry of all metaphysical speculations regarding the elements even if he did not do so effectively himself. For Scerri, Lavoisier's characterization of chemical elements should therefore be seen as purely empirical despite these exceptions. However, even if one were to accept this idea, I argue that there was a second kind of distinction implicit in Lavoisier's table of simple substances that also complicates any qualification of his view of elements as purely empirical. Lavoisier did not only distinguish between true elements and chemical elements in admitting his first group: he also distinguished between chemical elements and indecomposable substances.

Indeed, Lavoisier included chemical elements that had never been isolated as simple substances and omitted others even though they had not been decomposed. Despite the impossibility to decompose them, Lavoisier omitted the fixed alkalis, potash and soda, from his list of simple substances. In 1785, Berthollet (1785) had shown that ammonia was composed of nitrogen and hydrogen, and Lavoisier could thus infer by analogy that all alkalis were similarly composed. He explained that, although it was impossible to be certain what the constituents of the alkalis would be, "analogy leads us to suspect that azote [nitrogen] is a constituent element of all the alkalies, as is the case with ammoniac" (Lavoisier 1790, 156). The analogical inference justifying the omission of the alkalis could be summarized as follows: ammonia had alkaline properties and it had been shown to be a compound of nitrogen; the other alkalis had similar properties and it was therefore likely that they were similarly composed.

This means that Lavoisier did not just rely on metaphysical speculations regarding true elementary nature; he also used analogical inferences to distinguish between chemical elements and indecomposable substances. The alkalis were not the only substance that he

reasoned on in this way: he also did not see the indecomposable mineral acids as chemical elements. Since all acids he decomposed consisted of some sort of radical and oxygen, it was likely that all others acids had a similar composition and that radicals would be found in each of them.[32] He therefore predicted their composition on the basis of analogy and included the mineral acid radicals in his table despite the fact that they had never been isolated in the form of a simple substance.[33]

Therefore, I argue that Lavoisier's exceptions to his own definition of chemical elements were more than just leftovers from earlier chemistry. Moreover, he had good reasons to make these exceptions because it was in fact quite a pragmatic choice to omit certain indecomposable substances on the basis of analogical inferences. After all, Lavoisier was very aware of the limitations of identifying composition in a purely negative way: any currently indecomposable substance might very well be decomposed in the near future. It therefore made a lot of sense to adjust the results of decomposition attempts to include how they were likely to evolve. In other words, Lavoisier relied on analogical inferences to complete the identification of elementary nature because his definition alone could not suffice.

## Procedural and metaphysical difficulties following from Lavoisier's definition

Lavoisier's definition of the element led to uncertainty regarding the simplicity of the substances identified as elementary. Siegfried and Dobbs (1968, 292) identify two main difficulties resulting from the adoption of the definition of the element as a simple

[32] Hricko (2021) has described the successful prediction of boron as a radical of boracic acid as a problem for scientific realism because it relied on Lavoisier's theory of acidity, which was later proven to be false. I would instead argue that it shows the success of using chemical analogies: even when theories (of acidity) are proven false, the analogies that they are based on still remain. On the use of analogy in the formulation of Lavoisier's view of acidity see also Fisher (2018).

[33] It might seem surprising that Lavoisier listed no radicals of the alkalis in his table. However, Perrin (1973) has explained Lavoisier did not expect the alkalis to contain unknown radicals, because he suspected they were azurets (composed of nitrogen, hydrogen and caloric in various proportions).

substance: "metaphysical, what are the true elements and how many of them are there" and "procedural, how does one determine which of two chemically related bodies is simpler?"[34]

In the existing literature on this topic, the metaphysical difficulties have received most attention (see for example Farrar 1965; Brock 1985). The Lavoisian definition necessarily led to uncertainty, because no amount of failed decompositions could prove that no future means of decomposition might decompose the substance in question. Lavoisier had anticipated this difficulty and tried to solve it by arguing against any speculation, and his followers likewise insisted on the conditional nature of the list of simple bodies (for examples see Siegfried and Dobbs 1968, 283). This provisional identification caused a lot of metaphysical discomfort, and the lack of guarantee that substances were really simple left room for speculation regarding their true nature and internal composition.

When it comes to procedural differences, one key issue that has been pointed out is the circularity of Lavoisier's definition. Chang (2007, 13) has provided some examples of cases in which it was not straight-forward to identify which bodies where simple and which were composed. For instance, whereas phlogistonists argued that sulphuric acid and phlogiston combined to form sulphur, Lavoisier and his followers argued that sulphur was a simple substance and sulphuric acid a compound of sulphur and oxygen. Likewise, Lavoisians saw metals as simple whereas phlogistonists argued they were able to decompose them into phlogiston and calxes (which Lavoisians called oxides). The negative-empirical criterion could not solve these debates. In other words, the circularity of Lavoisier's definition was due to the fact that simple substances were defined as resulting from decompositions, and decompositions in turn were defined as the breaking down into simpler substances. Some additional criteria for distinguishing between decompositions and combinations were therefore necessary. In the words of Robin Hendry, the identification of a certain chemical transformation as a decomposition required "the skilful application of a web of compositional hypotheses" (Hendry 2005, 37).

In my discussion of the exceptions that Lavoisier made to his own definition, I have likewise distinguished between metaphysical speculations and analogical inferences,

[34] Following Bensaude-Vincent (1981, chap. 3), we might add linguistic difficulties: are 'simple substance' and 'element' really synonyms? Some followers of Lavoisier continued to use the terms 'elements' and 'principles' in addition to 'simple bodies', often without clearly distinguishing between these notions.

which I argue were Lavoisier's responses to the metaphysical and procedural difficulties of his own definition, respectively. These difficulties provide additional reasons why some care is needed in characterizing Lavoisier's view of elements as purely empirical or operational, as is often done (for example Brock 1992, 119; Siegfried 2002; Scerri 2006; Bensaude-Vincent 1981). While his identification of chemical elements relied on experimental results, it was not strictly operational in the sense that other considerations also played a role. Likewise, even provisional simplicity could not be established purely on the basis of chemical transformations, because additional knowledge of composition was required in order to interpret the results of those transformations.

# Weighing and chemical atomism

In order to identify which substances were elementary, chemists working in Lavoisier's system needed additional information regarding the composition of substances. It may seem as though weight measurements could provide the way out of this circularity: using Lavoisier's law of the conservation of matter in combination with weight tracking as a way to measure the quantity of matter, some operations could be identified as decompositions or combinations. Some historians have suggested that this may have provided a way to make the negative-empirical criterion work in practice (see for example Rocke 1984, 5–6). But did weight measurements really solve the difficulties resulting from Lavoisier's definition? What about the resulting acceptance of chemical atomism? This section will evaluate to what extent the tracking of composition by weight measurement provided a way out of the procedural and metaphysical difficulties surrounding the definition of the element as a simple substance.

## Weighing as a way to track composition

Lavoisier's long-lasting contributions to chemistry lay not only in his results or theories but also in his methods - specifically, in his systematic use of the balance (see Levere 1992; Bensaude-Vincent 1993, chap. 8). In his *Traité*, Lavoisier formulated the law of conservation of weight:

> "We may lay it down as an incontestible axiom, that, in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment; the quality and quantity of the elements remain precisely the same; and nothing takes place beyond changes and modifications in the combination of these elements" (Lavoisier 1790, 130–31).[35]

The idea of the conservation of weight enabled the use of the balance as a tool to track composition: if a substance became heavier, the reaction was a combination, and if the substance became lighter after a reaction, it had been decomposed. This presupposed not only the conservation of matter, but also the idea that weight was an indicator of the quantity of matter. Once these two hypotheses were accepted, weight could be used to identify reactions as either decompositions or combinations.

Hasok Chang (2011a; 2012b, 35–37) has highlighted how the importance of weighing may have led to the victory of Lavoisier's antiphlogistic system. For example, Lavoisier's interpretation of the decomposition and recomposition of water could only be seen as superior to that of the phlogistionists if one accepted his premises regarding the conservation of weight. Cavendish and Priestley saw the same reaction as the production of 'phlogisticated water' (hydrogen) and 'dephlogisticated water' (oxygen). This interpretation perfectly explains why the combination of the two products would reproduce water – however, it does not account for phlogisticated water being so much lighter than water itself. If weight is seen as an indicator of composition, the existence of a compound that is lighter than one of its constituents is an issue. For compositionists, Lavoisier's interpretation of the phenomena was therefore better.

This is one example of the additional compositional hypotheses needed for the identification of simple substances. The cases discussed in the following chapters of this thesis will illustrate that the use of weighing was often insufficient to identify composition because many experiments could still be interpreted in different ways that were coherent with the conservation of weight (see especially chapters two and three). For now, I will

[35] "(…) car rien ne se crée, ni dans les opérations de l'art, ni dans celles de la nature, et l'on peut poser en principe que, dans toute opération, il y a une égale quantité de matière avant et après l'opération : que la qualité et la quantité de principes est la même, et qu'il n'y a que des changements, des modifications." (Lavoisier 1789, 140–41).

first discuss another reason why this focus on weight was important. Besides providing a way to identify (in some cases) operations as decompositions, it led to the identification of quantitative regularities in the combinations of substances.

## Chemical atomism

The late eighteenth-century interest in weighing was also of crucial importance in the early history of chemical atomism. The interest in gravimetry quickly led to the observations of regularities in the proportions in which substances combined with each other (Rocke 1984, 6–15; Brock 1992, chap. 4). In 1794, Joseph-Louis Proust (1754-1826) generalized this into a law according to which components always combined in the same proportions in order to form certain substances. Thus, for example, oxygen and hydrogen would always combine in the same ratio in order to form water. For other substances, like oxides, this was more complex to establish because metals and oxygen tend to combine in multiple different proportions (metals have multiple degrees of oxidation). Proust argued that there were only two oxides per metal, which each consisted of a fixed proportion of oxygen, rather than a whole range of combinations. All other proportions would simply be mixtures. Although this led to a debate with Berthollet, Proust's law eventually became a consensus.

In parallel, the term stoichiometry was coined by Jeremias Richter (1762-1807), a student of the philosopher Immanuel Kant who aimed to mathematize chemistry. In 1792, Richter showed that acids and bases can be compared in neutralizing power: for example, taking 1000 parts of sulphuric acid, one might identify the amounts of base needed to neutralize that quantity and assign a dimensionless relative 'equivalent' value to them. The ratios between two equivalents stays the same independently of the neutralizing substance, and it is therefore possible to compare to various types of acids besides sulphuric acid to see how much of each acid would be equivalent to 1000 parts of sulphuric acid. Such an identification of equivalents can be done purely empirically without any underlying theory, and it is not in itself a form of chemical atomism.

John Dalton (1766-1844), a Quaker who made his living as a private elementary teacher in Manchester, was the one to link stoichiometry to the millennia-old idea of atoms (see Brocke 1992, chap. 4). In 1808, Dalton published his *New System of Chemical Philosophy*, of which five pages were dedicated to his atomism. He formulated the theory that all of

matter consisted of microscopic particles surrounded by an atmosphere of caloric (heat) that combined together in various, fixed proportions because of attractions and repulsions between them. Chemical reactions would thus be the rearrangements of such particles. Various versions of atomism had been around for thousands of years, so the real novelty of his theory was a new approach to stoichiometry. Dalton provided a kind of calculus of chemical reactions which turned chemical atoms into really useful quantified entities. Besides the assumption that all of matter consisted of hard, indivisible atoms, he relied on the law of the (qualitative as well as quantitative) conservation of matter and proposed that each chemical element corresponded to a different kind of atom characterized by a specific weight. He suggested that these atoms combined to formed chemical compounds in small integer ratios.

In order to determine the atomic weight of each element, Dalton needed to know the chemical formula of various substances. He decided to follow the simplest approach by supposing the smallest combination of two bodies to be a binary one, in other words AB. If A and B combine in multiple proportions, these proportions are $A_2B$ or $AB_2$. For example, since water was the only known compound of oxygen and hydrogen at the time, he supposed its composition to be HO (using today's symbols). Knowing the proportions in which hydrogen and oxygen combined, this enabled him to establish an atomic weight for oxygen (fixing hydrogen at 1): O=7. These rules were explicitly arbitrary – there was no way to know the actual formula so one had to start somewhere, and why not with the simplest assumption?

From quite early on, Dalton's theory had various supporters. The Scottish chemist Thomas Thomson learned of the theory in 1804 and invited Dalton to lecture on it in Edinburgh in 1807 (these lectures provided the basis for his *New System*). Dalton's system was mostly defended and publicized by Thomson, William Hyde Wollaston and later Jöns Jacob Berzelius. Dalton's contemporaries saw his theory first and foremost as a series of laws of composition, most importantly the law of multiple proportions. It had already been known that elements combine in fixed proportions, but the law of multiple proportions helped explain why their various equivalents were often multiples of one another. Taking a current-day example, since oxygen and hydrogen combine as water or peroxide, 8 and 16 are equivalent weights of oxygen relative to hydrogen as unity. Such series of equivalents

can be calculated for each binary combination, directly from the analytical data. Following Dalton's law this would correspond to hydrogen combining with one or two atoms of oxygen, and the fact that the quantity of oxygen doubles is explained as the doubling of the amount of atoms. This was immediately recognized as a very helpful tool for calculating chemical combination.

The rest of Dalton's theory was criticized as containing too many hypotheses about the nature of atoms. Many of his colleagues liked his laws of composition but did not agree with the idea of atoms, and they often chose terms other than 'atomic weight'. Most of them only wanted to adopt a conventional system of equivalent or combining weights, because this would enable them to adopt the system without saying anything about particles that matter possibly consisted of. The term "equivalent" was popularised by Wollaston in 1814 when he published an influential paper proposing a single, invariant equivalent for each element based on the lowest oxide. He defended his approach as empirical and free from hypotheses about the structure of matter. While the equivalent weights were very popular, the idea of chemical atoms received much criticism. David Knight (1967) has argued that the wide success of Wollaston's attitude towards atoms shows "the astonishing infertility of a specifically atomic theory in chemistry before the 1860s" (*ibid*., 25). However, Alan Rocke (1984) has since convincingly argued that chemical atomism was universally adopted throughout the nineteenth century.

Chemical atomism, according to Rocke, is the idea that "there exists for each element a unique 'atomic weight', a chemically indivisible unit, that enters into combination with similar units of other elements in small integer multiples" (*ibid*.,12). Both Dalton and his opponents adopted this approach and the two groups differed only in their views towards *physical* atomism, the idea that matter is actually composed of small particles that have a specific shape and size. At the time, chemists themselves did not clearly distinguish between the physical and chemical atomism, and this explains why they attacked atomism in general (on this distinction, see also Rocke 1978). Chemical atomism did not require the adoption of any hypothesis about the structure of matter, and Rocke has argued that even though Wollaston's system was purely conventional and distinct from microscopic interpretations of chemical atoms, the seemingly empirical 'equivalent weights' of Wollaston and his followers were actually atomic weights.

According to Rocke (1984, 10–15), chemical atomism therefore lies between physical atomism and the purely empirical laws of stoichiometry. Stoichiometry assigns multiple, purely empirical equivalent weights to each element on the basis of the law of fixed proportions. Such equivalent weights often form series of small integer multiples of each other (such as 8 and 16 in the example of hydrogen and oxygen). Chemical atomism on the other hand, *explains* the regularities in the weight proportions, rather than simply describing them. It explains them by postulating that elements combine in a minimal unit, a chemically indivisible minimum that can combine with the units of other elements in small integer multiples. The quantity of matter corresponding to such a unit, as measured by its weight, is different for each element, which means that each element can be characterized by one specific weight. In order to identify the atomic weight, chemical formulae need to be identified because one has to know (or conjecture) of how many atoms a specific substance is composed. In the beginning of the nineteenth century, this consisted in assuming a formula for the simple oxides of the elements and using that to calculate atomic weights relative to the known weight of oxygen. Once they were identified, the atomic weights could then be used to establish formulae for all the other compounds of the elements (see also Chang 2012b for this iterative relation between formulae and weights).

The equivalent weights of Wollaston and his colleagues relied on the assumption of chemical formulae that could not be directly derived from the laws of stoichiometry, and this meant that their equivalent weights could not be purely empirical. Even if chemical atomism did not have a visual model of what chemical atoms would look like, Rocke has argued that it was theoretical because it explained the law of multiple proportions. Rocke's argument that chemical atomism was (almost) universally accepted during the nineteenth century is commonly accepted by historians today. Hasok Chang (2012b, chap. 3) has identified various different systems of chemical atomism and he has added that atoms were not only characterized in terms of weight; they could be seen as minimal units of matter identified in various ways, for example by volume in addition to weight (see *ibid*., 152). Klein (2003) prefers to speak of the theory of chemical proportions.

The fact that atomic (or equivalent, or combining) weights came to be seen as a property of elements is very significant for the history of the notion of chemical element: it seems like this would provide a positive attribute by which they could be characterized, rather

than the negative and provisional criterion of indecomposability. Now that I have provided an overview of the early history of chemical atomism, I can return to the main question of this section: did this new theory solve the difficulties regarding the identification of simple substances?

## Atoms and simple substances (1): metaphysical speculations

Siegfried and Dobbs (1968) have argued that Dalton's system should be seen as the completion of the chemical revolution, because it solved the issues left open by the Lavoisian view of composition. In their words, "the problem of the chemical element ceased to be critical about the time of the appearance of Dalton's atomic theory the elements" because it provided chemists with a new set of problems and a practical approach toward them that led them away from the issue of the truly elementary nature of bodies (Siegfried and Dobbs 1968, 293). According to their account, chemists had already known that the question of elementary nature could not be answered, but the atomic theory really led them in a different direction, focusing on purely pragmatic questions.

In his own book, Siegfried has taken this argument even further, stating that "ultimately, Dalton's theory completely transformed chemical from a chaos of unorganized empirical knowledge into a science centered on the concept of atomic weight" (Siegfried 2002, 235). Siegfried has argued that by assigning an atomic weight to each element, it became possible to mathematize composition. Historians of eighteenth-century (and earlier) chemistry have shown in various works that pre-Daltonian knowledge should not be dismissed as unorganized and chaotic, as has hopefully been made clear in earlier parts of this chapter. Putting aside these dismissals of earlier knowledge, it is nevertheless possible to investigate Siegfried's claim that Dalton "permanently" solved the problem of composition (*ibid*., 262). Siegfried argued that Dalton's idea of assigning a single atomic weight to each element made it possible to not only explain the fixed proportions in which elements combine, but also to express empirical composition as the combination of quantitative units of matter. He interprets this as a mathematization of chemical composition. On first view, this seems like a reasonable claim, and coherent with the potential that chemists saw in the law of multiple proportions at the time.

However, the idea of composition did not cease to be problematic after Dalton's theory. Dalton's assumption that each simple substance would be composed of only one

type of completely indecomposable atom was questioned by reductionists who thought that simple substances would ultimately be composed of even simpler elements. The clearest sign of this reductionism was the continued success of Prout's hypothesis throughout the nineteenth century.

William Prout (1785-1850) was one of many people who speculated on the complexity of chemical elements; he had developed some of his ideas during his studies under the influence of Thomas Thomson, John Miers and Humphry Davy. These speculations took on a new dimension thanks to Dalton's idea of atomic weights. In two famous papers from 1815 and 1816, Prout noted expressed two hypotheses (see Brock 1985): on the one hand, Prout noted (and attempted to empirically establish) the mathematical relations that existed between the atomic weights of many elements. Specifically, various elements appeared to be exact multiples of the weight of hydrogen. On the other hand, Prout speculated about the cause of these relations: he conjectured that all elements were composed of units or atoms of a primary matter that had the weight of hydrogen atoms. These ideas motivated the research of entire groups of chemists at various points during the nineteenth century. In other words, Dalton's hypothesis did not in any way change the idea that simple substances might actually be compounds for most chemists. Quite on the contrary, Dalton's approach opened up the way for an entirely new type of speculation on the inner complexity of simple substances using mathematics.

Nineteenth-century speculations on the inner complexity of elements were not just based on the seemingly arithmetic relation that seemed to exist between atomic weights; a deeper underlying feeling of uncertainty also remained. Nineteenth-century chemists saw a profound contradiction between the rich quantities of simple substances that they continued to discover and their conviction that nature was ultimately simple and harmonious (Levere 1977b). Following Prout's example, some of them therefore ascribed the numerical regularities in atomic weights to the idea that elements were composed of multiple units of a simpler, primary matter. These endeavours lasted throughout the nineteenth century (see also Knight 1978). In short, chemists continued to feel a metaphysical discomfort regarding the idea of provisionally simple substances despite the adoption of chemical atomism.

This also leads to an important point regarding weight and its role in resolving the circularity of Lavoisier's definition. During Lavoisier's lifetime there were indeed various cases in which the use of weight resolved questions regarding the composition of substances by providing a method to distinguish between composition and decomposition. However, even once the law of conservation of weight was commonly accepted, various issues regarding composition remained unsolved. As will become clear in later chapters as well, various types of speculations were completely compatible with weight conservation. This was the case for speculations regarding the inner complexity of elements (weight could not be used in order to know whether atoms were composed of some even simpler primary matter) but also for the interpretation of concrete reactions (for instance, some claims of having decomposed chlorine and nitrogen were perfectly coherent with the use of weight to track composition, as will become clear in chapters two and three). In those cases, Lavoisier's definition remained circular and more positive arguments were needed in the form of supplementary hypotheses regarding the composition of substances. This point will be further argued in the following chapters. Before then, one question remains: did the atomic theory lead to a new concept of chemical element?

## Atoms and simple substances (2): a new concept of element?

It may seem as though atomism added the positive criterion to the elements that the definition of simple substances was lacking: the atomic weight. This potentially constituted a stable characteristic by which elements could be identified, rather than the purely negative criterion of the impossibility to decompose them. Whereas indecomposability could only be identified provisionally, at least atomic weights could be detected and traced.

Indeed, in Dalton's view, the elements were distinct individuals composed of only one type of atom that could not be reduced to simpler components. He had quite an unusual view of chemical elements, probably – as Rocke (1984, 39–40) remarks – because he was not a chemist, since chemists generally thought of the list as uncertain and provisional. In order for Dalton to formulate his theory that each of Lavoisier's simple substances consisted of a different type of atom, he had to uncritically accept this list. When it came to the definition of chemical elements, however, Dalton did echo Lavoisier in the second part of his *New System*:

> "By elementary principles, or simple bodies, we mean such as have not been decomposed, but are found to enter into combination with other bodies. We do not know that any of the bodies denominated elementary, is absolutely indecomposable; but it ought to be called simple, till it can be analyzed" (Dalton 1810, 1 part 2:221–22).

This dissonance between Dalton's definition and his implicit ideas regarding chemical elements appears to be characteristic for the views of chemists in the nineteenth century. In her study of the history of the concept of element, Bensaude-Vincent (1981) has shown that the wide adoption of chemical atomism further complicated the linguistic difficulties regarding elements by adding an additional notion: besides elements, principles and simple substances, the concept of atoms now also played a role in chemical theory. Although the atomic theory, and various developments in the same line of investigation, drastically improved knowledge of simple substances and their properties throughout the nineteenth century, Bensaude-Vincent has shown that did not stimulate any conceptual work on the part of chemists. Chemists did not find the need to work on their definition of the concept of element and its relation to other concepts and even seemed averse to this kind of reflection. They continued to cite Lavoisier's definition of the element as a simple substance for decades, and it took decennia for chemists to explicitly identify the atomic weight as a positive criterion by which each individual element could be characterized. Indeed, Bensaude-Vincent has argued that a new concept of element was not generated until Dmitri Mendeleev explicitly distinguished between elements and simple substances.

## Conclusion

This chapter has both provided the historical background to the case studies that will follow and shown the difficulties of applying Lavoisier's definition of the chemical element in practice. I have described the emergence of Lavoisier's new system of chemistry in the context of the chemical revolution and the influences of eighteenth-century chemical practice on his views of composition. While the view of the composition of specific substances changed, a deeper ontological understanding of chemical composition remained: already since the mid-eighteenth century, chemists distinguished between simple and compound bodies, and classed them according to chemical behaviour within each level of composition. Rather than just a residue of decomposition, the simple

substance was therefore always also characterized as a constituent of compounds. This remained the case in Lavoisier's chemistry and in that of his nineteenth-century followers.

Although others had defined chemical elements by their indecomposability, Lavoisier was the first to do away with the four elements and center chemistry on a list of provisionally simple substances. Besides simple substances, this list also included a group that he referred to as 'the elements of bodies'. Lavoisier moreover speculated on the inner composition of some indecomposable bodies and predicted the existence of substances that had not yet been isolated. While the former were in part inherited from earlier views of matter, these latter inconsistencies were a response to the insufficiencies of Lavoisier's own definition. His definition of chemical elements on the basis of their provisional simplicity left room for metaphysical speculations on the true constitution of indecomposable substances. Moreover, in itself, this definition did not suffice for the identification of simple bodies, and complementary hypotheses were required. The identification of composition (or lack thereof) required various types of hypotheses in order to support the direct empirical evidence and provide a guide on how to interpret it.

The tracking of composition via weight measurement could provide additional empirical evidence in order to identify some operations and decompositions and others as combinations. However, the late eighteenth-century focus on gravimetry did not provide a solution to the metaphysical and procedural difficulties of identifying chemical elements. On the contrary, it was compatible with all kinds of speculations regarding their inner composition, as weighing alone could not provide an answer. Furthermore, chemical atomism did not lead to a new concept of chemical element: the definition of chemical elements as simple substances remained dominant at least until Mendeleev redefined the concept in 1869.

This conclusion therefore points towards a paradox. As the number of discoveries of new elements illustrates, post-Lavoisian chemists were incredibly successful in identifying, studying and characterizing elementary substances. If, as I have argued here, the difficulties of the negative-empirical criterion had not been resolved by the development of early chemical atomism, this means that nineteenth-century chemists could not have relied only on atomic weight and experimental indecomposability. Some examples illustrate this especially well: aluminium was accepted as an element long before

it was isolated in the form of a simple substance, and chlorine was seen as a compound by some and as a simple substance by others. In these cases, the negative-empirical criterion alone could not provide the necessary evidence for the identification of their elementary nature. Yet, chemists during the first half of the nineteenth century found a way to use other types of evidence in order to know which substances to view as chemical elements. In the rest of this thesis I will show how these chemists determined the elementary nature of aluminium, chlorine, tantalum and niobium, and how they rejected a number of other supposed elements.

# PART I - Aluminium, Chlorine and Ammonia: Composition and Analogy in the Early Nineteenth Century

Around 1810, not too long after the publication of Lavoisier's *Traité de Chimie*, the number of chemical elements rapidly rose. The traditional hero of this early nineteenth century boom is the English chemist Humphry Davy (1778-1829), who is credited with more discoveries of elements than any other individual.[36] He was able to isolate sodium, potassium, barium, strontium, calcium, boron, and magnesium and also contributed to the identification of aluminium, chlorine, iodine, and fluorine as chemical elements. During the first decades of the nineteenth century, he aimed to systematically decompose as many substances as possible in order to arrive at the "true elements of bodies" (H. Davy 1808b, 1). His research programme therefore seems like a logical first place to start for a study of the ways in which chemical elements were identified in the early nineteenth century. At first glance, Davy's discoveries appear to symbolize the triumph of the negative-empirical principle: by developing new techniques to decompose previously indecomposable substance, he was able to isolate a number of new elements in the form of simple substances. However, looking at these cases in more detail it becomes clear that their identification as chemical elements was often more complicated than it seems. The idea of a single moment during which these new substances were isolated and proven to be elementary is the result of a retrospective retelling of these stories.

Some cases stand out as especially puzzling or even seemingly contradictory to the Lavoisian definition of chemical elements. Aluminium appeared as a metal on lists of chemical elements from around 1810, more than fifteen years before it was isolated in the form of a simple substance. This happened following Davy's prediction of the metal as a

[36] For biographical information on Davy, see the biography by David Knight (1992a). Much has been published on Davy recently, see for example the papers making up the *Ambix* collection "Papers on Humphry Davy (1778-1829): Chemistry, culture and society in early nineteenth-century England", edited by Frank James.

constituent of the indecomposable compound alumina (now also known as aluminium oxide), which behaved like a metallic oxide and was therefore likely to contain a new metal. Chemists' willingness to accept Davy's prediction of the existence of aluminium, despite considering his attempts at isolating it unsuccessful, clearly contradicted the Lavoisian rule of never viewing an indecomposable body as a compound. Chlorine, on the other hand, had been isolated in the form of a simple substance. However, while Davy this time followed the Lavoisian definition in arguing that chlorine had never been decomposed and should therefore be seen as a chemical element, many chemists refused to accept his arguments. The elementary nature of chlorine divided the European chemical community roughly between 1810 and 1816, and the debate was not resolved until after the discovery of the analogous chemical element iodine. The cases of aluminium and chlorine constitute exceptions and controversies during which chemists had to explicitly argue on the nature of these substances and they can therefore help shed light on chemists' criteria for effectively accepting new chemical elements.

Although these cases were complex, chlorine and aluminium were relative success stories for Davy since they were both ultimately accepted as chemical elements. Davy also named and studied 'ammonium', the supposed metallic constituent of ammonia, which was not generally accepted as a chemical element. He justified this prediction with a similar analogical inference as in the case of aluminium, because ammonia also behaved in many ways like a metallic oxide. However, in this case his inferences were continually contradicted by experimental results, and he proposed a number of hypotheses between 1807 and 1812. Besides predicting the existence of ammonium, this also led him to question the elementary nature of nitrogen and hydrogen. Davy's difficulties in identifying the nature of ammonia and its constituents show that elementary nature was not self-evident or directly observable. It was fallible and closely linked to the nature and classification of compounds. All three first chapters of this thesis will show this in more detail.

Various aspects of the stories of the early investigations into the nature of these substances are still unknown, especially in the case of aluminium and ammonium. While the debate on the elementary nature of chlorine has been studied, it has generally been described as an isolated historical case rather than as part of a broader study of elementary nature. In each of these chapters I will make historical arguments that are specific to each

case, but these episodes are also philosophically interesting because they exemplify the ways in which early nineteenth-century chemists resolved the metaphysical and procedural difficulties of the negative-empirical criterion for elementary nature that I described in the prologue. The identification of chlorine and aluminium as chemical elements, and the various hypotheses proposed in the study of the composition of ammonia, all relied on the use of inferences on the basis of chemical analogy. Far from providing an unambiguous method for the isolation of elementary substances, I argue that the results of experimental decomposition attempts formed only part of a complex argumentation, in which new empirical findings had to be made coherent with analogical inferences, chemical classification and previous theoretical knowledge. Like Lavoisier, these early nineteenth-century chemists relied on chemical analogy in making an implicit distinction between chemical elements and indecomposable substances.

## Historical actors, context and sources

These three chapters are not just separate case studies: they overlap both chronologically and thematically, and they build on the same primary sources mostly from the period between 1807 and 1820. While Davy is sometimes presented as an individual heroic figure, his work during this time cannot be examined in isolation from that of other chemists. I will also focus on the contributions of the Swedish chemist Jöns Jacob Berzelius (1779-1848) and the French chemists Joseph Louis Gay Lussac (1778-1850) and Louis Jacques Thenard (1777-1857), as well as a number of their colleagues. Davy, Berzelius, Gay-Lussac and Thenard were members of the first generation of chemists following that of Lavoisier who were active during the first half of the nineteenth century: born within two years of one another, they had each been educated in the new system of chemistry. These chemists were all investigating the same groups of substances using similar methods during the period discussed here, which ranges approximately from Davy's discovery claim of sodium and potassium in 1807 to Berzelius' acceptance of the elementary nature of chlorine in the early 1820s.

Among their experimental apparatus these men each had access to a new type of instrument called the voltaic pile, the first battery capable of producing a relatively steady current of electricity. This instrument was named after Alessandro Volta (1745-1825), a professor of experimental physics in Northern Italy who had invented it in 1799.

It consisted of pairs of plates of two different kinds of metals, stacked on top of each other with a piece of moistened cardboard separating each pair. The pile immediately became a sensation throughout Europe: large-scale batteries were constructed at the Royal Institution in London and at the Ecole Polytechnique in Paris, the latter on direct orders from Emperor Napoleon (Sutton 1981). Berzelius and his Swedish colleagues had less impressive funding but were nevertheless able to significantly contribute to the early electrochemical investigations using their own piles. The pile provided a powerful new decomposition method and a way to study chemical substances using electricity, which was used in the study of aluminium, chlorine and ammonia.[37] They also used a variety of other methods which often consisted of decomposing and recombining substances.

For these men, the beginning of the nineteenth century was more than just an intellectually stimulating time marked by the development of the voltaic pile: this was also the period during which they rose to fame in the European chemical community. All four of them acquired prestigious institutional positions during the first decade of the century. In 1801, at only 22 years old, Davy was appointed to the Royal Institution where he lectured to an audience consisting mostly of well-read, wealthy women (see Lloyd Edmondson 2019; Golinski 1992). Berzelius was appointed professor of medicine and pharmacy in 1807 at the School of Surgery in Stockholm, which became the Karolinska Institute in 1810 (Jorpes 1970). Thenard acquired the chair of chemistry of the Collège de France in 1804 and Gay-Lussac became a professor at the Ecole Polytechnique in 1809 (Belmar and Bertomeu-Sánchez 2010; Crosland 1978). In addition, each of them was elected to the Academies of Science in their respective countries.

Although they were working during troubled times in European history, in different countries and even different languages, these chemists were in contact with each other through debates, rivalry and correspondence and sometimes even visited each other. These exchanges will provide the primary sources for this first part of the thesis. Davy's publications can mostly be found in the *Philosophical Transactions of the Royal Society of London*, though he sometimes published in French. Gay-Lussac and Thenard mostly

[37] On the establishment of the voltaic pile as an instrument for the decomposition of chemical substances, rather than an object of study in itself, see Golinski (1992, 203–12) and Chang (2012b, chap. 2).

preferred the *Annales de Chimie* and Berzelius published in a variety of Swedish, German, English and French journals (see Beckman 2016).[38] Outside of the laboratory, teaching was an important activity for their careers and each of their textbooks will provide important primary sources.[39] In addition, I will rely on a number of other textbooks that show how elements were characterized, most notably the *System of Chemistry* by the Scottish professor Thomas Thomson (1773-1852) which ran for many editions. Thomson also edited the journal *Annals of Philosophy* from 1813 to 1820, in which he wrote yearly reports on the advancement of chemistry.[40] Lastly, both Davy and Berzelius had rich correspondences that have since been edited, in which they provided additional protocols, hypotheses and more intimate thoughts that were not shared publicly.[41]

Each of these actors were working in very different institutional, political and cultural contexts and they each had their own style that was influenced by these contexts. While Berzelius was very attached to the formulation of general rules, Gay-Lussac and Thenard were more flexible in admitting exceptions. Davy was strongly influenced by romanticism and had a fairly unusual career that gave him a lot more freedom to speculate. I will explain these particularities and their evolution over time as well as the ways in which they influenced some of the stark oppositions on the elementary nature of substances.

[38] Publication of the *Annales de Chimie* had ceased after Lavoisier was captured in 1793 and later sentenced to death. In 1797 the publication of the journal resumed, initially mostly under the leadship of Guyton de Morveau and Fourcroy. After the death of Fourcroy, Gay-Lussac and Thenard were added to the editorial board of the journal as protégés of Berthollet (Crosland 1994).

[39] On the historical development of chemistry textbooks, see Bensaude-Vincent and Lundgren (2000) and Bensaude-Vincent, García Belmar and Bertomeu Sánchez (2003).

[40] The *Annals of Philosophy* was one of a number of scientific journals to be founded in Britain shortly after the Napoleonic wars with the aim of exploiting the growing market for periodicals (Topham 2016). Thomson co-founded the journal in 1813 together with the London publisher Robert Baldwin and it was one of his main sources of income until he became appointed as a lecturer in chemistry at the University of Glasgow in 1817. In 1826, Baldwin sold the journal to the editor of the *Philosophical Magazine* after which the two journals were combined.

[41] Davy's correspondence has recently been edited by Tim Fulford and Sharon Ruston (2020) and can be accessed online at http://davy-letters.org.uk/. Berzelius' correspondence has been published in a number of separate volumes in the early twentieth century. In the first part I will mostly rely on the collection edited by Henrik Söderbaum (1912a).

Nevertheless, I will show that despite these differences, they shared requirements for the identification of elementary nature in the early nineteenth century. Each of them explicitly relied on analogical inferences in a very similar way.

## The role of analogy in nineteenth-century studies of chemical composition

In his "Introductory Lecture to the Chemistry of Nature", delivered at the Royal Institution on 31 January 1807, Davy characterized analogy as an essential tool in science:

> "The *body* of natural science, then, consists of *facts*; its governing spirit is analogy, - the relation or resemblance of facts by which its different parts are connected, arranged, and employed, either for popular use, or for new speculative improvements" (H. Davy 1840, 8:67–68).

Davy often mentioned analogy in his lectures and publications, describing it as "beautiful and replete with promise" (H. Davy 1840, 8:317).[42] Though he sometimes dismissed analogy as mere speculation, Davy also heavily relied on analogical reasoning in order to design and interpret his experiments (Tate 2019). In his view, a "true philosopher" had to understand the connections between facts and put them to use: in scientific debates, he therefore highlighted his knowledge of analogy in order to increase his scientific authority (Ruston 2019).

Although Davy's reference to analogy was particularly frequent, his reliance on analogy and analogical reasoning was representative for men of science during the early nineteenth century. From the late eighteenth and well into the nineteenth century, the importance of analogy as a theme in scientific publications continued to increase.[43] Many examples of analogical inferences can be found in the history of eighteenth- and nineteenth-century chemical practice: for instance, Alessandro Volta (1745-1827) explored the

[42] Davy appears to have been fascinated by analogy throughout his lifetime. In his first manuscript, written in 1798, Davy already used analogical reasoning four times (James 2019). Davy reflected on analogy again in his last work *Consolations in Travel* (Ruston 2019, 138–39).

[43] In their survey of mentions of "analogy" and similar terms in the *Philosophical Transactions of the Royal Society*, Gingras and Guay (2011, fig. 1) have found a significant increase in the use of these terms, starting around 1780 and lasting throughout the nineteenth century.

various analogies between the imponderable fluids of heat and electricity (Heilbron 2000). Likewise, analogies formed the basis of the extension of concepts from the inorganic to the organic domain and promote the unity of chemistry during the first half of the nineteenth century (Brooke 1969). Dmitri Mendeleev (1834-1907) also used analogies in different ways. Firstly, he relied on the analogy between the distinctions molecule/atom and simple substance/element in the reconceptualization of the notion of chemical element (Bensaude-Vincent 2019). Secondly, he used his periodic system as a visualisation of the analogical properties of the chemical elements in order to predict the properties of elements that were yet to be discovered (Pulkkinen 2019b). In her overview of chemical philosophies, Mary Jo Nye (1993) has described a consistent reliance on analogies in the establishment of chemical explanations since the eighteenth century.[44]

The use of analogies and analogical inference was therefore widespread in chemical practice. The most frequent use of analogy during this period was as a principle of classification (Gingras and Guay 2011) and this is also the most relevant for the study of chemical composition. As I explained in the prologue, from the mid-eighteenth-century onwards, chemists classified substances not only according to their level of composition but also on the basis of their chemical properties in terms of tendencies to combine. Chemical analogy remained a widely accepted principle of classification during the nineteenth century (Knight 1978, chap. 9). Chemical substances were identified and characterized by the way they combined with other substances, and they were classed with other substances that exhibited similar patterns of chemical behaviour.

These 'chemical analogies' between substances of a same class or family could form the basis for an analogical inference. For instance, the fact that two substances were chemically analogous could be a reason to think that they would behave similarly under the same conditions, for example they would react similarly to an electrical current. This heuristic use of analogical inference was especially helpful in facilitating experimental research (Fisher 2018). Analogy enabled chemists to evaluate the relevant similarities in different experimental outcomes, formulate working hypotheses and design experiments

[44] The use of analogy was of course not limited to chemistry. Other nineteenth-century examples of scientific uses of analogy include Michael Faraday and James Clerk Maxwell (see Henderson 2014), Erasmus Darwin (D. Porter 2007) and Charles Darwin (Sterrett 2002).

to test them. Moreover, I argue that analogical inference also played a role beyond the formulation of working hypotheses: chemical analogies provided a way to indirectly study the composition of indecomposable substances. This use of analogy relied on a correlation between properties and composition. For many chemists at the time, similarities in chemical properties were thought to indicate similarities in chemical properties. As Davy himself summed up: "bodies that are similar should be classed together, and their composition is analogous" (H. Davy 1812, 47). This link between chemical analogy and composition enabled chemists to infer the chemical composition using the composition of other, similar bodies.

In some cases, chemical analogies could provide a counterargument against the worries that newly discovered chemical elements might actually be compounds. The fact that a substance was indecomposable in itself could not prove elementary nature, because its indecomposability might simply be due to insufficient experimental means. However, if an indecomposable substance could be classed with analogous substances that were generally considered simple, there was no reason to suppose it to be a compound – at least not more so than other chemical elements. Likewise, if an indecomposable substance had its place in a class of substances that were commonly admitted to be compounds, it was likely to be a compound as well. It was therefore justified to take it off the list of simple substances in anticipation of the development of an adequate decomposition technique. In other words, inferences on the basis of chemical analogy provided a way to ensure the reliability of experimental results and a method to choose between different possible ways to interpret them.

This role of analogy in chemistry is very similar to that described by Adrian Currie in his book *Rock, Bone and Ruin* (2018). Arguing against the idea that historical scientists only have very little evidence on which to base their studies of past events, Currie has described the ways in which they produce additional evidence by relying on analogies. Historical scientists are able to establish links between the various traces of the past they can uncover and identify patterns in the types of systems that they study. Using such patterns of regularities, they can establish analogies between various types of events that enable them to indirectly acquire knowledge about systems that they cannot access directly. By studying a system that is analogous to the one they are trying to study, they can produce

evidence that complements the direct trace evidence from the past. In Currie's view of the historical sciences, analogies do not justify hypotheses about the past in themselves: rather, they are integrated with all the other types of evidence. Historical scientists multiply their ways of studying the phenomena about which they are trying to gain knowledge in order to find out whether all different kinds of evidence point towards the same conclusion.

I argue Currie's account can be extended to include early nineteenth-century chemists who were eager to study chemical composition any way they could. By studying analogous substances, they could indirectly acquire knowledge of the composition of indecomposable substances. Analogical inferences did not themselves justify a conclusion regarding chemical composition. Instead, they were part of a more complex argumentation that integrated inferences on the basis of existing knowledge and various types of experimental results. Thus these first few cases studies will not only tell us about the arguments used to establish elementary nature in these specific cases, but also provide a new interpretation of the use of analogy in chemistry, and more generally give us some insight into the processes of chemical inquiry.

Chapter one will describe the prediction and acceptance of aluminium's elementary nature. Various analogical arguments regarding the nature of its compound alumina had been formulated since the middle of the eighteenth century, but around 1810 it became commonly accepted that alumina was the oxide of a new element called aluminium. I will study the arguments on which this acceptance was based, as well as the eventual isolation of metallic aluminium and its perceived significance at the time. Chapter two will investigate the attempts to identify the composition of the alkaline compound ammonia between 1807 and 1813, focusing on the work of Davy and Berzelius. Ammonia behaved like a metallic oxide in many ways but whenever it was decomposed, it only produced hydrogen and nitrogen. The ways in which Davy and Berzelius adapted to the repeated contradictions between analogy and experimental results will show the importance of each of these aspects in their evaluations of the elementary nature of nitrogen, hydrogen and the supposed metallic constituent of ammonia. Lastly, chapter three focuses on the debate on the elementary nature of chlorine between 1810 and 1816. Despite Davy's insistence on the impossibility to decompose chlorine using even the strongest available means, many chemists opposed the elementary nature of chlorine. The opponents of elementary chlorine

believed that chlorine had in fact been decomposed, because they interpreted the same reactions differently. Each of these three cases will therefore show a different aspect of the use of analogical reasoning in the study of elementary nature in the early nineteenth century.

# CHAPTER 1 - Aluminium: Analogy, Composition and the Discovery of a Chemical Element

In his Bakerian lectures of 1806 and 1807, Humphry Davy argued he could use his pile to decompose previously indecomposable substances and isolate their constituents.[45] Using this new method, he was able to decompose the fixed alkalis and produce the new metals potassium and sodium. Once he had decomposed the alkalis, Davy continued his attempts at decomposing similar chemical substances in the hope that his new instrument would enable him to identify their constituents. Although he was able to decompose barites, strontia, lime and magnesia, not all his decomposition attempts worked out as he had hoped. One of the substances that remained indecomposable was *alumina* (aluminium oxide).[46] Nevertheless, Davy predicted that alumina and other, similar substances, contained metals:

> "Had I been so fortunate as to have obtained more certain evidences on the subject, and to have procured the metallic substances I was in search of, I should have proposed for them the names of silicium, alumium [sic], zirconium, and glucium" (H. Davy 1808a, 353).[47]

By way of naming these substances, Davy attached his name to them even though he considered his own attempts to isolate them unsuccessful. Davy continued to attempt to

[45] On Davy's theoretical interpretation of the pile and the way in which it decomposed substances, see Russell (1959a; 1959b).

[46] In modern chemical terms, the earths could be identified as (hydrated) metallic oxides and carbonates. I have added current names for these substances in order to facilitate understanding, but the early nineteenth-century terms do not perfectly correspond to any pure chemical substance from the point of view of today's chemistry.

[47] Davy's "alumium" was criticized as a name because it implied that the metal was directly extracted from alum, the salt of alumina and sulphuric acid, rather than from its oxide. In order to stay consistent with the other metals' names, which were all named after their oxides, it was proposed that the metal be named aluminium instead. Based on these criticisms, Davy changed the name to aluminum, but most European chemists continued to prefer aluminium (Richards 1896, 5–6). Glucium was first renamed glucinium, and later came to be known as beryllium.

decompose alumina during the following year, but he never felt he was able to produce a sample of aluminium. Nevertheless, aluminium was added to lists of chemical elements, and it appeared in various textbooks following Davy's publications on the topic. Alumina, even though it had never been decomposed, was classed as a compound and identified as aluminium oxide.

Alumina remained indecomposable for more than fifteen years after Davy's prediction of its composition. The date of the first isolation of metallic aluminium depends on how one evaluates the attempts of Hans Christian Ørsted (in 1825) and Friedrich Wöhler (in 1827) at producing the metal and describing its properties. As opposed to potassium and sodium, which Davy both identified in the form of an isolated simple substance, Davy predicted the existence of aluminium as the constituent of a compound that had not been decomposed. The acceptance of aluminium as an element therefore shows that early nineteenth-century chemists were willing to rely on different arguments than the negative-empirical criterion in order to justify the addition to a list of chemical elements. What were these arguments? How did chemists at the time perceive the significance of its isolation? By studying chemists' characterization of alumina and aluminium around the time of its prediction and isolation we can identify their effective criteria for elementary nature.

So far, no studies have been aimed at answering these questions. As a light-weight, strong and widely available metal, aluminium has a long and fascinating history that is intrinsically linked with the history of industrialization and modernity. Aluminium's significance as a material has motivated historians to focus on its production in the form of a metal, describing the improvements in the industrial process that enabled the mass production of aluminium during the nineteenth and twentieth centuries (Ferrand 1961; H. N. Holmes 1930; Le Roux 2015; Sheller 2014). Likewise, most accounts of the history of aluminium date the discovery of the element during the 1820s. Davy's experiments have often been characterized as 'failed' or 'unsucessful' (H. N. Holmes 1930; Jagnaux 1891; Weeks 1956) and more recently, they have been excluded from the discovery process of aluminium (Ferrand 1961; Kragh 2019). However, the history of aluminium as a chemical element does not completely overlap with its history as a material, and the former has generally been overlooked.

This chapter will therefore focus on the early history of aluminium, from the identification of alumina in the middle of the eighteenth century to the first production of an industrial quantity of metallic aluminium a century later. The central part of the chapter will focus on the years around 1810, showing when it was accepted as a simple substance and for which reasons. I will analyse Davy's attempts to decompose alumina, the evidence he presented in favour of the existence of the new metal and the way in which it was received by his contemporaries. I will argue that chemists accepted the elementary nature of aluminium following Davy's prediction of the metal, despite considering his attempts at isolating the metal unsuccessful.[48] They were convinced by Davy's use of analogy to infer the presence of aluminium in alumina: as an earth, alumina behaved extremely similarly to the alkaline earths which Davy had experimentally shown to be metallic oxides. The acceptance of aluminium as an element illustrates that chemists did not accept all indecomposable substances as chemical elements: if there were reasons to believe that they were compounds, such substances were not included in lists of chemical elements. Likewise, elements could be accepted without having been isolated in the form of simple substances.

In addition to Davy's work, I will evaluate the significance of the eventual isolation of aluminium for chemists at the time. The changing ways in which the story of aluminium was retrospectively told during the nineteenth and twentieth century explain why the first isolation of aluminium is generally thought of as its discovery today. I will therefore argue that the fact that the discovery of aluminium is generally attributed to Wöhler and Ørsted does not tell us anything about the criteria for elementary nature, but rather about the ways in which credit for scientific discoveries is attributed.

## The identification of aluminium as the metallic constituent of alumina

The chemical substance alumina was first identified in the middle of the eighteenth century. Ever since its identification, its similarities to metallic substances were noted and it was suspected that a metal would one day be produced from alumina. Around 1810, these

[48] I have made a similar argument elsewhere (Hijmans 2022a).

views of the composition of alumina became more specific, as chemists explicitly identified it as a metallic oxide containing a new metal called 'aluminium'. This section will retrace these different views of alumina up to the moment when aluminium was identified.

## Alumina: from earth to metallic oxide

In 1754, Andreas Sigismund Marggraf (1709-1782) chemically distinguished the 'earth of alum' from lime (calcium oxide) after isolating it from a salt called 'alum' that could be found in clay (Ferrand 1961, 21–22). This distinction replaced the element Earth with a series of earthy substances, insoluble and incombustible white powders without much taste or smell (see prologue). Guyton de Morveau proposed to rename this earth "alumina" (from the latin *alumen*) in order to distinguish it from argil. Alumina was characterized as a salifiable base, because it combined with vitriolic (sulphuric) acid to form the salt alum. Since alum resembled vitriolic salts that had a metallic base, chemists suspected that a metal might one day be produced from alumina. According to Macquer (1766, 112–17) for example, alumina had the remarkable property of changing colour depending on heat and humidity, which to him seemed to indicate its disposition of uniting with phlogiston. This indicated that alumina was likely "of metallic nature" (*ibid*., 117). Despite multiple attempts, no metal could be produced from alumina during the eighteenth-century (see for example Savaresi 1791).[49]

When Lavoisier published his table of simple substances, alumina had not been decomposed and he therefore listed it as one of the earthy salifiable simple substances (Lavoisier 1789, 192).[50] Nevertheless, he suspected, like his predecessors, that alumina would one day be reduced to a metal.[51] Lavoisier had a view of salt formation according to which the acids and bases were held together by oxygen and he therefore thought it was

[49] Alumina was used in the production of ceramics and therefore, as Fourcroy (1800, 2: 149) summarized, "l'histoire des connaissances acquises sur l'alumine est liée à celle des progrès des arts". Part of that history is discussed in Lehmann (2012).

[50] By 'salifiable', Lavoisier meant their capacity of combining with acids to form salts (see prologue). The other earthy salifiable simple substances in his table were lime, magnesia, barites and silica.

[51] In other words, Lavoisier inversed the view of alumina: whereas the production of a metal was presented as a combination with phlogiston in Macquer's account, the same reaction was a decomposition for Lavoisier.

likely that all salifiable earths were in reality oxides, likely metallic oxides (Siegfried 1982). Moreover, the earths were the only salifiable substances that did not readily combine with oxygen, probably resulting "from their being already saturated with that element" (Lavoisier 1790, 177). The impossibility to decompose alumina could be explained fairly easily: since there were no stronger reduction methods than heating with charcoal, the oxides of metals that had a higher affinity for oxygen than charcoal could not yet be reduced. Lavoisier therefore predicted that many metallic substances were still to be discovered, among which were those that might be produced from the earths. He insisted, nevertheless, that this was only a hypothesis: since they had never been decomposed and their composition was unknown, it was best to consider the earths simple for the time being.

Lavoisier's successors likewise suspected alumina to be a compound, while also admitting that it was technically still a simple substance. Thomas Thomson's second edition of *A System of Chemistry* provides a good illustration of the ambiguous view of the earths around this time. While admitting that the earths had to be considered simple because they had never been decomposed (1804, 1: 548-9), Thomson did not actually include them in the first book of his *System*, which was dedicated to the simple bodies. Instead he described all salifiable substances as 'primary compounds' and admitted that they could not "with propriety be introduced among the simple substances" (*ibid.*, 462). In his system, alumina was listed as one of twelve 'undecompounded bodies' that Thomson omitted from the first book of simple substances: all nine earths, the two fixed alkalis and an acid. In other words, Thomson distinguished between indecomposable substances and chemical elements, just as Lavoisier had implicitly done. In Thomson's case, this distinction was actually coherent with the way he defined chemical elements:

> "By simple substances is not meant what the ancient philosophers called elements of bodies, or particles of matter incapable of further diminution or division. They signify merely bodies which have not been decompounded, *and which no phenomenon hitherto observed indicates to be compounds*. Very possibly the bodies which we reckon simple may be real compounds; but till this has actually been proved, we have no right to suppose it" (Thomson 1804, 16; emphasis added).

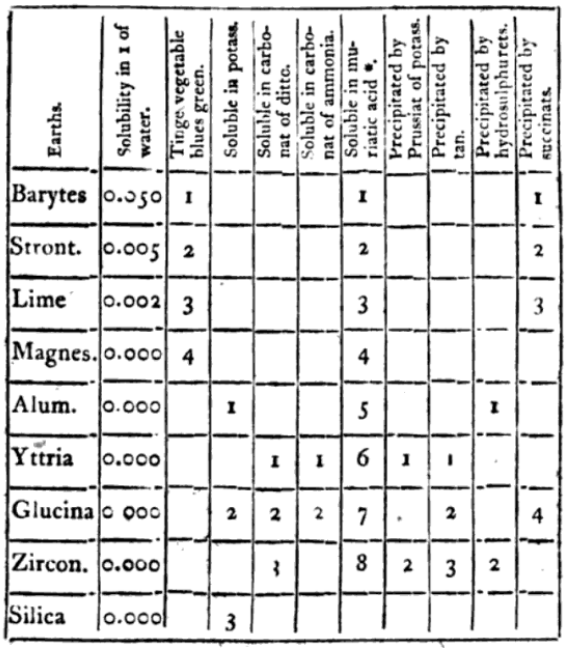
For Thomson, not all indecomposable bodies were chemical elements. If there were good reasons to believe that they were compounds, he implied that they should not be seen as

simple. Although this sounds fairly intuitive, it contradicted Lavoisier's rule of not supposing bodies to be compounds unless they had actually been decomposed.

In the case of alumina and the other 'undecompounded bodies', there were good reasons to suspect that they were compounds. Thomson provided two justifications for his distinction between undecompounded and simple bodies. Firstly, the undecompounded bodies resembled known compounds so closely that Thomson thought it would be "improper" (*ibid*., 452) to separate them from these compounds in a classification. This resemblance made it very likely that they too would one day be proven to be compounds. Specifically, the fixed alkalies (potash and soda) closely resembled the volatile alkali (ammonia) which had been shown to be a compound (*ibid*., 473). The earths in turn closely resembled the fixed alkalies, so much so that they could "scarcely be placed into different classes" (*ibid*., 545). Instead of separating between these bodies, he chose to view the entire class as (probable) compounds.

This first justification reflects Thomson's view of the salifiable substances as a group of substances that should always be classed together. Thomson (1804, 545–47), described the alkalies and earths as constituting a "regular series" that "graduate into each other": the extremities, potash and silica, significantly differed from each other, but the difference in properties from each body to the next was extremely small (see Figure 2). On one end, the series would be connected to ammonia through potash, and on the other, silica provided the link to the metallic oxides. Within the series of earths, one might distinguish between alkaline and common earths but those two groups should not be separated from one another, nor from the alkalis.[52] There was indeed some disagreement on whether and how to distinguish between the different groups of salifiable substances (for a summary of different views, see Gay-Lussac and Thenard 1811, 2:253–57).

[52] Thomson characterized the earths by the following properties: when pure, they had the form of a white powder with little or no taste and smell, of a density that did not exceed 4.9, that was insoluble (or poorly soluble in water), incombustible (and inalterable by the fire) and capable of being heated with combustible substances without reacting. The difference between the alkaline earths (lime, magnesia, barite and strontian) and the common earths (alumina, yttria, glucina, zircon and silica) was that the former coloured vegetable blues green and neutralised acids, whereas the latter did neither. Thomson did not effectively apply the distinction between alkaline and common earths until the third edition of his textbook (Thomson 1809, 365).



| Earths. | Solubility in 1 of water. | Tinge vegetable blues green. | Soluble in potass. | Soluble in carbonat of ditto. | Soluble in carbonat of ammonia. | Soluble in muriatic acid *. | Precipitated by Prussiat of potass. | Precipitated by tan. | Precipitated by hydrosulphurets. | Precipitated by succinats. |
|---|---|---|---|---|---|---|---|---|---|---|
| Barytes | 0.050 | 1 | | | | 1 | | | | 1 |
| Stront. | 0.005 | 2 | | | | 2 | | | | 2 |
| Lime | 0.002 | 3 | | | | 3 | | | | 3 |
| Magnes. | 0.000 | 4 | | | | 4 | | | | |
| Alum. | 0.000 | | 1 | | | 5 | | | 1 | |
| Yttria | 0.000 | | | 1 | 1 | 6 | 1 | 1 | | |
| Glucina | 0 000 | | 2 | 2 | 2 | 7 | | 2 | | 4 |
| Zircon. | 0.000 | | | 3 | | 8 | 2 | 3 | 2 | |
| Silica | 0.000 | | 3 | | | | | | | |

*FIGURE 2 - Table representing "some of the characteristic properties of the different earths" (Thomson 1804, 547). Solubility is the only measured property; the other numbers simply indicate that the substance has the property, showing that they form a gradual series. Source: Google Books.*

Thomson's second reason for excluding the undecompounded bodies from his first book of simple substances was that their inclusion would have disturbed the logical arrangement of the first book. According to Thomson, the thirty-two simple bodies in his first book constituted "a beautiful whole, which has much more of scientific arrangement than any other part of chemistry is yet capable of assuming" (*ibid*., 453). Thomson saw the simple bodies as connected to each other, either by common properties or by their way of reacting with oxygen. The fact that he did not see such connections between the earths and alkalis on the one hand, and the rest of the indecomposable bodies on the other, justified their exclusion from the book of simple bodies.[53] Thomson's second justification for the separate identification of a group of undecompounded substances shows that he did not see classifications of chemical bodies as mere lists of indecomposable substances but rather as

[53] Thomson did not believe the earths would turn out to be metallic oxides because "the properties of most of them [the earths] are so exceedingly different from those of metallic oxides, that the supposition of their being composed of the same ingredients is contrary to every fact, and to every analogy with which we are acquainted" (Thomson 1804, 549).

more complex arrangements. Any indecomposable substance that did not fit into such a classification was less likely to be a simple body. Fourcroy (1800, 111–15) made the same decision to exclude all salifiable bases from the simple substances and justified it by the same reasons, which gives reason to think that Thomson's view was not just an exception. I will further discuss this distinction between chemical elements and indecomposable bodies below.

In short, in the early nineteenth century, chemists saw alumina as a body that was likely composed, but as of yet undecompounded. Analogical inferences regarding the possible constitution of alumina date back to the eighteenth century but it remained impossible to produce a metal from alumina. Lavoisier and his followers suspected that alumina was a compound but they were still relatively cautious when it came to formulating hypotheses regarding its exact composition – sometimes resulting in seemingly contradictory statements. Thomson and Fourcroy classified it as an indecomposable compound.

Around 1810, chemists' view of alumina changed: instead of just being suspected to be a compound, it explicitly came to be accepted as one (see Table 1).[54] Moreover, a new metal appeared in textbooks and classifications of simple substances: aluminium, the metallic constituent of alumina. This shows that aluminium was already commonly thought of as a chemical element, years before it was effectively isolated. I argue that it was Davy's work on the decomposition of the earths that caused this shift.

[54] The exception to this was Dalton (1810, 1 part 2:504) who remained sceptical of aluminium in 1810. It must be noted, however, that Dalton also did not accept the compound nature of the fixed alkalis either: he saw potassium and sodium as compounds of the alkalis with hydrogen (*ibid*., 467-68). Despite all of this, he did class both the earths and the fixed alkalis as 'compounds of two elements'.

| | (1) | (2) | (3) | (4) | (5) | (6) |
|---|---|---|---|---|---|---|
| Lavoisier (1789) | X | | | X | | |
| Fourcroy (1800) | | | X | | | |
| Thomson (1802) | | X | X | X | | |
| Thomson (1804) | | X | X | X | | |
| Thomson (1807) | | X | X | X | | |
| Berzelius (1808b) | | X | X | | | |
| Thomson (1810) | | | X | | | X |
| Dalton (1810) | | X | X | | | |
| Berzelius (1811a) | | | X | | X | X |
| Berzelius (1812a) | | | X | | X | X |
| Davy (1812) | | | X | | X | X |
| Thenard (1813) | | | X | | X | X |
| Chevreul (1816) | | | X | | X | X |
| Thenard (1817) | | | X | | X | X |
| Berzelius (1817) | | | X | | X | X |
| Thomson (1817) | | | X | | X | X |
| Deterville (1818) | | | X | | X | X |
| Thenard (1821) | | | X | | X | X |
| Delafosse (1822) | | | X | | X | X |
| Thenard (1824) | | | X | | X | X |
| Berzelius (1825a) | | | X | | X | X |

*Table 1 - Overview of different characterizations of alumina and aluminium in textbooks, classifications and dictionaries, showing how they evolved over the course of multiple editions. (1) Alumina classed with simple substances; (2) Alumina explicitly stated to be an undecompounded substance; (3) Alumina classed with compounds; (4) Alumina suspected to be a compound; (5) Aluminium classed with simple substances; (6) Aluminium named as a metal.*

## Davy's experiments on the decomposition of the salifiable substances

In the Bakerian lectures of 1806 and 1807, Davy had announced the decomposition of the fixed alkalis, soda and potash, and argued that they were compounds of oxygen and the previously unknown metals sodium and potassium.[55] Generalizing from this result, he speculated that the property of being composed of oxygen and a metal likely extended to the entire class of salifiable substances:

> "From analogy alone it is reasonable to expect that the alkaline earths are compounds of a similar nature to the fixed alkalies, peculiar highly combustible metallic bases united to oxygene. I have tried some experiments upon barytes and strontites; and they go far towards proving that this must be the case. (…) Barytes and strontites have the strongest relations to the fixed alkalies of any of the earthy bodies; but there is a chain of resemblances, through lime, magnesia, glucina, alumina, and silex. And by the agencies of batteries sufficiently strong, and by the application of proper circumstances, there is no small reason to hope, that even these refractory bodies will yield their elements to the methods of analysis by electrical attraction and repulsion" (H. Davy 1808b, 41–42).

In other words, Davy followed a similar reasoning as Thomson had when it came to the constitution of the salifiable bodies: the earths resembled the alkaline earths which in turn resembled the alkalis; since the alkalis were now shown to be compounds, the other substances likely had a similar constitution. Furthermore, the decomposition of the alkalis further increased the plausibility of the idea that all salifiable substances might be metallic oxides. In this reasoning, Davy relied on chemical analogies as a way to formulate working hypotheses and design experiments to test them (see Fisher 2018).

In order to test his hypothesis, Davy (1808a) first attempted the decomposition of the alkaline earths since they were most similar to the fixed alkalis. This proved to be a lot more difficult than decomposing soda and potash, and multiple attempts using different methods failed. Davy's battery had started to corrode and he felt that it had lost part of its power. He had to wait for the construction of a new battery, consisting of 500 six square inch plates, which was finished in May 1808 (*ibid.*, 339). Using a method developed by

[55] Following the Lavoisian method of naming metals, the names sodium and potassium were simply meant to mean "the metals produced from potash and soda" (H. Davy 1808b, 32).

Berzelius and Pontin (1808), he was able to form an amalgam (an alloy of mercury) of the metallic constituents of the alkaline earths and distil away the mercury. The method consisted in moistening the alkaline earths, mixing them with red mercury oxide and electrifying this mixture using a globule of mercury as the negative electrode. As a result, the metallic bases of the alkaline earths formed amalgams with the mercury, which Davy then distilled in glass tubes in order to evaporate the mercury. Complete distillation was quite difficult because the heat required for the distillation of the mercury caused the bases of the alkaline earths to react with the glass.[56] Despite these difficulties, Davy could ensure himself that he produced enough of the new metallic substances to describe their properties and prove that he had decomposed barite, strontian, lime and magnesia. Following the same principle as for the fixed alkalis, he chose the names of barium, strontia, calcium and magnium.[57]

The next step was to decompose the common earths, one of which was alumina. This proved even more difficult, and Davy tried various methods (H. Davy 1808a; 1810c). Besides the formation of an amalgam, he attempted to decompose a mixture of alumina and potash using platinum electrodes. When he inserted a negatively electrified platinum rod into the mixture, he observed the production of a lot of light as well as globules that rose to the surface and immediately burned. He left the mixture to cool and saw that the platinum rod was heavily corroded and covered in a thin metallic film. When he treated this metallic film with acid, alumina was recovered from it. Next, Davy heated alumina in a platinum tube and passed potassium vapour over it; this produced tiny metallic particles on top of the remaining alumina. He was also able to fuse together potassium, iron filings and alumina to form a metallic mass that was whiter and harder than iron but still malleable, and from which iron oxide, potash and alumina could be reproduced.

Though the results of these experiments gave some reason to think that alumina had been decomposed, Davy did not consider this proven. In 1808, Davy (1808a, 352) stated that there was "very great a reason" to believe that alumina was a metallic oxide, because

[56] These difficulties illustrate the fact that even decomposition methods rarely produced pure simple substances because it was hard to keep them from reacting with other substances as soon as they were produced.

[57] Magnium was later renamed magnesium. Davy could not choose the name magnesium at the time because it had been used by Bergman to describe manganese (H. Davy 1808a, 346).

this was the simplest explanation of the phenomena. After he had finished his experiments on the earths, Davy (1812, 356) concluded in his *Elements of Chemistry* that "it [could] not be doubted" that alumina was an oxide. Moreover, although the metallic nature of aluminium could not yet be considered demonstrated, he argued it was "very likely, both from the facts detailed, and from analogy". How come Davy argued he had identified a new metal without isolating it? What was the role of analogy in his argumentation? The next section will answer these questions.

# Chemical analogy as evidence in favour of aluminium

Before the acceptance of aluminium as a metal can be considered, we must first take into account the evidence supporting Davy's claim. In Davy's words, the "evidences" in favour of the decomposition of alumina were not "of the same strict nature as those that belong to the fixed alkalies and alkaline earths" (H. Davy 1808a, 352). Whereas he was able to establish the composition of the latter group of substances by isolating their constituent metals, the internal composition of alumina remained inaccessible. Davy therefore had to rely on analogical reasoning as additional evidence of its nature. In accepting the elementary nature of aluminium, Davy's contemporaries followed a similar reasoning.

## The evidence in favour of aluminium

In order to understand Davy's argumentation in favour of the existence of aluminium, we might compare it to the way in which he defended his discoveries of the alkaline earth metals. Davy's experiments on magnesia, lime, barites and strontium produced enough of the constituent bases of these substances to show that they had the properties usually associated with metals, such as lustre, opacity, combustibility, and the conduction of heat and electricity (H. Davy 1808a, 343–46).[58] Strontium and barium had a white metallic shine and could be fused and flattened. They were heavier than water and reacted with oxygen from the air to form oxides, that were the alkaline earths. Calcium was difficult to

[58] Before the isolation of potassium and sodium, which were very light, an additional property of the metals was their high density (H. Davy 1812, 319).

study because it oxidised too rapidly when exposed to air, but before it burned it had the colour and shine of silver. Magnesium was very hard to purify because it also burned before the mercury was completely distilled; however, Davy was able to observe that it had the same colour and shine as the other metals he isolated. It was also heavier than water.

Furthermore, all of these new metals combined with oxygen to form the corresponding alkaline earth.[59] Though he could not determine the proportion in which the metals combined with oxygen, he was able to reproduce the alkaline earths from the metals he had isolated and reported that they became heavier as they combined with oxygen – a sign that this reaction was indeed a combination.[60] Lastly, the alkaline earths were decomposed by electricity in a similar way as metallic oxides, producing the metal at the negative pole and oxygen at the positive pole of the voltaic pile. Davy (1808a, 346) therefore concluded that the evidence for his claim regarding the composition of the alkaline earths was "of the same kind" as that invoked in support of the composition of all other metallic oxides.

Davy had relied on a very similar argumentation in favour of the metallic nature of the alkaline metals, sodium and potassium, a few years earlier. Among others, Gay-Lussac and Thenard claimed that potassium was a compound and Davy therefore had to defend his claim that there were elementary. Robert Siegfried (1963) has shown that Davy emphasized the analogies between sodium and potassium and the other metals in order to show that he had carried out a decomposition and produced two new chemical elements. Sodium and potassium looked and behaved like metals, and since metals were generally accepted to be (at least provisionally) simple, potassium and sodium should be accepted as such as well. Furthermore, Davy argued that the decomposition of potash and soda was analogous to the

[59] This may have also been a way for Davy to ensure that the new metals he isolated were not artefacts, because he was able to reproduce the original substance. Indeed, Klein and others have pointed out the need for synthesis as a confirmation of analytical results, see for example Klein (2014) or Klein and Lefèvre (2007, sec. 6.3).

[60] On weight as the proof of composition, Davy (1812, 182) stated: "By analysis compounded bodies are resolved into their constituents; by synthesis they are produced in consequence of the union of these constituents; and when the weight of the compound corresponds to that of the constituents, the processes are considered to be accurate."

decomposition of other metallic oxides.[61] The examples of the alkaline and alkaline earth metals show that even the isolation of a new simple substances required the support of analogical arguments in order to show that they were indeed simple.

Davy could not rely on the same arguments in the case of aluminium, because his decomposition attempts had not yielded the same results. For example, he saw two possible explanations for the production of metallic particles by potassium vapour: either the potassium had decomposed alumina and produced tiny quantities of the earth's metal, or potassium had entered into combination with the earth, forming these little particles. The latter, he said, was "unlikely, and contrary to analogy" (H. Davy 1810c, 61), but it could not be completely ruled out. The metallic film was also likely to be a film of aluminium resulting from a decomposition of alumina, but the quantity of metal produced was too small to study its properties or to detect any weight change as alumina was reproduced. Likewise, Davy was unable to definitively identify the metallic mass he had produced: it was likely to be an alloy of aluminium and iron, especially since he had succeeded in producing alloys of calcium and magnesium by the same method. However, it could have also been a mixture of iron, potassium and alumina.

Despite these difficulties, Davy argued that alumina should be seen as a metallic oxide and its constituent aluminium as a metal. Chemical analogy provided him with the additional evidence in favour of his claim. The nature of the alkaline earths had been established experimentally and Davy therefore argued that all of the salifiable substances should be classified as metallic oxides. Until that time, the salifiable bases (common earths, alkaline earths and alkalis) had been distinguished from the oxides according to the following properties: the earths generally were not precipitated by triple prussiates or tincture of galls, and the alkalies and alkaline earths were soluble in water (though the common earths were not). However, Davy (1810c, 64–66) argued that if these differences were seen as sufficient in order to separate between the earths and oxides, one should also separate the oxides into different classes. In other words, he argued that the differences

[61] In their *Recherches Physico-Chimiques*, Gay-Lussac and Thenard (1811, 2:257) explained how they eventually came to accept sodium and potassium as metals.

among the metallic oxides themselves were larger than the differences between the salifiable substances on the one hand and the oxides on the other:

> "Platina and gold in specific gravity, degree of oxidability, and other qualities, differ more from arsenic, iron, and tin, than these last do from barium and strontium. The phaenomena of combustion of all the oxidable metals are precisely analogous. In the same manner as arsenic forms an acid by burning in air, potassium forms an alkali and calcium an earth;" (H. Davy 1808a, 364).

Moreover, he argued the similarities between earths, alkalis and oxides should outweigh their differences:

> "The oxide of tin and other oxides abounding in oxygene, approach very near in their general characters to zircon, silex and alumine; and in habits of amalgamation, and of alloy, how near do the metals of the alkalies approach to the lightest class of oxidable metals? It will be necessary, I trust, to pursue these analogies any further" (H. Davy 1810c, 66).

This was true especially since Davy had been able to show the alkaline earths to be metallic oxides, because this meant that the earths were extremely similar to a group of newly decomposed metallic oxides. The reclassification of the entire family of salifiable substances would enable them all to be included in a new coherent classification without having to separate them into different classes.

For Davy, these similarities - chemical analogies - between the different salifiable substances made it likely that they were all similarly composed. As Davy (1812, 480) stated, "as far as our knowledge of the nature of compound bodies has extended, analogy of properties is connected with analogy of composition". This meant that proof of the internal composition of one body pointed towards an analogous composition for analogous bodies. In other words, if some of the salifiable substances were proven to be metallic oxides, the others should also be accepted as metallic oxides. Even if it violated the negative-empirical criterion, Davy argued it was justified to adjust classifications on the basis of this inference because it would result in a classification that reflected the chemical analogies between substances. It was more important to respect those analogies in order to form a coherent classification rather than to respect *à la lettre* the rule of never supposing an indecomposable body to be compound. Davy was therefore implicitly working with a

similar distinction as Thomson: just because a body could not be decomposed, this did not necessarily mean that it should be seen as a chemical element.

For Davy, the justification of the reclassification of the entire group of salifiable substances as metallic oxides lay in the idea that analogies between chemical substances would last even as further facts about their inner constitution would be discovered. According to Davy (1808b, 33), no matter the future discoveries regarding the internal constitution of his newly identified simple bodies, their classification as metals would still remain valid:

> "Whatever future changes may take place in theory, there seems however every reason to believe that the metallic bases of the alkalies, and the common metals, will stand in the same arrangement of substances; and as yet we have no good reasons for assuming the compound nature of this class of bodies."

Elsewhere, he stated that even if the metals might one day be proven not to be absolutely simple substances, "still the alkalies, the earths, and the metallic oxides will belong to the same class of bodies" (H. Davy 1808a, 363–64). Names such as 'aluminium', 'potassium' or 'sodium', meaning 'the metals from alumina, potash or soda', could not be proven to be wrong, for even if these metals were shown to be compounded in the future, they would still be classified as metallic constituents of these compounds. The realization that alkalis and alkaline earths were compounds did not affect the chemical analogies that existed between them, and likewise the metals would still be analogous to each other even if it turned out that they were all compounds.

For Davy, chemical analogy was therefore perhaps even more important than experimental simplicity because it was more durable. More than anyone, Davy was aware that the limits of empirical indecomposability could shift rapidly: after all, he himself had worked on developing methods to decompose previously indecomposable substances. It seemed perfectly plausible to him that this method would be further perfected, or that other technologies would be invented that could enable new decompositions. This made the identification of undecomposed substances even more provisional, because there was no guarantee that they would not be decomposed shortly thereafter. Chemical analogies, on the other hand, were established independently of the ultimate composition of the classified substances, and would remain valid irrespective of the future discoveries regarding their

internal constitution. This idea constituted a counterargument against the worries that Davy's newly discovered simple substances might actually be composed: since they were analogous to substances which were generally considered simple, there was no reason to suppose them to be compounds. This way, classification based on analogy provided a guide in navigating the uncertainty of the 'true' simplicity of the provisionally accepted elements and resolve the uneasy feeling that resulted from the impossibility of knowing the ultimate nature of the simple substances.

## The role of analogy in the acceptance of aluminium as a metal

Other chemists readily accepted the existence of aluminium on the basis of Davy's analogical reasoning, even though they still considered alumina to be an indecomposable substance. Among the first to accept the existence of aluminium was Berzelius, who listed aluminium as one of the metals and even classified it according to electronegativity in his 1811 essay on chemical nomenclature (Berzelius 1811a). He did so without offering any reflection on its acceptance as a simple substance which indicates that he did not see this as a controversial decision. In 1816, he explained his acceptance of aluminium in a reflection on the use of analogical argument in chemistry:

> "Since Davy has discovered that the alkalies and alkaline earths are true oxides, we conclude that alumina, zirconia, glucina, and yttria, are likewise oxides, although hitherto nobody has succeeded, so far as I know, in his attempt to separate oxygen from these bodies. Yet no chemist has any doubt about the accuracy of the conjecture, as he sees the analogy between these bodies and the oxides of zinc, manganese, cerium, &c." (Berzelius 1816, 263–64).

In this citation, Berzelius emphasized the importance of analogy in the acceptance of alumina as a metallic oxide and argued in favour of it. Indeed, he did not base his acceptance of aluminium on Davy's experiments alone, since he did not consider them as sufficient proof of the compound nature of alumina.[62] Dictionaries from this period confirm Berzelius' claim that aluminium was accepted by all or most chemists (Chevreul 1816; Delafosse 1822; Deterville 1818, 378).

[62] Later, Berzelius also referred to the "dubious success" ("zweifelhaftem Erfolge*"*) of Davy's attempts of the isolation of the metal (Berzelius 1827a, 6:118).

Thenard likewise accepted the elementary nature of aluminium. In his *Traité de Chimie* (1813, 208), he named aluminium as part of a family of metals which was accepted based on analogy, despite never having been isolated:

> "Six of [the 38 metals] have not yet been obtained, and are admitted as metals by analogy, or because the materials from which we extract them have the strongest relations with the metallic oxides. These six presumed metals are silicon, zirconium, aluminium, yttrium, glucinium and magnesium."[63]

Thenard explained the impossibility of isolating these six metals based on their presumed high affinity for oxygen. In the chapter on oxides, he stated why he thought they should be accepted as metals:

> "Before the works of M. Davy, these salifiable bases [silica, zirconia, alumina, yttria, glucina and magnesia][64] were seen as simple bodies; we could even see them as such today, because as of yet no different bodies have been separated out of them; but there are such strong relations between these types of bases and the former salifiable alkaline bases, that is, lime, baryte, strontian, potash and soda, that it is extremely probable that they are all of the same nature. Now, it is proven that the latter are truly oxides: so we must also, by analogy, accept the former to be oxides;" (Thenard 1813, vol. 2 pp. 36–37).[65]

[63] "Six d'entre eux [les 38 métaux] n'ont point encore pu être obtenus, et ne sont admis qu'au rang des métaux par analogie, ou parce que les matières d'où nous les extrayons ont les plus grands rapports avec les oxides métalliques. Ces six métaux présumés sont le silicium, le zirconium, l'aluminium, l'yttrium, le glucinium et le magnésium." Note that Thenard included silicon as a metal, which was still fairly common at the time. Davy had originally named it silicium but Thomson (1817, 1: 252) argued it should be renamed 'silicon' because of its similarities to carbon and boron. Silicon was eventually isolated by Berzelius, see below.

[64] Note the difference between Thomson, Davy and Thenard's classification of these bodies: magnesia was sometimes classified as a common earth, and by others as an alkaline earth. According to Thomson (1804, vol. 1 p. 546) it could be seen as the link between the two groups, since it had properties that were perfectly intermediary between the two. Surprisingly, it appears that Thenard considered Davy's isolation of magnesium to be unsuccessful as well.

[65] "Avant les travaux de M. Davy, on regardait ces bases salifiables comme des corps simples ; on pourrait même encore aujourd'hui les regarder comme tels, puisqu'on n'en a point encore séparé des corps différéns ; mais il y a de si grands rapports entre ces sortes de bases et les anciennes bases salifiables alcalines, savoir, la

Thenard therefore followed the same reasoning as Berzelius. Similarly, Thomson (1817, 363) stated that Davy's experiments left "little doubt on the subject, though he did not succeed in obtaining the metal in a separate state." In the fifth edition of Thomson's system, aluminium became part of a family of metals, together with yttrium, glucinium and zirconium, which were characterized by forming compounds that were "formerly distinguished in chemistry by the name of *earths proper*" (Thomson 1817, 356). Seeing the characterization of aluminium in these accounts, it becomes clear that chemists accepted aluminium as a metal based on Davy's results, despite judging his decomposition attempts as unsuccessful. This was because the evidence was supported by analogies that pointed to the existence of a metal called aluminium.

Here I have discussed only a relatively small sample of chemists accepting aluminium, but the views of Berzelius, Thenard and Thomson were influential in the chemical community at the time. Thenard's textbook was used by the French Ministry of Public Instruction as the model for chemistry education, and his classification of substances was copied by most French textbooks of the early nineteenth century. It was incredibly successful in France, running for six editions and selling more than 18.000 copies (Bensaude-Vincent, García Belmar, and Bertomeu Sánchez 2003, 82). Berzelius' *Lärbok i Kemien* likewise ran for many editions and its translations in five languages enjoyed a tremendous success (Jorpes 1970, 94–96). Thomson's *System* was equally successful, with new editions continuing to be published between 1802 and 1831. These three textbooks can be seen as the standard textbooks of the time (Bensaude-Vincent, García Belmar, and Bertomeu Sánchez 2003, 82–83). Any views defended by their authors would have been known by a large audience.

The discovery of the internal composition of some of the salifiable substances did not affect the classification of the salifiable substances as such: they remained a single group of substances, and the proof that some of them were metallic oxides sufficed for the others to be viewed as metallic oxides as well. Thenard (1813, 2: 36) classed the earths as

chaux, la baryte, la strontiane, la potasse et la soude, qu'il est extrêmement probable qu'elle sont toutes de même nature. Or, il est prouvé que celles-ci sont de véritables oxides : dont on doit aussi, par analogie, mettre celles-là au rang des oxides ; de même qu'on a mis l'acide borique au rang des corps brûlés, longtemps avant d'en avoir opéré la décomposition."

compounds despite the impossibility of decomposing them. This way, the class of salifiable bases remained intact, moving as a whole from the rank of simple bodies to that of compounds. Thenard created two new families of metals consisting of the constituents of the salifiable bases, one of which contained only postulated substances. Similarly, Thomson (1817) left the family of common earths intact, and classified their supposed metallic constituents as a separate family of metals.[66] Alumina had long been classified as part of a well-established group of bodies, and keeping this group together was more important than strictly adhering to the definition of a simple body as an indecomposable substance: after all, the impossibility of decomposing certain substances could simply be due to the unavailability of adequate decomposition techniques, which might be developed in the future.

Some chemists included this condition in their definition of the chemical element, as Thomson had done in his *System.*[67] Berzelius (1808b, 6) distinguished even more explicitly between simple and undecompounded bodies. In his *Lärbok*, he divided the ponderable bodies into three types: simple bodies, undecompounded bodies and compounds. He formulated the distinction between 'simple' and 'undecompounded' as follows:

> "We call *simple* bodies those of which we believe to know with complete certainty that they are not composed, and which we encounter everywhere as constituents of the rest of nature. (...) We call *undecompounded* those bodies which we have valid reasons not to regard as simple, but which we have not yet been able to decompose into simpler elements, and whose constituent parts, in case these bodies were composed, are still completely unknown to us."[68]

[66] Except for silicon; it had become clear that this substance was more closely related to carbon and boron than to the metals (see Partington 1964, 4:150).

[67] This definition remained the same throughout the different editions of Thomson's *System.*

[68] "*Enkla* kroppar kalla vi sådana, som vi tro oss med full säkerhet veta icke vara sammansatta, och hvilka öfverallt träffas såsom beståndsdelar af den öfriga naturen. (…) *Odecomponerade* kallas sådana kroppar, som vi väl icke hafva giltiga skäl att anse för enkla, men som vi icke hafva kunnat åtskilja i några enklare grundämnen, ock hvilkas beståndsdelar således, i fall de äro sammansatta, hittils äro fullkomligt obekannte." Emphasis original. Berzelius retained this distinction in later editions of the textbook.

This definition of simple substances, as well as the decision to include aluminium among the metals despite the fact that it had never been isolated, show that early nineteenth-century chemists relied on multiple types of evidence in order to identify the composition of substances. The impossibility of decomposing a substance could be due either to their actual simplicity, or to the insufficiency of the means of decomposition. The impossibility of decomposing a substance was not sufficient for it to be seen as simple if there was other evidence pointing in the direction of it being composed. In the case of alumina, the analogies that indicated that it was a metallic oxide provided sufficient evidence for it to be seen as a compound. Alumina was no longer simply an undecompounded body: from 1810, it was commonly viewed as a compound of which the constituents were known.

## The retrospective attribution of credit for the discovery of aluminium

In the previous section, I have shown how Davy's work on the decomposition of the earths provided sufficient evidence for chemists to accept the elementary nature of aluminium. Yet, this episode is often excluded from its discovery. Helge Kragh (2019, 85), for example, has claimed that aluminium "was known to exist and Davy had even coined a name for it …, but it had not yet been discovered." This statement seems very contradictory: how come aluminium could be discovered if it was already known to exist? Kragh probably meant that the credit for the discovery was retrospectively attributed to Wöhler (and later reattributed to Ørsted) rather than Davy. But if aluminium came to be accepted as an element following Davy's work on the subject, how come he is not seen as its discoverer? Where does this focus on the moment of isolation in the form of a simple substance come from? What was the perceived significance of the isolation of the metal at the time? This section will answer these questions by showing how the story of aluminium has been told and retold over the centuries, and thereby point towards a broader reflection on the construction of discovery stories. I will begin by explaining how aluminium eventually came to be isolated.

## The production of pure aluminium

Davy's publications on aluminium are relatively unique in that they describe failed decomposition attempts in a detailed way. He may have done so in order to attach his name to aluminium early, because he was aware others were working on similar questions. Increasingly throughout the nineteenth century, chemists tended not to publish failed attempts at isolating substances, and this makes it difficult to know how many people tried to isolate aluminium during the fifteen years following Davy's work. However, multiple European chemists were studying the earths and how to decompose them, such as glucina (beryllium oxide), zirconia (zirconium dioxide) and silica (silicon dioxide), and it is likely they also experimented with alumina. Moreover, there is evidence that a small group of chemists exchanged on alumina and related topics; though we can only speculate what they discussed while meeting in person, some of their exchanges can be traced via correspondence.

One of these chemists was Berzelius. In April 1824, Berzelius (1912b, 69–71) wrote to Davy about his recent work on silica; using potassium, he was able to decompose double fluorides of silicon and potassium or sodium. Once he had isolated silicon using this method, Berzelius tried it on other earthy substances that could form similar double fluoride salts.[69] He succeeded in producing zirconium but his attempt to isolate aluminium failed because of the difference in solubility of the aluminium salts.[70] Contrary to Davy, Berzelius did not publish a detailed description of his attempt at decomposing alumina. He did not mention this work in his 1824 article on the decomposition of silica, and only vaguely alluded to it in a later publication (Berzelius 1824; 1827a, 6:6). He did, however, exchange with other chemists about his work on the earths. Wöhler was his student and assistant when he isolated silicon and zirconium in 1824. The same year, Ørsted was visited by Davy in Copenhagen and the two men went to Sweden, where they spent a few days traveling with Berzelius and Wöhler. During this and other encounters that summer, it can

[69] A natural occurrence of such a double fluoride salt is the mineral cryolite, which would later become an important source of aluminium (see Kragh 1995).

[70] Wöhler (1827, 158) later explained that Berzelius likely used too much potassium, which made the solution alkaline and caused the aluminium to dissolve.

be assumed that they discussed their work on the previously indecomposable earths (Christensen 2013, 425–27).

These exchanges demonstrate that there was a network of European chemists working on the isolation of aluminium and other similar issues. The decomposition of the earths was a well-known chemical problem, and Davy had shown how rewarding such an endeavour could be. For instance, according to Dan Christensen (*ibid*., 426), Ørsted's interest in this topic could be explained by an admiration for Davy and the wish to arrive at similar achievements: he started investigating the earths in 1823 following a trip to England where he visited Davy. Berzelius had already spent decades investigating this question, in collaboration with many of his students and colleagues.[71] The exchange of knowledge between these chemists was crucial for the eventual successful isolation of aluminium.

In early 1825, Ørsted presented a lump of aluminium at the Danish Academy of Sciences. His method consisted of two steps: first he produced anhydrous aluminium chloride by heating chlorine, alumina and charcoal in a porcelain tube. The resulting chloride was then heated with a potassium amalgam, producing potassium chloride and an aluminium amalgam. Out of this amalgam, the mercury could be evaporated, leaving behind a lump of tin-like metal. Ørsted did not inform Berzelius or Davy of this result, and he did not announce it as a discovery in any official way. The work was abstracted in the *Journal für Chemie und Physik*, but despite three reminders from its editor, Johann Schweigger (1779-1857), Ørsted did not provide a longer German version. Altogether, his findings failed to attract much interest (Christensen 2013, 428–29).

In September 1827, Wöhler visited Ørsted, who showed him his method for producing aluminium from its chloride and encouraged him to investigate the metal further since Ørsted did not have the time to do so himself. That same year, Wöhler's first paper on aluminium was published in the *Annalen der Physik* (Wöhler 1827). After his trip to Denmark, Wöhler had tried to replicate Ørsted's experiments but found that he could not obtain the same results. The distillation of the amalgam produced a grey metallic mass,

[71] Besides Wöhler, John August Afwerdson (1792-1841) also studied the earths in Berzelius' lab, for instance. On Berzelius' life and work see Jorpes (1970).

which released a green gas when heating intensified and left behind only potassium. He therefore started looking for a different method and found that he succeeded by exchanging the potassium amalgam with pure potassium. He heated aluminium chloride and potassium together in a platinum crucible, which produced a liquid black-grey mass. Once the mixture cooled down, the remaining potassium chloride could be dissolved in water in order to leave behind a metallic powder, which Wöhler believed to be pure aluminium.

As Wöhler himself acknowledged, his isolation of aluminium clearly built on his predecessors' work. Wöhler cited Davy, who in his view had succeeded in reducing aluminium without being able to separate it from the other reaction products. He also cited Ørsted's "ingenious" method for producing aluminium chloride which constituted an essential step in his new method. However, on the basis of his own replication, Wöhler concluded that Ørsted's method did not yield pure aluminium. Wöhler explained that he had not intended to get involved in someone else's unfinished research, but that it was Ørsted himself who encouraged him to continue the work on aluminium. It seems that Ørsted wasn't too interested in obtaining priority for the isolation of aluminium, as he did not contradict Wöhler on the impurity of his sample; in a lecture on the subject in January 1828, he admitted that his lump of aluminium may have indeed contained potassium (Christensen 2013, 430). There were no signs of bad feelings or rivalry between him and Wöhler. Thus, in absence of any real debate, the consensus was that Wöhler had been the first to successfully isolate aluminium. Wöhler continued his investigation of aluminium, announcing in 1845 that he had produced small globules of the fusible and flexible metal, which could be hammered into thin sheets without tearing (Wöhler 1845).

The first successful isolation of a metal was of course a very prestigious achievement. When it came to the elementary nature of aluminium, however, Wöhler's results were more so a confirmation of something that was already known. In the years following Wöhler's publication, no one seems to have thought that aluminium had just been 'discovered': Wöhler was seen as the first to isolate a metal which had already been predicted to exist. For instance, in his annual report on the progress of chemistry, Berzelius (1829, 8:108) reported that aluminium, "which so many chemists sought to isolate in vain", had "at last" been produced by Wöhler, thereby adjusting his earlier reporting of Ørsted's attempts as a success (see Berzelius 1827a, 6:118). Likewise, textbooks descriptions of aluminium were

adapted to include Wöhler's isolation of the metal (for example Dumas 1828, 399; Thenard 1834, 200; Gmelin 1843, 289). Some mentioned only Wöhler, whereas others cited a varying number of predecessors; none, however, identified Wöhler as the 'discoverer' of aluminium. As the chemistry professor of University College London, Edward Turner (1796-1837), summed up in his textbook:

> "That alumina is an oxidized body was proved by Davy (...); and it was inferred, chiefly by analogical reasoning, to be a metallic oxide. The propriety of this inference has been demonstrated by Wöhler, who has procured *aluminium* (…) in a pure state" (E. Turner 1834, 501).

The fairly unproblematic recognition of Wöhler as the first to isolate aluminium became an issue again when aluminium came to be recognized for its industrial potential. Deville's work on aluminium changed its status from merely one of the metals to an important commodity, a discovery with tremendous economic stakes.

## (Re)telling the story of aluminium

Around the middle of the century, the properties of the earths and different types of metallic compounds remained a topic of investigation for a number of chemists, one of which was Henri Sainte-Claire Deville.[72] After studying under Jean-Baptiste Dumas (1800-1884), Deville's impressive results from his research on mineral waters in Besançon earned him a position at the Ecole Normale Supérieure (ENS) in Paris. Upon his arrival there in 1851, he acquired government funding to set up a teaching laboratory where he investigated the properties of various metals and metallic compounds. Deville's arrival in Paris marked the beginning of an especially close friendship to his old professor, which lasted for the rest of his life and likely influenced his research interests. Indeed, his choice to study metals coincided with a reawakening of Dumas' interest in classifying the elements, which required detailed knowledge of chemical elements and their compounds (Klosterman 1985).

In February 1854, Deville (1854a) presented a new method to produce large quantities of pure aluminium to the French Academy of Sciences. Deville's (1854a) method for the

[72] For biographical information on Deville, see Paquot (2005).

isolation of aluminium was similar to Wöhler's, but instead of potassium, he used sodium for the reduction of aluminium chloride. The distillation of the excess aluminium chloride yielded metallic globules which could be fused together. In August 1854, he announced a second method to produce aluminium, using electrolysis as Davy had initially tried. However, instead of mixing alumina and potash, Deville (1854b) electrified a heated mixture of sodium chloride and aluminium chloride.[73] Deville thus further developed both types of methods for the production of aluminium that had been explored by his predecessors (displacement as well as electrolysis). Deville's chemical method enabled him to produce a metallic mass big enough to see what it would be like to fabricate aluminium objects. Because of its strength, low density, high malleability and low tendency to oxidize, he immediately noticed the industrial potential of the new metal. This captured the attention of the Academy: Deville was awarded funding for further research, various members came to visit his laboratory and later reproduced his experiments (see Sainte-Claire Deville 1854b, 322; 1854c). Soon, Emperor Napoleon III (1808-1873) became interested in the metal.[74] He arranged for a hall in the state-run Javel works in Paris to be dedicated to the production of aluminium: at this long-established chemical factory, there was more space to carry out large-scale tests.

Less than 18 months after Deville's initial presentation, the first bars of aluminium produced at Javel were presented before the Academy (Dumas 1855). Besides Javel, Deville was involved in the creation of two other factories in and around Paris and one near Rouen. Deville's collaborators and assistants moved between the ENS laboratory and the different industrial sites, where research and development took place as well (Le Roux 2015). Outside of France, aluminium also sparked an interest, but the early closure of two British factories meant that France remained the only producer of aluminium until the 1880s (Ferrand 1961, 115–28). Deville and many others continued to perfect the production procedures for industrial quantities of aluminium at a lower cost, but the fascinating story of how aluminium became such an affordable metal is beyond the scope of this chapter.

[73] The salt mixture, which was inert in this reaction, helped ensure that aluminium chloride did not evaporate.

[74] Dumas, by then an important member of the imperial government, helped acquire funding and recognition for Deville.

It is important to note, however, that the industrial potential of the new material meant that it was seen as a major achievement – even more so than the discovery of any other chemical element. This becomes especially clear from the reaction of Napoleon III, who exposed the first ingot of aluminium next to his crown jewels at the 1855 Universal Exhibition in Paris (Paquot 2005, chap. 4; Renaux 2019). The recent Emperor was keen to show off his country's technological achievements to the international audience at this world fair, and the new material served as proof of France's modernity. This shows the tremendous amount of prestige that came with the discovery of aluminium and the high stakes of identifying the legitimate discoverer. Elsewhere, I have argued that Deville largely shaped the narrative surrounding aluminium by presenting himself and Wöhler as the two fathers of aluminium.[75] Here, I will only provide a short summary of this argument.

Wöhler's priority when it came to the isolation was already established, but Deville actively reinforced it, creating the idea that aluminium was "known only thanks to the beautiful works of Mr. Wöhler" (Sainte-Claire Deville 1855, 9). His many compliments and references to Wöhler contrast with the fact that he cited no other contributions on aluminium. In this new narrative, there seems to have been no room for the earlier failed attempts at producing the metal, nor for any collective endeavours that may have led to the birth of the aluminium industry.[76]

Moreover, Deville actively defended his own work in three priority disputes. His first priority dispute was with Robert Bunsen (1811-1899) on the question of who had been the first to use the electrolytic method for the production of aluminium. Two other priority disputes between Deville and his students show how unwilling he was to share the priority for industrial aluminium. The first of these controversies involved the Tissier brothers, Charles (1832-1864) and Alexandre (1835-1860), who had worked at the Javel plant on

[75] See my chapter "The many fathers of aluminium: collaboration, credit and the construction of discovery" in the collective volume *From 'Eureka' to Narrative Process: Studies on the Discovery of Chemical Elements*, edited by Brigitte van Tiggelen and Annette Lykknes. The book manuscript is currently under review.

[76] Likewise, Lissa Roberts (2016, 344–47) has argued that Deville's monograph erased the material trajectories of aluminium and its mineral ores by presenting it purely as a laboratory substance. Studying these trajectories and the many ways in which aluminium has been handled outside of the laboratory can provide another way to question the notion of scientific discovery (see Osborn 2016).

the first trials of the industrial production of aluminium. The second was his refusal to share a prize with his assistant and collaborator Jules Henri Debray (1826-1888). These disputes ultimately motivated Deville to publish a monograph on aluminium, establishing himself as the founder of the aluminium industry.

We can only speculate whether Deville was motivated by sheer humility, or whether he consciously made this diplomatic choice. Either way, the decision to credit Wöhler for the discovery of aluminium worked out in his favour, as Deville (1858, 504) himself explained:

> "Knowing well that I had predecessors in the study of [sodium and aluminium], I did my best to highlight the importance of their work, and for that I have been rewarded. … Mr. Wöhler has honoured me with a friendship of which I am extremely proud, and since becoming his collaborator and host, I am happier than ever to have asked only for a small share in the esteem that scientists owe to the discoverer of aluminium."

Indeed, Deville's humble decision to reaffirm Wöhler's priority as the true discoverer of aluminium marked the beginning of a friendship between the two men. Deville travelled to Göttingen in 1856 and 1858, and became a member of the Göttingen Academy of Sciences (Paquot 2005, chap. 12). Rather than opposing the well-known chemist in a priority dispute, Deville aligned himself with Wöhler and was thereby able to share the recognition for aluminium with him. Moreover, Deville and Wöhler were jointly awarded the "Légion d'Honneur" by Napoleon III in 1855 (*ibid*., 43-44). Thus, for Deville, the social implications of the priority for aluminium surpassed his friendship with Wöhler: the shared credit also firmly established his scientific authority and position in society, nationally as well as internationally.

For the remainder of the nineteenth century, Wöhler was explicitly identified as the sole discoverer of aluminium (see for example Lejeal 1894; Moissonnier 1903; Richards 1896). However, this changed in the 1920s. The celebration of Wöhler had caused Ørsted's work to mostly be ignored, and Danish chemists wanted to celebrate their fellow countryman in honour of the anniversary of his work on electromagnetism. Likely motivated by national pride, chemist and historian J. Fogh reconstructed Ørsted's experiments in 1921 and showed that, contrary to what Wöhler had said, pure aluminium could be obtained using this method. Fogh and his colleagues concluded that Ørsted

deserved to be given priority as the discoverer of aluminium (Bjerrum 1926). They had considerable success and managed to effectively rewrite the history of aluminium, with the result that most twentieth-century accounts of the discovery of aluminium credited Ørsted rather than Wöhler (Kragh 2019; see for example Partington 1964, 4:323).

The focus on the roles of Wöhler and Ørsted in the history of aluminium is therefore not a sign that their work was seen as establishing the nature of aluminium at the time but rather a result of the retrospective focus of the attribution of credit by later chemists and historians. While the isolation of an element was a very prestigious achievement, aluminium had already been known to exist and its elementary nature had long been established by the time it was isolated. The attention for the isolation of aluminium is therefore an example of the ways in which discovery stories are shaped by the retrospective attribution of credit, and do not necessarily correspond to the ways in which chemists perceived the events at the time they took place. When it comes to the identification of the elementary nature of aluminium, this section has also shown that the retrospective focus on isolation should not be interpreted as a sign that isolation was necessary in order to prove the elementary nature of aluminium.

# Conclusion

Ever since the mid-eighteenth century, it was suspected that alumina might eventually be reduced to a metal, and after Davy's decomposition of the alkalis, this became even more likely. Acting on these suspicions, Davy attempted to decompose alumina in 1808 and 1809. Despite considering his own attempts unsuccessful, Davy argued that alumina should be seen as the oxide of aluminium on the basis of its chemical analogy to substances that were known to be metallic oxides. Davy's contemporaries accepted the existence of the metal aluminium following his publications on the topic, despite judging the direct evidence of the decomposition of alumina as insufficient. By the time metallic aluminium was produced, the metal had been known to exist for over fifteen years. The economic importance of aluminium as a material then motivated chemists, and later historians, to tell its early history focusing on the isolation of the metal itself.

The classification of alumina as a metallic oxide despite the impossibility to decompose it in the laboratory shows that chemists based their identification of chemical

composition on more than just direct evidence of chemical decomposition. As Thomson's and Berzelius' definitions of simple substances indicate, indecomposable substances were not necessarily seen as simple; after all, such substances could very well be compounds that could simply not be decomposed using the available means. Chemical analogies could provide an additional method for the evaluation of composition so that chemists could have an indication of whether or not to trust the provisional simplicity of the substances they attempted to decompose. Starting from Davy's argumentation in favour of aluminium, I have shown that classifications on the basis of analogy could serve as a guide in assessing the composition of substances because they were viewed as stable compared to the criterion of experimental (in)decomposability which continually shifted as laboratory techniques improved. Whereas the possibility of decomposing a substance depended on the adequacy of the laboratory techniques at hand, classes of analogous substances were thought to hold independently of decomposability. The premise on which these inferences were based was the idea that analogous substances were composed of similar elements.

We might therefore see the identification of chemical analogies between substances as a way to assure the reliability of the results of experimental decomposition attempts: the results of decomposition attempts had to be coherent with the chemical analogies and classifications based on them. The impossibility to decompose alumina could either be explained by the idea that it was a simple substance, or by the idea that it was an indecomposable compound. The fact that it was chemically analogous to substances of which the compound nature had been established made it much more likely that alumina was also a compound, for which an adequate decomposition method had yet to be developed. The chemical analogy between alumina and the other earths therefore provided chemists with additional, indirect evidence of the composition of alumina. The role of analogy in the identification of aluminium is therefore similar to its role in the historical sciences (such as archaeology, palaeontology and geology) as described by Adrian Currie (2018). Analogies could provide indirect evidence of the composition of indecomposable compounds.

This use of analogy went beyond that of a heuristic or strategy for formulating working hypotheses, as described by Fisher (2018). Analogy did help Davy advance in his research in this way: because of the similarities between alkalis, alkaline earths and common earths,

he inferred it was likely that they all had a similar composition. However, even without being able to confirm this hypothesis by directly decomposing alumina, Davy's prediction of the composition of alumina could be established as a form of knowledge of its composition. This strategy employed by early nineteenth-century chemists is also comparable to what Hasok Chang (2004, chap. 3) has described as the 'mutual grounding' of measurement standards. Chang developed this idea on the basis of his historical study of the development of temperature, specifically when temperature scales were extended beyond their original domains to measure temperatures below freezing or above the boiling point. Thermometers were only calibrated to measure temperatures between the freezing and boiling point of water and the operations that established their validity could not be carried out beyond this domain. The scientists studying temperature therefore chose to simultaneously develop multiple ways to measure temperature and maximise the coherence between them. Likewise, when studying composition, chemists made sure to increase the number of ways in which they studied it in order to increase the reliability of their results.

In the case of alumina, this knowledge became commonly admitted and chemists did not see a reason to question it. They relied on a kind of pragmatic justification of their analogical inferences: as long as the resulting knowledge of composition was coherent with experimental results and enabled them to carry out operations as they wished, there was no reason to revise their conclusions. In the case of aluminium, this convergence was arrived at fairly easily, as the eventual isolation of the metals shows. This leads to a question: what happened in cases where there was no coherence between the results of analogical inferences and actual decompositions? How much trust did these chemists place in their analogical inferences and classifications as representations of chemical analogies? In order to truly understand the strategies that this community of chemists employed for studying chemical composition, a more problematic case has to be studied. The next chapter will therefore show how chemists attempted to make sense of the composition of ammonia.

# CHAPTER 2 - "A Curious Exception Among the Alkalis": Identifying the Composition of Ammonia (1807-1813)

In the previous chapter, I have shown how the English chemist Humphry Davy and his contemporaries relied on analogical inferences in the identification of aluminium as a chemical element. These chemists were able to infer the composition of chemically indecomposable substances such as alumina (aluminium oxide) by analogy because they knew that chemically analogous substances were generally similarly composed. This use of analogy was part of their strategy to multiply the ways in which they studied composition: experimental studies of substances by decomposition and recomposition were not always reliable and often difficult to interpret, and they therefore used chemical analogies as indirect evidence of the composition of bodies. I have argued that the trust in such analogical inferences was justified by pragmatic considerations. Whereas the possibility of decomposing a substance depended on the available laboratory techniques, chemical analogies were seen as much more stable. It was therefore more useful to keep well-established classes of substances together rather than to separate them strictly on the basis of experimental results that might evolve as new techniques were developed. A question naturally follows from this conclusion. In the case of alumina, the analogical inference predicting its composition was consistent with experimental results, even if it could not be confirmed by chemical decomposition until decades later - but what happened when experimental results continually contradicted hypotheses regarding inferred composition? How did chemists deal with incoherence between various types of evidence?

In this chapter, I will analyse a more complicated case in which analogy and experimental results contradicted each other: the attempts at identifying the composition of ammonia that took place during the period 1807-1813. Ammonia ($NH_3$) is a colourless gas which has the alkaline property of neutralizing acids. By the eighteenth century, chemists generally referred to ammonia as the 'volatile' (gaseous) alkali and classed it with the 'fixed' (solid) alkalis potash and soda (see Klein and Lefèvre 2007).[77] Together, these

[77] For a chronological summary of historical views of ammonia, see Kopp (1845, 3:236–51).

three alkalis formed a subgroup of the salifiable substances, a class formed of substances that combine with acids to form salts, which also comprised the alkaline and common earths. During the last decades of the eighteenth century, Scheele, Priestley and Berthollet independently showed it to be composed of nitrogen and hydrogen and by the early 1800s there was, in Davy's (1808b, 35) words, "no doubt of its nature in the mind of the most enlightened chemists."[78] However, between 1807 and 1810, chemists first came to agree that the fixed alkalis were metallic oxides and then extended this view to all salifiable substances. These results caused Davy and his colleagues to question their knowledge of the composition of ammonia once again: how could it be possible that ammonia behaved in so many ways like a salifiable substance and yet did not have the same composition?

This chapter will show how chemists dealt with this contradiction between analogical inference and experimental results, focusing on the work of Davy and his Swedish colleague Jöns-Jacob Berzelius. Davy and Berzelius shared a correspondence and they quite strongly influenced each other on these questions, especially during 1808 and 1809.[79] From 1809 onwards they increasingly disagreed on the most likely interpretation of the facts, and each attempted to develop their own theories explaining the properties of chemical substances. Both of them changed their mind a number of times between 1807 and 1813 and this period can be seen as transitional for them: whereas Davy gradually abandoned the conviction that the presence of principle-like constituents might explain the properties of matter, Berzelius was in the course of developing a complex research program that would become central to his chemistry. For both of them, the composition of ammonia was of key importance for their general explanation of the properties of chemical substances. In light of the contradiction between analogy and experiment, both Davy and Berzelius tested out a number of hypotheses, including various speculations about the inner complexity of simple bodies. They were unable to find a definite solution to the issue that

[78] Davy's claim seems to be confirmed by textbooks from this period (for example Thomson 1804, 286–88; Berzelius 1808b, 256). For Berthollet's work on ammonia, see Lemay (1960).

[79] Colin Russell has highlighted especially the influence that Davy had on Berzelius, stating that "the greatest achievement of Davy in *theoretical* chemistry was to give to Berzelius the initial impetus for the latter's system of electrochemistry" (Russell 1959b, 24). See also Russell (1963a).

could establish a consensus. After 1813, Berzelius' position remained stable for almost a decade, and Davy abandoned the question altogether.

Even though ammonia itself is a compound and not an element, this chapter has its place in a study on the identification of chemical elements. The history of ammonia provides new insight into elementary nature in the early nineteenth century because the study of its composition was always closely linked to the nature of its constituents. Davy coined the name 'ammonium' for the predicted metallic constituent of ammonia. As his views of ammonia evolved, Berzelius first added the metal ammonium to his classification of elements, and later replaced this with the element 'nitric'. Both Davy and him also questioned the elementary nature of hydrogen and nitrogen, the latter of which Berzelius did not admit as a chemical element until the 1820s. Their work on ammonia therefore provides a wealth of information on the prediction of elementary nature from the study of compounds, as well as the relation between such predictions, general views of chemical composition and experimental results.

It appears that no study has so far aimed at analysing these historical investigations into the nature of ammonia and its possible metallic constituent ammonium. This gap in the literature is likely due to the fact that from today's point of view, Berzelius and Davy failed. For example, Davy's work on ammonia has been dismissed as and 'embarrassing mistake' (Crosland 1980, 113) that was 'unhappily based on problematic analyses' (Levere 1977a, 374). Davy's views on ammonium have been described mainly by Robert Siegfried (1964) because of their importance in his revival of the idea of phlogiston, but no thorough overview of his views on ammonia has been published. Berzelius's views have been studied in more detail by Evan Melhado (1981) and Anders Lundgren (1979; 1992) but only in so far as they were important for the establishment of his system of laws of chemical composition. This chapter assembles these references and complements them with a study of Davy and Berzelius' publications and correspondence. This gap in the literature illustrates the bias resulting from the focus on historical research that is viewed as successful today. No matter how we view their endeavours retrospectively, it is clear that the composition of ammonia was an interesting and useful problem to these chemists themselves, and that in itself makes this episode worth studying.

Moreover, this historical episode provides further material for the study of the role of analogical reasoning in establishing knowledge of composition, and it will both illustrate and refine some of the ideas I brought forward in the previous chapters. Like in the identification of aluminium, analogy functioned as a method for the indirect study of chemical composition. Likewise, as in the case of aluminium, these inferences relied on the observation that generally, chemically similar substances shared a similar composition. The central assumption that motivated this research on ammonia, as summarized by Berzelius in a letter to Berthollet, relied on the similarities between the fixed and volatile alkalis:

> "It would be very inconsistent to believe that only ammonia provides phenomena that are *externally* so analogous to those of the fixed alkalis, the earths and the metallic oxides, and yet *internally* of an entirely different nature" (Berzelius 1811b, 79).[80]

While this idea was shared by Davy, Berzelius and their contemporaries, choices on how to deal with it varied depending on each individual's goals and the contexts within which they were working.

Berzelius, for example, was very attached to the link between properties and composition. From his appointment at the Karolinska Institute, Berzelius started publishing various editions of his textbook *Lärbok i Kemien* (see Jorpes 1970). This likely played a role in his wish to develop relatively simple and systematic explanations of chemical composition. However, Berzelius went further than most textbook writers in developing a theoretical system: his central aim during the period discussed here was to develop a sophisticated explanation of chemical properties on the basis of composition (Melhado 1981). With this aim in mind, he followed a systematic research programme that combined the quantitative analysis of first and second order compounds (oxides, sulphides and the more complex compounds they formed) with their qualitative characterization (in terms of properties such as acidity and basicity). Berzelius used all of this data to establish laws of composition, and he was extremely reluctant to admit any exceptions. This

[80] "(…) il serait très-inconséquent de croire que l'ammoniaque seule fournit des phénomènes *extérieurement* si analogues à ceux des alcalis fixes, des terres et des oxides métalliques, mais *intérieurement* d'une nature tout-à-fait opposée" (Berzelius 1811b, 79; emphases original).

contrasted with Thenard and Gay-Lussac, who were not investigating the same general patterns of composition and were much more willing to admit that ammonia might simply present an exception.

Meanwhile, Davy had his own peculiar style of considering a lot of different hypotheses without clearly committing to any. As opposed to Berzelius, Gay-Lussac and Thenard, Davy did not fit the description of a professional scientist, which in many ways gave him a lot more freedom to take risks and speculate on various topics including phlogiston (see Crosland 1980). Since his non-expert audience at the Royal Institution paid a subscription fee, his career was particularly dependent on pleasing them. He was able to acquire a lot of independence in his research through his success in pleasing his audience, using a style that often integrated much broader views about nature, natural order and beauty (Golinski 1992; Lloyd Edmondson 2019). Furthermore, Davy was also a romantic and a poet, and he constantly switched between genres in his writing (see Knight 2005). After his marriage to Jane Apreece (née Kerr, 1780-1855) in 1812, he quit his position at the Royal Institution since he no longer needed a salary thanks to his wife's fortune.[81] It was also around this time that he stopped investigating the nature of ammonia.

In what follows, I will give a chronological overview of the different hypotheses regarding the composition of ammonia that Davy and Berzelius pursued between 1807 and 1813 and show how they moved from one idea to the next. Both of them started out their research with the basic assumption that all alkalis would be composed of similar elements; eventually, the problem of the nature of ammonia came to play a central role in the development of broader theories of chemical composition. As each of their hypotheses were contradicted by experimental results, this chapter will show how they adjusted their interpretations of the composition of ammonia in order to avoid incoherence.

[81] Jane Davy inherited her wealth from her father, Charles Kerr, who acquired it through partially illegal practices on Antigua. Although Kerr did not own a plantation himself, James (2021) has argued he shared in the legacy of Caribbean slavery.

# Ammonia as a potential metallic oxide

Analogy was used to predict the composition of the alkaline substances at least since the late eighteenth century. When Davy decomposed the fixed alkalis and showed that they were metallic oxides, chemists reconsidered the composition of ammonia and investigated whether it was also a metallic oxide. The discovery of the possibility to produce an amalgam from ammonia further increased the probability that it was a metallic oxide, since only metallic substances were known to form amalgams. In this section I will describe Davy and Berzelius' views of ammonia as a potential metallic oxide and the ways in which they adapted this view to integrate contradictory results.

## The decomposition of the fixed alkalis

Since the last decades of the eighteenth century, knowledge of the composition of ammonia had motivated predictions of the composition of the other two alkalis. In 1785, Berthollet (1785) had decomposed the substance using an electric spark, producing water and nitrogen gas, and calculated the original proportions of its constituents from the reaction products. The observation that ammonia was composed of nitrogen and hydrogen was sufficient for Lavoisier and various other chemists around 1800 to omit all three alkalis from their lists of simple substances (Lavoisier 1789; Fourcroy 1800; Thomson 1802). Davy made a similar inference and predicted the composition of the fixed alkalis using the example of ammonia.[82] He thought that since the lightest alkali, ammonia, was composed of nitrogen and the lightest inflammable body, perhaps the combination of nitrogen with a denser inflammable body would produce the other two heavier alkalis.[83] It was with this idea in mind that Davy embarked upon the decomposition the fixed alkalis using his voltaic

[82] Davy felt especially sure of the composition of ammonia because he had been able to reproduce Berthollet's experiment (H. Davy 1800, 56–62).Their results slightly differed but Davy explained this by the improvement of knowledge of the composition of water between 1785 and 1800. He thus concluded that ammonia consisted of 35 volumes of nitrogen for 105 volumes of hydrogen (or in terms of weight: 121 parts nitrogen for 29 parts hydrogen).

[83] Davy's reasoning is explained in a footnote by John Davy retracing the history of the relation between metallic oxides and earths (H. Davy 1839, V: 102-3). Davy himself also remarked this in a footnote to his Bakerian Lecture for 1807 (H. Davy 1808b, 42).

pile. Therefore this constitutes an example of analogy working as a heuristic in moving from one experiment to the next by enabling the formulation of working hypotheses: Davy could rely on the patterns of similarities in the chemical behaviour of the alkalis in order to design his experiments (see Fisher 2018).

In this case, Davy's working hypothesis did not last very long. In the Bakerian Lecture for 1807, Davy (1808b) announced his decomposition of soda and potash to the Royal Society of London: contrary to his predictions, they did not contain any nitrogen. Instead, Davy found that they were the oxides of two new metals, which he named potassium and sodium. Rather than abandoning his analogical reasoning altogether, this result motivated him to reverse his original inference and doubt the well-established nature of ammonia: though its composition had been known, all new facts were accompanied by "a train of analogies, and often by suspicions with regard to the accuracy of former conclusions" (H. Davy 1808b, 35). It seemed more likely to him that previous experiments showing the composition of ammonia had been erroneous, than that the three alkalis had a different composition. Davy therefore set up experiments to test whether ammonia might contain any oxygen that may have gone unnoticed in previous analyses. His initial results indicated that ammonia was the oxide of a compound nitrogen-hydrogen radical (see below).

Davy's decomposition of the alkalis was important news, and it soon reached Berzelius in Sweden who by then had been working for a few years on a very similar research program involving the voltaic pile (see Russell 1963a; 1963b). From his summary of Davy's results for the *Economiska Annaler* of April 1808 (Berzelius 1808a), it becomes clear that he was convinced by Davy's claim that the ammonia was also an oxide:

> "The similarity of the volatile alkali with the fixed is so great, that their constituents must also be similar, and *analogy* here almost moves over to the rank of *proof*" (Berzelius 1808a, 119).[84]

One of the reasons why Berzelius may have been eager to accept this analogical inference is that the idea that all three alkalis were oxides fit in well with the central role that was attributed to oxygen in the Lavoisian system of chemistry.

[84] "Likheten af det flygtiga alkali med de eldfasta är så stor, att deras beståndsdelar äfven måste vara likartade, och *analogien* går här nästan öfver till rangen af *bevis*". Emphasis original.

Davy and Berzelius each interpreted the importance of the presence of oxygen in the alkalis in their own way. Davy, who at the time was searching for an explanation of chemical behaviour in terms of constituents which acted as the causes of properties, saw it as an indication that oxygen was the cause of both acidity and alkalinity:

> "Oxygen then may be considered as existing in, and as forming, an element in all the true alkalies [sic]; and the principle of acidity of the French nomenclature, might now likewise be called the principle of alkalescence" (H. Davy 1808b, 41).

At this time, Davy was still convinced of the Lavoisian idea of principles, and here he used 'element' in a Lavoisian sense to refer to a constituent that could cause specific properties.[85] For Berzelius on the other hand, the fact that both acids and bases contained oxygen gave reason to think that acidity and alkalinity did not depend only on the amount of oxygen but also on the nature of the oxidized radical. He had already been interested in the composition of acids, but this finding motivated further research into the composition of bases, as well as the electrochemical properties of simple bodies. This was the first step towards the development of his complex laws of composition that occupied him during the 1810s (see Melhado 1981, chap. IV, V and below).

In short, Davy and Berzelius were both willing to adapt their initial view of the composition of ammonia to incorporate newly found evidence about the composition of the alkalis. On the basis of analogy, it seemed very likely to them that all alkalis would be oxides. They both saw this possibility as an interesting and important hypothesis that had to be pursued further. Berzelius put on hold everything he was working on in order to spend a month investigating this question together with Magnus Martin Pontin (1781-1858). He even postponed the preparation of his textbook, possibly because he wanted to include these additional findings in it. This attitude towards the possibility that ammonia might be a metallic oxide shows how attached both Berzelius and Davy were to analogical inference as an indication of chemical composition.

[85] By 1816 he would come to reject the idea of a single element as the cause of this kind of properties (see Brooke 1980). See also next chapter.

## The ammonia amalgam

One of Pontin's and Berzelius' discoveries during their month-long electrochemical work was that of a curious phenomenon: the ammonia amalgam (Berzelius and Pontin 1808).[86] In order to compensate for the low strength of their battery, they developed an alternative method for the decomposition of the alkalis that relied on the use of mercury as a negative electrode. Instead of directly decomposing the fixed alkalis into oxygen and a metal, this enabled them to combine potassium and sodium with mercury to form an amalgam, before evaporating the mercury to leave behind the metal. They then tried to decompose the other salifiable substances in the same way, including ammonia.[87] Since ammonia was so similar to the fixed alkalis, they suspected it would also be capable of forming an amalgam. When they closed the circuit on mercury and ammonia, they saw "a metal build up before [their] eyes, from a fluid of which the constituent parts and their proportions are fairly precisely determined" (Berzelius and Pontin 1808, 121).[88] Ammonia, or one of its constituents, appeared to have combined with mercury into a metallic alloy.

Berzelius informed Davy of the amalgam by letter in May 1808.[89] Within a month after receiving the letter, Davy announced his own production of an amalgam from ammonia before the Royal Society. His method consisted of placing a drop of mercury in a cavity in a piece of 'muriate of ammonia' (ammonium chloride) and connecting the mercury to the negative electrode of his voltaic pile. As soon as the circuit closed, the

[86] The amalgam was simultaneously discovered by Thomas Seebeck (1770-1831) in Jena.

[87] This is another example of the use of analogical reasoning as an experimental stratagem (Fisher 2018): the analogies between the salifiable substances made it likely that they would react to electrical currents in the same way. This supposition also formed the basis for experimental design.

[88] "(…); men då vi i följande försök sett ammoniakens kända beståndsdelar sammanträda på den negativa polen och formera en metallkropp; då vi anföra att en metall under våra ögon blifvit sammansatt i en vätska, hvars beståndsdelar äro oss fullkomligt bekanta, och till deras inbördes förhållanden i det närmaste bestämda, berätta vi ett mirakel, som kanske många af våra läsare skola misstro, och sjelfve misstrodde vi i början våra egna sinnen, till dess att försöken, behörigt repeterade och på flera olika sätt omgjorde, undanröjde alla tvifvelsmål" (Berzelius and Pontin 1808, 121–22).

[89] Davy seems to have received the letter, which is now lost, in early June. See Davy and Berzelius' correspondence, note 1 from editor Söderbaum (Berzelius 1912b, 76).

mercury absorbed part of the salt, growing to five times its size in a few minutes. The soft solid that was formed had

> "the appearance of an amalgam of zinc; and metallic crystallizations shot from it, as a centre, round the body of the salt. They had an arborescent appearance, often became coloured at their points of contact with the muriate; and when the connection was broken, rapidly disappeared, emitting ammoniacal fumes, and reproducing quicksilver" (H. Davy 1839, V:124).

The metallic appearance of this amalgam was a striking observation. Berzelius and Pontin had even referred to it as "a miracle" which anyone would have difficulty believing until they saw it with their own eyes.[90]

The reason for this kind of enthusiasm was that mercury was known to produce amalgams only with metallic substances: amalgams were alloys of mercury with another metal, whereas its compounds with non-metals, such as cinnabar (mercury sulphide), were non-metallic and could therefore not be characterized as amalgams.[91] As Davy (1808a, 361–62) put it, it was "scarcely possible to conceive that a substance which forms with mercury so perfect an amalgam, should not be metallic in its own nature": in other words, ammonia behaved like metallic compounds in producing an amalgam, it therefore had to contain a metal as well. He therefore suspected that the substance entering into the amalgam was some kind of metallic component of ammonia, which Davy proposed to call 'ammonium'. Thus, Davy had changed his interpretation again: rather than an oxide of a compound nitrogen-hydrogen radical, he now identified ammonia as the oxide of ammonium. In Berzelius' and Pontin's words, the discovery of the ammonia amalgam "embellished" the discovery of the fixed alkalis' metallic nature because it indicated that the alkalis not only each contained oxygen, but also a metal.[92] This finding had added even more similarities between the alkalis.

---

[90] See citation in footnote 88.

[91] Alloys, likewise, were only formed by metals. Thus, for example, Thomson (1804, 275) explained the formation of alloys was one of the best ways to determine the metallic nature of a substance.

[92] "Upptäckten af ammoniakens analogi med metallerna, har (...) ganska mycket förskönat upptäckten af de eldfasta alkaliernas metalliska natur" (Berzelius and Pontin 1808, 128).

The logical next step was to attempt to isolate ammonium, the supposed metallic constituent of ammonia. This proved impossible, because as soon as the electrical circuit was broken, the amalgam disappeared and produced hydrogen, nitrogen and mercury. Davy (1808a, 353–61) found that the speed at which this decomposition happened made it impossible to evaporate the mercury with the hopes of obtaining pure ammonium. Berzelius and Pontin obtained the same result and explained the decomposition by the presence of a bit of remaining moisture: metallic ammonium would thus be transformed back into ammonia by absorbing oxygen from this water, producing ammonia and leaving behind mercury and the remaining hydrogen from the water (Berzelius and Pontin 1808, 122–27).

Despite the difficulty isolating metallic ammonium, Davy was not willing to let go of the idea that this metal existed. He provided further arguments in favour of the metallic nature of ammonium on the basis of chemical analogy. In Davy's view, all metals could be aligned in a chain of analogies, each metal being almost indistinguishably similar to its neighbours. Ammonium fit well into this series:

> "From platina to potassium there is a regular order of gradation as to their physical and chemical properties, and this would probably extend to ammonium, could it be obtained in the fixed form" (H. Davy 1808a, 363).[93]

Ammonium would be both the lightest metal and – supposing that ammonia was an oxide – the most easily oxidizable, followed by potassium and sodium. All phenomena involving ammonium were perfectly coherent with this classification of ammonium as a metal, and its predicted affinity for oxygen could explain the fact that it was so difficult to isolate. The argument regarding the metallic nature of ammonium could thus be summarized as follows: ammonia had properties in common with metallic compounds, most notably that of being capable of producing an amalgam with mercury; therefore, it probably contained a metal as well.

[93] Berzelius and Pontin (1808, 129) likewise placed the metals in a row going from platinum, the heaviest, to the metal of ammonia, the lightest.

## Gay-Lussac and Thenard' criticism of ammonium as a metal

When it comes to the rest of the European chemical community, it seems that opinions on the amalgam were divided. According to Delamétherie (1812, 63), the idea that ammonia was a metallic oxide was "most commonly accepted", but others saw "an uncertainty hanging over the subject, which the exertions of subsequent experimenters have not been able to remove" ("Review of Science" 1810, 412). Whereas a similar argumentation had worked well for the prediction of aluminium as a constituent of alumina, the decomposition of ammonia into nitrogen and hydrogen reduced the plausibility of the analogical inference regarding ammonium. This explains, for example, why Berzelius included both aluminium and ammonium as simple metals in his classification of chemical elements, but referred only to ammonium as a "problematic body" despite the fact that neither of the two had been isolated (Berzelius 1811a, 282).

The clearest opposition to ammonium came from Gay-Lussac and Thenard (1810b) who refused to accept the existence of the ammonia amalgam as proof of the metallic nature of ammonium. Since electricity was necessary for the production of the amalgam, they thought it was possibly an artefact due to electrical action rather than chemical forces. Furthermore, they argued that the decomposition of the amalgam with the resulting production of hydrogen could not be seen as the oxidation of ammonium through the decomposition of water. When they repeated the experiment under a flask they did not observe any modification of the air inside the flask; since all moisture had been eliminated from the flask, no oxygen could have been provided by leftover water either. In their view, the produced hydrogen had to come from the amalgam itself. Therefore, they concluded that the ammonia-amalgam was not a metallic alloy but a compound of nitrogen, hydrogen and mercury.

Davy (1810a) criticized Gay-Lussac and Thenard for failing to acknowledge that the amalgam was possibly the most extraordinary fact of all of chemistry and explaining it away "as if it were in accordance with all our established systems" (*ibid*., 391).[94] He argued

[94] "MM. Gay-Lussac et Thenard trouvent facile d'expliquer de quelle manière est formé cet amalgam, et ils raisonnent sur ce fait (peut-être le plus extraordinaire de la Chimie) comme s'il étoit d'accord avec tous nos systèmes établis."

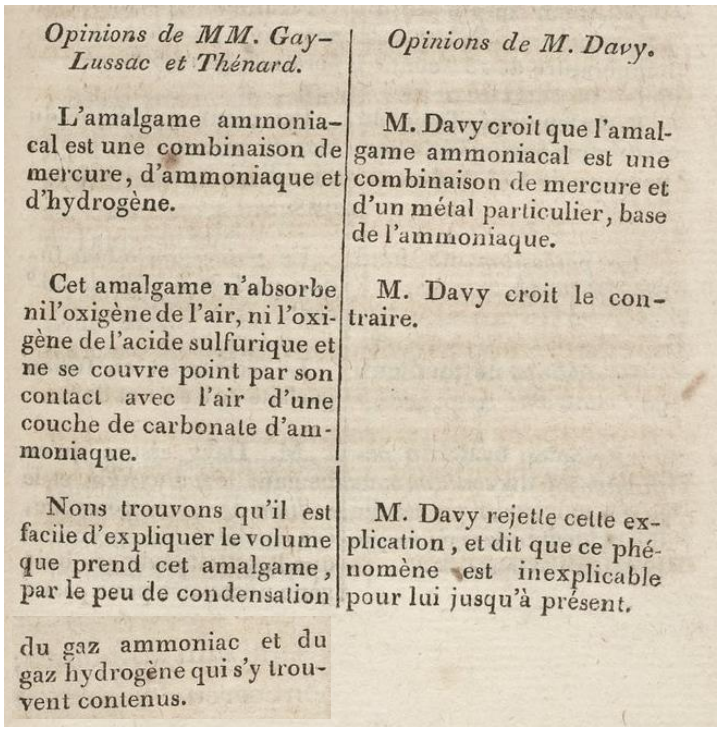
that they should pay more attention to the analogies between ammonium and the metals instead of just dismissing this phenomenon as an exception. Yet, Gay-Lussac and Thenard were not opposed to the use of analogical inferences in the study of chemical composition.[95] They admitted that one could invoke the similarities between the alkalis in order to argue that they all had a similar composition. They simply interpreted 'similar composition' in a different sense, arguing that this inference gave just as much reason to think that potassium and sodium were compounds of hydrogen as it would prove the simple nature of ammonium. In fact, they did initially argue against the acceptance of potassium and sodium as simple bodies (Siegfried 1963), but eventually they became convinced of the metallic nature of these substances. Contrary to ammonium, they argued there existed "better founded analogies" between potassium, sodium and the other metals (Gay-Lussac and Thenard 1811, 2:234). For them, the facts surrounding ammonia gave insufficient reason to think that it contained a metal, and the possibility of producing an amalgam in itself did not suffice. Therefore, they continued to see ammonia as nothing more than a "curious exception among the alkalis" (*ibid*., 257). In 1814, Gay-Lussac proposed that the nitrogen in ammonia perhaps played the same role as oxygen did in the alkalis (see Levere 1980). This shows that he, too, was looking for an explanation that could preserve the analogies among the alkalis.

Why then were Gay-Lussac and Thenard willing to accept this exception, contrary to Davy and Berzelius? A possible explanation lies in the influence of Gay-Lussac's mentor, Claude-Louis Berthollet (1748-1822). Gay-Lussac and Thenard were part of an elite group of researchers at the centre of French chemistry which was marked by Berthollet's authority as the main heir to the Lavoisian research group (Crosland 2003). After returning from Napoleon's expedition to Egypt, he took on an important role in the editorial board of the *Annales de Chimie*. He also bought a country house in the nearby village of Arcueil, where chemists gathered and presented their work. In 1807, Berthollet and Pierre Simon Laplace (1749-1827), another former collaborator of Lavoisier, officially founded the Society of Arcueil. Gay-Lussac had been Berthollet's assistant since 1801, and Thenard

[95] See for example their remark that "les conclusions les plus probables sont celles qui s'accordent le plus avec l'analogie générale de la chimie" (Gay-Lussac and Thenard 1810a, 294).

(who had studied under Nicolas Vauquelin) quickly joined the group. The young members of the group rapidly became elected to the first class of the Institut de France (the successor to the French Royal Academy of Sciences) thanks to the influence of Berthollet and Laplace. Berthollet also invited his young colleagues to join the board of the *Annales*. It was Berthollet who had famously analysed ammonia in 1785 and shown that it was a compound of nitrogen and hydrogen, and seeing the influence of Berthollet on Gay-Lussac it is likely that he was confident in the results of his teacher.

Furthermore, Gay-Lussac and Thenard had no problem opposing Davy, as their ongoing debate between 1807 and 1814 shows. While Berthollet himself did not contribute to this debate with his own publications, he did play a role in the publication of Davy's and his opponents papers in the *Annales de Chimie* (see MacArthur 1985). In their *Recherches Physico-Chimiques*, Gay-Lussac and Thenard dedicated an entire section to presenting their ideas in opposition to those of Davy (see Figure 3). Whether it was attracting an audience, multiplying publications or pleasing their peers and superiors, it appears that there was some advantage for them in cultivating this debate. It may seem as though this was simply a matter of national opposition between France and England since the two countries were at war with each other, but the French view of Davy was more complicated than just his nationality. Napoleon himself was quite fond of Davy's work: after the announcement of the discovery of potassium and sodium, he awarded Davy with a prize and ordered the construction of the pile at the Ecole Polytechnique, the very same that Gay-Lussac and Thenard used (Sutton 1981). Davy also travelled to France in 1813 on Napoleon's invitation and exchanged with the group at Arcueil (see Golinski 1992). While there was a definite rivalry between Davy and Berthollet's group, they seem to have been relatively friendly enemies.



| *Opinions de MM. Gay-Lussac et Thénard.* | *Opinions de M. Davy.* |
| --- | --- |
| L'amalgame ammoniacal est une combinaison de mercure, d'ammoniaque et d'hydrogène. | M. Davy croit que l'amalgame ammoniacal est une combinaison de mercure et d'un métal particulier, base de l'ammoniaque. |
| Cet amalgame n'absorbe ni l'oxigène de l'air, ni l'oxigène de l'acide sulfurique et ne se couvre point par son contact avec l'air d'une couche de carbonate d'ammoniaque. | M. Davy croit le contraire. |
| Nous trouvons qu'il est facile d'expliquer le volume que prend cet amalgame, par le peu de condensation du gaz ammoniac et du gaz hydrogène qui s'y trouvent contenus. | M. Davy rejette cette explication, et dit que ce phénomène est inexplicable pour lui jusqu'à présent. |

*FIGURE 3 - Part of a four-page-long table summarizing the differences of opinion between Davy and Gay-Lussac and Thenard (Gay-Lussac and Thenard 1811, 2:159–60). Source: Bibliothèque nationale de France.*

## How to account for the oxygen in ammonia

In the identification of ammonia, the metallic nature of ammonium was not the only issue at hand: in order for ammonia to be a metallic oxide, it not only had to contain a metal but also oxygen. The possibility of forming an amalgam was itself evidence in favour of this idea and for some, such as Thomson (1810, 2:17) it could "prove the presence of oxygen in ammonia in a very decisive manner". Moreover, there was also direct experimental evidence of the oxygen in ammonia which dated from before the discovery of the amalgam, as described by Davy (1808b) in his Bakerian Lecture of 1807. His clearest experimental result was a (partial) decomposition of pure ammonia over a heated iron wire, in which water was formed: Davy thought that the oxygen to form this water had probably come from the ammonia itself. Moreover, when he decided to repeat the electric decomposition of ammonia in order to verify that all reaction products had been identified, he found that one eleventh of the original mass of the decomposed ammonia was lost. This loss, he said, could only be ascribed to the presence of oxygen in ammonia. He concluded

that ammonia was a triple compound of nitrogen, hydrogen and oxygen, containing at least 7 or 8 per cent oxygen.

Yet, repeated efforts to empirically detect the presence of oxygen in ammonia could not confirm this conclusion as the decomposition of ammonia continued to only produce nitrogen and hydrogen. In France, Amédée Berthollet (1780-1811, son of Claude Louis) investigated Davy's claim that ammonia contained oxygen even before the publication of the 1807 Bakerian Lecture arrived in France. In March 1808, Berthollet reported before the *Institut National* that he had been unable to confirm Davy's results: firstly, he had been unable to oxidize iron wire in ammonia gas, and secondly he could not verify the weight discrepancy in the decomposition of ammonia (the total weight of hydrogen and nitrogen produced corresponded to the initial quantity of ammonia). Berthollet concluded these results gave no reason to believe that ammonia contained any oxygen.

In England, the oxygen content of ammonia was also investigated by William Henry (1774-1836), who reported in May 1809 that he too was unable to detect any oxygen in ammonia. Besides decomposition by electric spark and burning it in oxygen, Henry (1809) developed a new decomposition method which consisted of burning ammonia in two portions (first in too little oxygen gas, then burning the remainder again).[96] Henry's numerous attempts gave slightly varying results, but overall they corresponded to the composition that Davy himself had come to identify through repeated decomposition attempts. By 1809, Henry and Davy agreed that ammonia consisted of about 74 parts hydrogen and 26 parts nitrogen (in volume). In Davy's words, no "free oxygen" could be detected in it (Berzelius 1912b, 16).

Davy was now faced with a puzzling contradiction between ammonia's chemical behaviour on the one hand (its analogies to metallic compounds, most importantly the amalgam) and the products of its decomposition on the other (the fact that it only produced hydrogen and nitrogen). Numerous repetitions had eliminated the possibility that the problem was due to previous errors in the decompositions of ammonia, so there had to be another explanation. Once again, Davy was reluctant to admit the possibility that ammonia

[96] Henry reported this from Manchester to Davy, who read the letter before the Royal Society in London. It was published alongside an annex to Davy's 1808 Bakerian Lecture in July 1809.

might simply have a different composition than the substances it was analogous to. In 1809, Davy proposed an alternative solution: if oxygen could not be detected directly, perhaps it was contained in a different manner within ammonia, for example as a constituent of nitrogen or hydrogen. Instead of being 'free' and directly obtainable, the oxygen of ammonia would thus be contained within another body, and this allowed Davy to explain both why it could not be directly obtained and why ammonia behaved like an oxide.

Moreover, Davy was not just making a theoretical speculation. Besides its explanatory power, the idea that nitrogen was an oxide was supported by a series of experiments involving a compound of ammonia and potassium, during which Davy thought he had decomposed nitrogen. The study of this compound was part of his ongoing debate with Gay-Lussac and Thenard about the nature of potassium and whether or not it contained hydrogen (see Siegfried 1963). The details of their debate lie beyond the scope of this chapter, but of relevance here is their study of a reaction between potassium and ammonia: when heated in ammonia gas, potassium absorbed the gas and formed a blue-green non-metallic compound (see H. Davy 1808b, 141–57). When the blue-green compound came into contact with moisture, Davy found that it decomposed and produced ammonia of which the proportions of hydrogen and nitrogen were slightly off. Some nitrogen seemed to have been lost and some water was produced – he interpreted this as a sign that nitrogen had been decomposed intro hydrogen and oxygen.

The significance of such an experimental result meant that it had to be verified a number of times and Davy continued to work on this question for months, continually adjusting his conclusion. In an appendix to his third Bakerian Lecture which he presented in February 1809, Davy (1809a) reported that he had repeated the experiment over 20 times, often in the presence of distinguished chemists, and using instruments made of various materials, in order to avoid all error. Each time, he observed that some nitrogen was decomposed with the production of oxygen and hydrogen (H. Davy 1809b, 250). His correspondence with Berzelius shows that he gradually shifted towards this new interpretation from May 1809. By October 1809, Davy was "strongly inclined to suspect" that hydrogen was a protoxide of ammonium, ammonia a dioxide and nitrogen a trioxide (Davy to Berzelius, 18/10/1809, see Berzelius 1912b, 16). Davy was aware that this would mean that ammonia and water would both be compounds oxygen and ammonium, and he

explained the differences between these bodies with the idea that they were two "different modifications of the same substance under different electrical states" (Berzelius 1912b, 11).

It might seem surprising that Davy was more willing to see nitrogen and hydrogen as compounds than to simply accept ammonia as an exception to the rule that similar properties indicated a similar composition. However, hypotheses regarding the complex nature of nitrogen were not new, nor were they exceptional. In 1800, there had been a controversy between Dutch and German chemists on the potential composition of nitrogen (Knight 1978, 38–39). In 1814, both Thomas Thomson and John Miers also argued that nitrogen was probably a compound (see Brock 1985, chap. 5). Davy was therefore not considering extremely obscure hypotheses, but rather engaging with a research question that had been investigated by various other chemists. Hypotheses regarding the complex nature of hydrogen, on the other hand, were much less common. This might be why Davy and Berzelius both relatively rapidly abandoned this idea (see below).

Davy's suggestion that hydrogen and nitrogen were oxides also illustrates the difficulties in experimentally determining the simplicity of substances. There were many signs that nitrogen was indecomposable, yet there were also experiments that seemed to show that it had been decomposed. In cases like that of nitrogen and hydrogen, the law of conservation of weight could not provide a solution to this question, as John Hedley Brooke (1980, 126) has explained:

> "This kind of confusion in early nineteenth century chemistry can still come as a shock to those who like to believe that Lavoisier's criterion of the conservation of weight could be used once and for all to decide what was inside what. But … the criterion was not always applied when it might have been and in other cases it was impossible to apply. Sometimes it was impossible to obtain a reliable weighing of the product; sometimes it was impossible to combine the supposed constituents of a substance; and always there was the problem that the existence of a recurring minimum weight did not prove that an 'element' was *not* complex."

Experimental results were often coherent with multiple explanations, and chemists had to rely on additional evidence in order to help them choose the most likely hypothesis.

Like in his other argumentations regarding the composition of bodies, Davy supported his experimental results with analogical arguments in favour of the compound nature of nitrogen and hydrogen: in some ways, they behaved like compounds. An important argument was the fact that nitrogen was not very reactive: at this time, Davy still believed that the simpler a body was, the stronger its tendency to form compounds (H. Davy 1839, 324). When it came to hydrogen, Davy cited the fact that it formed an acidic compound with tellurium, which made it probable that hydrogen contained oxygen (Knight 1978, 132–33; Berzelius 1912b, 17). This argumentation exemplifies Davy's combined use of analogy and experimental decomposition throughout his study of ammonia. Each new result led to further analogical inferences, which in turn helped design further experiments of which the results could be further interpreted with the help of analogy. In this progression, the correlation between chemical properties and composition functioned as the key premise.

Although he was sceptical of compound nitrogen at first, Berzelius had completely adopted the idea by the spring of 1810.[97] For Davy as well as for Berzelius, the question of the nature of ammonia took on a central place in the development of broader visions on the composition of chemical substance. Both of them developed their own theory about the composition of chemical substances and their approaches gradually diverged, as will be described in the following sections.

# Berzelius' theory of oxidation

## The Versuch and Berzelius' identification of patterns of oxidation up to 1813

Berzelius' study of ammonia allowed him to combine two of his previous interests: the electrochemical properties of various substances and stoichiometry (Melhado 1981, chap. IV). Berzelius' first encounter with stoichiometric laws had occurred

[97] According to Lundgren (1979, 189), Berzelius did not accept this hypothesis until 1811. However, a letter to Davy from the spring of 1810 suggests that Berzelius had already adopted it (see Berzelius 1912, 19-20). This is confirmed by two letters he sent to Gilbert: in April 1810 he still seemed to hesitate, but in October he was certain that hydrogen and nitrogen were oxides (Berzelius 1810a; 1810c).

during the preparation of his textbook *Lärbok i Kemien* (Berzelius 1808b). He read Jeremias Richter's (1762-1807) work and learned of his law of equivalent proportions according to which the ratio between the amount of two different acids needed to saturate a given base remained constant no matter the specific base used (and vice versa for acids). Shortly after, in 1809, Berzelius also learned of Dalton's law of multiple proportions, according to which elements always combined in series of fixed proportions that were small integer multiples of one another. This was a crucial moment in Berzelius's chemistry, after which he gradually took on an empirical version of atomism that would come to play an essential role in the development of his chemical system (Rocke 1984, 66–78).[98] Because it combined his existing interests, the question of ammonia acquired a central place in Berzelius' ongoing research regarding the properties and composition of salts and their constituents.

Stoichiometric laws provided Berzelius with a way to calculate the composition of substances that could not be identified directly using decomposition. He first suggested to Davy in June 1809 that they might use the laws of stoichiometry to calculate the oxygen content in ammonia, since it was impossible to detect oxygen experimentally (Berzelius 1912b, 12).[99] Although Richter's work had enabled him with a method to calculate the composition of salts (second order compounds), the determination of the amount of oxygen in ammonia required the calculation of the composition of first order compounds (oxides). During the following years, Berzelius continued to perfect his method for the calculation of the composition of ammonia and in doing so he developed a number of stoichiometric laws himself in order to connect these different levels of composition (see Melhado 1981, chap. IV, V).

[98] Berzelius learned of Dalton's law from Wollaston's work. Wollaston was one of the first chemists to adhere to Dalton's atomic theory but he based his atomism more strongly on empirical results rather than Dalton's rule of simplicity or the idea of spherical, physical atoms. For Wollaston's views on atomism, see Rocke (1984, 61–66). For Wollaston's influence on Berzelius, see Lundgren (1979, 88–89). For Berzelius' view on Dalton's theory, see Lundgren (1992).

[99] This initial calculation relied on the amount of ammonia needed to neutralize a fixed quantity of acid: the more oxygen a base contained, the less of it was needed to neutralize a certain quantity of acid. Using this method, he calculated ammonia to contain 31,5% oxygen. This relied on Richter's law.

Berzelius empirically established his laws of composition in a famous paper: "Versuch, die bestimmten und einfachen Verhältnisse aufzufinden, nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind" (hereafter cited as the *Versuch*).[100] The *Versuch* consisted of a systematic survey of the proportions in which acids, bases and salts combined that provided an empirical basis to the law of multiple proportions and contained the foundation of much of Berzelius' later work. This experimental work was a direct continuation of his work with Pontin and established independently from any theoretical views of atoms (see Lundgren 1992). The initial paper, written in late 1809, consisted of two parts that first appeared in the *Afhandlingar i fysik, kemi och mineralogie* in 1810 and (with some minor additions) in Gilbert's *Annalen der Physik* in 1811 (Berzelius 1810b; 1811c; 1811e). Subsequently, Berzelius wrote three supplements expressly for Gilbert's *Annalen* which were published during 1811 and 1812 (Berzelius 1811d; 1812c; 1812b).

The first half of the *Versuch* contained the analysis of a series of oxides, with the explicit goal of supplying empirical foundations to Richter's rule of equivalent proportions and Dalton's law of multiple proportions.[101] This is also where Berzelius added his first additional law, the rule of basic oxygen, according to which there was an equal amount of oxygen in the bases (alkalis, earths or metallic oxides) of all the salts that a specific acid could form.[102] This law found its application in the second part of the paper, which consisted of a study of the alkalis and a determination of their composition both by calculation and by decomposition. Berzelius used the law of basic oxygen to determine the amount of oxygen in a base from the composition of a number of salts. Thus, since a certain quantity of muriatic acid always combined with bases that contained the same amount of oxygen, he could compare the quantity of ammonia that combined with a fixed amount of

[100] For a detailed summary of the contents of the *Versuch*, see Partington (1964, 4:153–58). The title of the paper can be translated as "Attempt to determine the definite and simple relations according to which the constituent parts of inorganic nature are combined with one another".

[101] For the formulation of the laws in his own words, see Berzelius (1810b, 163–64), translated in Berzelius (1811c, 252–53). In Lundgren (1992), the former is called "the law of unity".

[102] Berzelius later realized that Richter had already formulated this rule as well. See Melhado (1981, 170–73) for the way he arrived at this rule.

muriatic acid to the quantity of any other base needed, and calculate the amount of oxygen in ammonia to be 47,286% of its weight (Berzelius 1811e, 449).[103]

As Berzelius further developed his methods to calculate the composition of salifiable bases and other oxides, his new knowledge caused him to revise his views on the nature of ammonia. At the time of writing the first two parts of the *Versuch*, Berzelius was still convinced that ammonia was the oxide of some sort of metallic base, but he abandoned this view in part because he formulated another law of composition which would become the "keystone of his chemistry": the rule of oxides (Melhado 1981, 179).[104] This rule established a relationship between the amounts of oxygen in any two oxides that combined to form a neutral compound. The amount of oxygen in the most electronegative oxide had to be an integral multiple of that contained in the other, following an experimentally established pattern: the most electronegative oxide (the acid) contained 2, 3, 4, 5 or 6 times as much oxygen as the base. Berzelius formulated the rule of oxides between the publication of the original *Versuch* and that of the three supplements. He first shared it in a letter to Gilbert in October 1810 (Berzelius 1810c, 217), where he also defended the idea that nitrogen and hydrogen were oxides for the first time as a result of his new rule.

The idea that nitrogen and hydrogen contained oxygen was necessary for Berzelius to avoid any exceptions to his laws of composition and the empirical patterns of oxidation that they were based on. His archetype for the patterns of oxidation was that of sulphur (Melhado 1981, 198–99): for a given weight of sulphur, its acidic oxides contained oxygen in the proportions ½, 1, 2 and 3 (in modern terms: $SO_{1/2}$, SO, $SO_2$, $SO_3$).[105] In its salts, the amount of acidic oxygen was a multiple of 2 or 3 of the amount of basic oxygen (e.g. in modern terms: $PbO.SO_2$ for neutral sulphites and $PbO.SO_3$ for sulphates). Berzelius empirically confirmed the sulphur pattern for carbonic, phosphoric and muriatic acid, of

[103] In the translation this was corrected from 47,7% in the original paper (Berzelius 1810b, 260).

[104] For the way in which Berzelius arrived at his rule of oxides, see Melhado (1981, 179–84).

[105] With this pattern, Berzelius implied that sulphur combined with a half atom of oxygen, which shows his ambiguous attitude towards atomism at the time. He later did away with halves as he came to see atoms (at least instrumentally) as indivisible, see Lundgren (1992).

which the salts were also conform to the rule of oxides. Nitrogen compounds only matched this pattern if nitrogen (and initially, hydrogen) was a lower oxide itself (Melhado 1981, 203–11).

## Berzelius' circular argument on the nature of ammonia and nitrogen

Thus, long after Davy had given up on the presence of oxygen in ammonia, Berzelius became increasingly convinced of it. His initial analogical inference and the rule of oxides mutually reinforced each other in supporting this hypothesis. Like Davy, he argued the presence of oxygen in ammonia was likely because the other alkalis were known to be oxides, and the impossibility to detect free oxygen in ammonia could be explained by it being contained within nitrogen and hydrogen (Berzelius 1811d, 183). An additional argument came from a comparison with sulphuretted hydrogen (hydrosulphuric acid or hydrogen sulphide), an exception among the acids because it did not contain oxygen. If ammonia did not contain oxygen either, Berzelius argued it should conform to the patterns of combination of sulphuretted hydrogen, which it did not. This argument relied on the symmetry between alkalis and acids, which Berzelius all saw as containing oxygen (see Melhado 1981, chap. IV.1). If ammonia was an exception, an alkali without oxygen, he thought it should behave just as the acid without oxygen. Once he had provided these arguments in favour of the presence of undetectable oxygen in ammonia, he used his rules of composition to calculate the amount of oxygen in hydrogen, nitrogen and ammonia. He established a series of oxides of ammonium, inspired by the sulphur pattern and supported by gas density data supplied by Gay-Lussac (see Figure 4).

The second supplement to the *Versuch* consisted of a systematic study of nitrates and nitrites which was explicitly aimed at proving nitrogen's composite nature. Berzelius showed that nitrogen had to contain oxygen in order for the composition of various different nitrites to conform to the rule of oxides. All of these results were based on Gay-Lussac's erroneous eudiometric analysis of nitric acid (in modern terms the anhydride of nitric acid, $N_2O_5$) according to which the acid's formula would be $NO_2$(Gay-Lussac 1809). Using this data, Berzelius found that nitrates were not conform to the rule of oxides if nitrogen was taken to be a simple body, because the oxygen content of nitric acid would lie between 4 and 5 times that of the base. However, he argued that this problem could be

solved by taking the oxygen contained within nitrogen into account, making the oxygen content six times that of the base (Melhado 1981, 209–11). By then he had doubled the amounts of oxygen in his sulphur pattern, which meant nitrogen perfectly followed it. Berzelius considered this proof for the compound nature of nitrogen: "If the *nitrogen* in nitric acid compounds (…) *cannot be regarded as an elementary constituent*, then this cannot be the case anywhere in organic nature" (Berzelius 1812c, 173).[106]

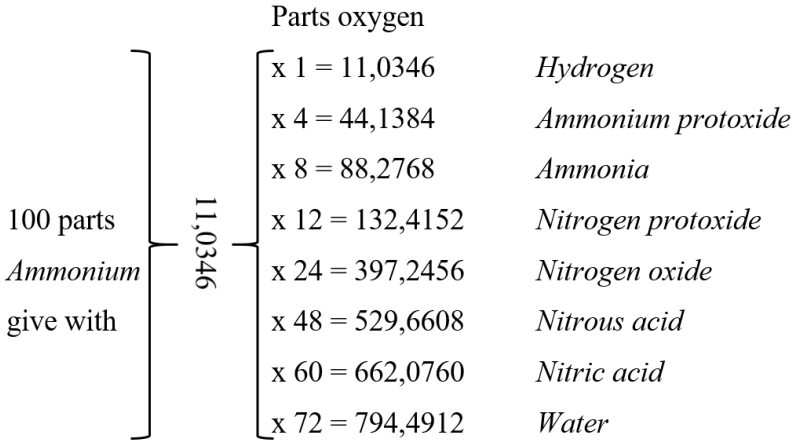



*FIGURE 4 - Berzelius' series of oxides of ammonium (Berzelius 1811d, 186).*

Thus, the laws of composition enabled Berzelius to reinforce his initial inference regarding the oxygen in ammonia, and to show that nitrogen was an oxide. Conversely, Berzelius' success in making nitrogen salts fit into the sulphur pattern increased his trust in his system of composition. The rule of oxides was supported by nitrogen oxides conforming to the sulphur pattern, and the oxide nature of nitrogen was supported by the conformity of its oxyacid salts to the rule of oxides. As Melhado (1981, 201) has argued, "Berzelius' persistence in upholding the oxide nature of nitrogen must be traced to the gratifying character of this interlocking relationship."

There were a few possible objections to Berzelius' view, and his way of dealing with them illustrates this circularity. In the second supplement to the *Versuch* (Berzelius 1812c), Berzelius discussed a possible objection to his own views: the constitution of nitrogen

[106] "Kann aber der *Stickstoff* in den salpetersäuren Verbindungen, wo das Ammonium sich in der positiv-elektrischen Modification befindet, *nicht als Elementar-Bestandtheil betrachtet werden*, so dürfte dieses wohl nirgends in der organischen Natur der Fall seyn." Emphasis original.

oxyacid salts only followed the rules of composition if nitrogen was taken as a simple substance in the calculation of their composition (Berzelius 1812c, 201). Berzelius concluded that in this case, nitrogen behaved as if it were a simple body, and it should be viewed as such in the calculations – but only in this case. On the one hand, Berzelius established his laws in absence of theoretical considerations, purely on the basis of empirical results. On the other hand, once they were established, Berzelius gave them tremendous importance in determining how experimental results should be interpreted. In Berzelius' system, no exceptions were allowed.

Berzelius also relied on this idea of nitrogen behaving as if it were simple in resolving another issue. As Berzelius (1811d, 187) himself remarked, his view left one striking question unanswered: if hydrogen, nitrogen, ammonia and water were all oxides of the same radical, how come reactions between hydrogen and oxygen always produced water, and reactions between nitrogen and oxygen always nitric and nitrous acids? The answer contained complex electrochemical considerations that cannot be discussed here (see Melhado 1981, 208). One notable argument however, was the suggestion that nitrogen and hydrogen were the proximate constituents of ammonia, just as acids and bases were the proximate constituents of salts. They behaved as if they were simple bodies without actually being simple. In some sense, ammonia could itself be seen as a kind of salt since it was composed of two oxides. This argument relied on a significant distinction between actually simple bodies and composed bodies that behaved as if they were simple (proximate constituents), a distinction that would later become a recurring theme in Berzelius' work on organic chemistry.

In short, once Berzelius had established his empirical patterns of oxidation he used them in order to interpret experimental results in the hope of retaining regular patterns of chemical combination without exceptions. The idea of compound nitrogen fit well into those patterns, and this increased their plausibility for Berzelius. The idea of compound hydrogen was not supported in the same way. While Berzelius initially used the rules of stoichiometry to argue for the composite nature of hydrogen as well, he already stated in the second supplement to the *Versuch* that this conclusion was much less certain than the composite nature of nitrogen (Berzelius 1812c, 175–76). In 1813 he abandoned the idea

completely and returned to a view of hydrogen as a simple body. He also proposed a new interpretation of the nature of nitrogen and ammonia that he would retain until the 1820s.

## Nitric and the development of Berzelius' system after 1813

In 1813, Berzelius' paper "Experiments on the nature of azote, of hydrogen and of ammonia, and on the degrees of oxidation of which azote is susceptible", a direct continuation from the second supplement of the *Versuch*, was published in two parts in the *Annals of Philosophy* (Berzelius 1813a). It is in this paper that Berzelius introduced his famous chemical notation which is still used today.[107] Here, Berzelius also replaced his previous view of ammonium as the radical of nitrogen with a new radical: nitric. In Berzelius' new view, nitrogen became the first degree of oxidation of nitric (whereas he had previously seen hydrogen as the lowest oxide of ammonium). Berzelius proposed five different proofs that all of the oxygen of ammonia was all contained within nitrogen and hydrogen had to be an "element" (*ibid*., 365-366).

Berzelius now thought of ammonia as composed of "two combustible bodies, combined with a single portion of oxygen common to both" (*ibid*., 366). In other words, it was the oxide of a compound radical which he noted as N+3H, making ammonia $NH^3$+O in his new notation. This meant that ammonia followed a pattern of composition which Berzelius had already identified for organic bodies with a compound base, such as sugar and tartaric acid. Just as there were organic acids, Berzelius therefore concluded that ammonia simply was an organic alkali. He used this new view to explain why the decomposition of ammonia produced only nitrogen and hydrogen: upon decomposition, the oxygen from ammonia would combine with nitric and form nitrogen, expulsing the hydrogen from the compound radical. This process was analogous to the decomposition of sugar, during which the compound radical was broken down and each of the simple bodies oxidized.[108] "By this explanation", he said, "the phenomena presented by ammonia will

[107] Berzelius' chemical notation began to spread from the 1820s onwards and proved extremely useful in chemistry. Ursula Klein (2001a; 2003) has shown how these symbols came to be used as 'paper tools' in the study of organic substances.

[108] Therefore, in Berzelius's (1813a, 367) words: "We can no more say, then, that ammonia is composed of azote and hydrogen, than we can that sugar is composed of carbonic oxide and hydrogen, or of carbon and water; because the very instance that these last substances are formed the organic compound ceases to exist as such."

cease to be anomalous, and … the analogy of ammonia with other bodies is perfectly restored" (*ibid*., 367). The only remaining anomaly was the ammonium amalgam, for which Berzelius simply saw no explanation.[109]

During the following years, Berzelius continued to work on his system, which was published in full form in his *Essai sur la théorie des proportions chimiques* (Berzelius 1819). The system was built on a 'dualistic' view of composition, building on (and expanding far beyond) that of Lavoisier and his colleagues: in Berzelius' view, salts were composed of oxides and acids, which in turn were each composed of oxygen and a radical. Like Lavoisier, Berzelius linked the properties of compounds to the amount of oxygen they contained, but he also explained their properties on the basis of electronegativity. At each of these different levels of composition, one played the role of a relatively electronegative body while the other was relatively electropositive (Russell 1963b).

Besides the establishment of patterns of chemical composition, Berzelius' systematic view of the composition of chemical substances was extremely useful for the early development of both chemical atomism and organic chemistry. In order to determine atomic weights, one had to know chemical formulae – and likewise the other way around. It was especially useful to know the composition of oxides, since the weight of oxygen was known and it was therefore easiest to use an oxide to calculate further atomic weights. Because they facilitated the identification of chemical formulae, Berzelius' patterns of composition enabled the calculation of atomic weights. Berzelian atomism was very influential, especially in Germany where it was commonly accepted during the 1830s (Rocke 1984, chap. 6).

For Berzelian atomism, the simple or compound nature of indecomposable bodies was not really of importance because he was not committed to any kind of indivisible atoms – there could very well be compound atoms that behaved as if they were simple in some cases. In fact, this idea of groupings of atoms as proximate constituents of more complex compounds gained a central place in the second application of Berzelius' system: the study

[109] He still saw it as a possibility at this time that the amalgam was a combination of mercury with the radical of ammonia: if this was the case then this would be "the curious phenomenon of a compound metallic body" (Berzelius 1813a, 367). The last page of the paper contains some conjectures regarding the possibility of transmutation, starting from this idea of compound metals.

of organic compounds. Berzelius expanded his dualistic view of chemical substances to the organic substances. This constituted another fruitful use of analogy, based on the idea that complex organic substances were composed of radicals just as inorganic substances were composed of chemical elements (Brooke 1969).

When Berzelius eventually changed his mind on ammonia again, his new view also relied on this idea of compound groupings behaving like simple constituents. He finally let go of the idea that ammonia and nitrogen contained oxygen around 1820 and admitted that nitrogen was a simple body (Söderbaum 1899, 125–27). Berzelius adopted a solution proposed by André-Marie Ampère in a footnote in 1816: that ammonium was a compound which in many of its chemical combinations behaved as if it were a simple body (specifically, an alkaline metal). Thus, for example, a volume of ammonia formed an oxide-like compound with a half volume of water, and salt-like compounds with one volume of hydrochloric acid or a half volume of hydrosulphuric acid (Ampère 1816b, 16). While this idea did not really explain why ammonia behaved in this way, it did preserve the analogies between the alkalis. Moreover, other bodies were known to behave in a similar way, most notably cyanogen which, although it was a compound, behaved in many ways like iodine and chlorine (see next chapter). The only disturbing exception that remained was the fact that free ammonia did not contain oxygen even though it behaved like a salifiable base.

From the way that Berzelius held on to the idea that ammonia and nitrogen were oxides, and even from his eventual acceptance of nitrogen as a simple body, it becomes clear that Berzelius was extremely attached to the link between the properties of bodies and their composition. This can be understood in terms of his research program during this period. For Berzelius, the idea that analogous substances shared a similar composition was more than a generalization of an empirical finding: it was a goal in itself, because it was the central premise on which any systematic account of chemical composition would be based. After all, it would not be possible to establish a system correlating the properties of bodies to various aspects of their composition if there was no such correlation to begin with. His wish to establish such a system in the first place is possibly linked to his textbook writing, for which it would of course be useful to be able to provide a general theory of chemical composition. Berzelius' started his work on ammonia during the writing of his first

textbook, and he postponed the publications of various editions because the nature of ammonia and nitrogen remained unsolved in his eyes (Jorpes 1970, 26).

This wish to establish a general account of chemistry and chemical composition was shared by Davy as well, although he followed a very different approach. While Berzelius was working on developing this system, Davy had gone into an entirely different direction towards a revival of the notion of phlogiston.

## Further development of Davy's ideas

By the time that Berzelius adopted the hypothesis of nitrogen being an oxide, Davy had already changed his mind again on the composition of ammonia. Between mid-October and mid-November 1809, he came to see ammonia as composed of three volumes of hydrogen and one volume of nitrogen.[110] In the Bakerian Lecture read on 16 November 1809, Davy (1810c, 58) proposed that the metallic appearance of some compounds of ammonia "perhaps might be more easily explained on the notion of nitrogen being a basis, which became alkaline by combining with one portion of hydrogen, and metallic, by combining with a greater portion." Davy stuck with this explanation as the most plausible one until 1812: the non-metallic substance ammonia became metallic by combining with hydrogen (H. Davy 1810a, 392; 1812, 481–82). Using this idea, he once again reversed his analogical inference in order to predict the composition of all metals on the basis of the idea that ammonium was a compound metal. In other words, the existence of ammonium provided Davy with a key argument in favour of the idea that all metals were compounds of hydrogen.

[110] Davy explained how he came to this new conclusion in a letter to Prieur from 9 November 1809 which was published in the *Annales de Chimie* (Prieur 1810). His continued investigation of the potassium-ammonia compound as part of his debate with Gay-Lussac and Thenard eventually led him to the conclusion that ammonia lost one third of its hydrogen when it combined with potassium (in modern terms: it formed an amide). This mean that no nitrogen was lost or decomposed, and this result was perfectly consistent with ammonia containing one part nitrogen and three parts hydrogen.

## Davy's phlogistic theory

Davy's new view of ammonia fit in nicely with a certain type of speculation that he had already presented. Davy (1839, V:89-90) first remarked that "a phlogistic chemical theory might certainly be defended" in a footnote in the Bakerian Lecture for 1807. According to such a theory, the metals would be compounds of unknown bases and hydrogen, and the metallic oxides would be compounds of the same bases with water. Similar to the way in which phlogiston had been thought to cause metallic properties in pre-Lavoisian chemistry, hydrogen would be the principle of metallicity in Davy's view. Though he never definitely rejected Lavoisier's anti-phlogistic chemistry, Davy exhibited an "extensive flirtation with phlogiston" throughout the next five years (Siegfried 1964, 118).

Early on in this period, he had already raised the hypothesis that ammonium might be an example of a compound metal; however, I argue that he did not see it as the most likely explanation of ammonia's nature until 1809.[111] From that moment on, ammonium became "a kind of type of the composition of the metals" for Davy (1812, 481). The nature of ammonia and ammonium was of central importance in Davy's revival of phlogiston, because metallic ammonium constituted the first and only example of a substance that became metallic by combining with hydrogen. This was the only available evidence, because Davy could not provide other experimental proof of metals containing hydrogen. Any finding on the nature of ammonia therefore necessarily influenced his view of chemical composition in general (H. Davy 1810c, 72).

Since there was no way to experimentally show the presence of hydrogen in metals, Davy's hypotheses regarding the inner composition of metals were mainly based on analogical inferences. Davy summarized his central premise as follows:

[111] For example, in his paper on the decomposition of the earths, though he considered the possibility that ammonium was a compound metal, Davy (1808a, 368 footnote) still argued that the most likely explanation was that nitrogen was an oxide of the simple body ammonium.

> "As far as our knowledge of the nature of compound bodies has extended, analogy of properties is connected with analogy of composition; if one of the inflammable solids or metals is proved to be compound, there would be strong evidence for supposing that the others were likewise compounded" (H. Davy 1812, 480).

Since similarly composed substances were known to behave similarly, chemical analogy among groups of similar substances might very well be caused by the presence of the same element in all of them. Likewise, according to Davy, the fact that metals resembled each other made it likely that they all had a similar internal composition. In a lecture at the Royal Institution in 1811 he explained:

> "The analogy of the properties of the metals, - their conducting power, - the magnitude of the number representing them [their atomic weight], - their splendour, - the similarity of their crystals, would all lead us to the idea of their not being entirely different kinds of matter; but would rather incline one to suppose that they contain some common element or elements" (H. Davy 1839, VIII:330).

The 'common element' that would explain metallic properties in Davy's theory was hydrogen. He also proposed that variations in the proportion of hydrogen were likely linked to differences in density and reactivity with oxygen. Thus, the lightest metal would contain the most amount of hydrogen and therefore have the strongest attraction for oxygen (H. Davy 1808a, 363–64).

The hypothesis of the internal composition of metals was also supported by the way in which ammonium combined with other substances. Davy had previously thought that the simpler the substance, the stronger its attraction to other bodies. According to that view simple bodies combined together to form a difficultly decomposable primary compound, whereas more complex compounds were easier to decompose. The way in which ammonia combined contradicted this idea: for example, it formed a compound with phosphorus and chlorine which was "incredible, according to all the existing analogies of chemistry" (H. Davy 1810b, 248) because two gases combined with a volatile solid to form a substance that did not decompose or even melt at a red heat. The fact that such a complex yet difficultly decomposable compound existed made it more likely that the impossibility of decomposing substances was not a sign of their actual simplicity:

> "the common chemical proposition, that complexity of composition is uniformly connected with facility of decomposition, is not well founded. (…) Is it not likely, reasoning from these circumstances, that many of the substances, now supposed to be elementary may be reduced into simpler forms of matter?" (H. Davy 1810b, 248)

In other words, Davy suggested that the fact that metals combined with other substances as if they were simple bodies could no longer be taken as a sign that they were actually simple.

Throughout the years that Davy brought up his phlogiston-inspired views, he never affirmed them as a definitive theory; however, the frequency with which he brought up these ideas indicates that they were more than just casual explorations of alternative views of matter (see also Siegfried 1964; Chang 2012b, 33–34). In Davy's view, "to inquire whether the metals be capable of being decomposed and composed [was] a grand object of true philosophy" (H. Davy 1839, VIII:331, from an 1811 lecture at the Royal Institution). After the publication of his 1812 textbook *Elements of Chemical Philosophy*, Davy never again suggested that a phlogistic theory of matter could explain the phenomena. In 1814 he openly rejected his previous conjectures, stating:

> "The chemists in the middle of the last century had an idea that all inflammable bodies contained phlogiston or hydrogen. It was the glory of Lavoisier to lay the foundations for a sound logic in chemistry, by shewing that the existence of this principle, or of other principles should not be assumed where they could not be detected" (H. Davy 1814b, 71–72).

Siegfried (1964, 124) concludes from this citation that "Davy's deep commitment to empiricism had reasserted itself" from 1812 onwards. I suggest instead that Davy's commitment to an empirical view of simple bodies emerged during these transitional years. His strict definition of the element as a simple (or even undecompounded) body seems to have resulted, or at least refined, by his research on ammonia and related questions. Until 1812, Davy felt perfectly comfortable speculating on the inner complexity of indecomposable bodies. His main goal during that period was to establish a systematic theory of chemistry that explained the properties of matter on the basis of composition

in terms of only a few elementary bodies. It was only from around 1813 that Davy completely abandoned this idea and restricted himself to purely empirical statements. The rest of this section will be dedicated to developing this argument.

## Davy's changing view of elements

Until around 1812, Davy distinguished between true elements, which played a role in causing the properties of compound substances, and insignificant simple bodies that could not explain any of the properties of matter. He had initially considered the idea that each metal might be a compound of hydrogen with an unknown basis, meaning that each decomposed metal would give rise to the discovery of a new body. However, this would not provide a simpler explanation of the phenomena, since this required the existence of the exact same number of simpler constituents. Davy therefore replaced his idea of unknown metallic bases with the idea that there was a single, unknown radical present in every single one of the metals in addition to hydrogen (see Siegfried 1964).

Davy's main goal during this time was to establish a simple, systematic theory of chemistry which explained all matter on the basis of only a few constituents. In his view, it was very unlikely that nature was messy and complex. The fact that chemists admitted the existence of so many simple substances was therefore a sign that chemistry was still very far from arriving at a true understanding of matter:

> "Whoever compares the complication of the systems which have been hitherto adopted, and the multitude, as it were, of insignificant elements, with the usual simplicity and grandeur of nature, will surely not adopt the opinion, that the highest methods of our science are already attained; or that events so harmonious as those of the external world, should depend upon such complex and various combinations of numerous and different materials" (H. Davy 1839, VIII:326; from a lecture in 1809).

Davy's effort to reduce the number of elements raises a question: how did he identify true elements and distinguish them from other, 'insignificant' simple bodies? There is no single reply to this question as his views changed over time. In 1808, Davy characterized oxygen as "the only body which can be supposed to be elementary" (H. Davy 1808a, 363). Oxygen was the most electronegative body known at the time, and Davy suspected that its presence caused the relative electronegativity of oxides. Hydrogen was also a possible

candidate for him, because it was the most electropositive body and perhaps the cause of the relative positivity of bodies like metals (if his phlogistic theory was true). However, in 1809 he also considered the possibility that hydrogen contained oxygen, an idea that contradicted its elementary nature. Later, he would first adopt hydrogen as the only true element before abandoning the idea of true elements altogether.

In 1812, Davy (1812, 480) characterized hydrogen as a true element:

> "We know nothing of the true elements belonging to nature; but as far as we can reason from the relations of the properties of matter; hydrogen is the substance which approaches nearest to what the elements may be."[112]

According to Davy, hydrogen could not be one of the 'insignificant' simple bodies, because was lighter than all the other undecompounded bodies and capable of combining with many different other bodies. It was also the most positively charged simple substance and its presence might therefore explain the positive charge of many inflammable compounds. Oxygen was almost as likely to be an element as hydrogen, because it too was reactive and light and it was the most negatively charged simple substance (Davy 1812, 480; 1839, V:132-33). In contrast, in the same work he still described nitrogen as a potential compound that had never been decomposed despite numerous attempts (H. Davy 1812, 270).

To Berzelius, this characterization of hydrogen appeared quite arbitrary. He asked Davy: "What are the characteristics of an element that are so eminent in hydrogen – or rather, is there an elementary characteristic, and what is this characteristic?"[113] This question was one of a long list of critical remarks that Berzelius sent to Davy after reading his textbook. By then, their correspondence had already become less frequent and their friendship was already significantly weakened by their disagreement regarding the

[112] Likewise, he stated that "of all gaseous substances, hydrogene is most distinctly characterized as an element" (H. Davy 1812, 254).

[113] "Quels sont ces caractères d'élément si éminents chez l'hydrogène – ou plutôt y a-t-il un caractère d'élément, et quel est ce caractère?" (Berzelius 1912b, 45). Berzelius himself did not formulate similar speculations on true elements, but he did state that oxygen "[constituted], as it were, the central point of chemistry" (Berzelius 1813a, 359).

existence of chlorine (see next chapter).[114] Berzelius had visited London in the summer of 1812 but they only met once, as Davy left for travels to Scotland, and their disagreements only increased after discussing in person (see Berzelius 1912b, 29–33).[115]

From the remainder of their correspondence, it becomes clear that Davy had adopted a new attitude towards the question of elementary nature around 1813. Davy never addressed all of Berzelius' remarks in detail, but they did have a final exchange in August 1813, during which Davy criticized Berzelius for placing too much trust in his hypotheses regarding the nature of (among other things) nitrogen:

> "I consider your *composition of azote* as *mere hypothesis* like your *composition of oxymuriatic gas;* and I shall continue to consider *all bodies* as undecompounded the elements of which have not been separated into any other forms of matter. I think it *very probable* that azote, chlorine, and the metals and inflammable bodies are compounds. I think it *probable* that the two first contain oxygene [sic] and the last contains hydrogene [sic]; but it is absolutely necessary to distinguish between what is *very probable* and what is *known*" (Berzelius 1912b, 59; emphases original).

While Berzelius replied that he too considered his ideas regarding the composition as mere hypotheses, he immediately contradicted this statement by adding that his latest experiments "decisively" proved its composition (*ibid*., 62). To Davy's point regarding the nature of undecompounded bodies, Berzelius replied:

> "I dare to object to you that among all the truths that we recognize as such, there are only very little that we can so to speak touch upon [*toucher du doigt*], and that it is by means of a consistent reasoning that most of our knowledge is verified. […] – My proofs of the composition of nitrogen are very simple; that is to say, I have shown that if nitrogen does not contain oxygen, there are combinations of which the quantitative composition is contrary to the law of chemical proportions; and since it is impossible for such cases to exist, nitrogen must be an oxide" (*ibid*., 62).[116]

[114] Russell (1963a) notes their different opinions on the atomic theory as an additional problem.

[115] For a summary of Berzelius ambiguous feelings towards Davy after their lunch together, see Jorpes (1970, 59–61). For his activities on this trip and his later European traveling, see Bernhard (1992).

[116] "(…) j'ose vous objecter que parmi toutes les vérités que nous reconnaissons comme telles, il n'y en a que bien peu que nous pouvons pour ainsi dire toucher du doigt, et que c'est par le moyen d'un raisonnement

At stake in this exchange was not just their interpretation of the composition of specific bodies, but also their underlying views about the relation between theory and experiment. Whereas Berzelius became increasingly confident about the possibility to calculate chemical composition, Davy no longer felt comfortable stating anything but experimental facts. By 1813, he had clearly abandoned the idea of true elements that he defended between 1807 and 1812.

## Davy and Berzelius' (increasingly) different views of chemistry

Although Davy and Berzelius heavily influenced each other during 1808 and 1809, they were also working in fundamentally different contexts, and they had different attitudes towards the ways in which one should distinguish between 'what is probable' and 'what is known'. Berzelius had no problem expressing his trust in hypotheses that were not commonly adopted. Despite admitting it was controversial, he classed ammonium as a metal in 1811, stating that he made this decision "in the conviction that [chemists would] sooner or later agree with [him]" (Berzelius 1811a, 283). Berzelius wanted a chemistry that could be useful. He operated within the Swedish tradition of common-sense applied chemistry (as exemplified by Torbern Bergman's work on affinity). Even though he eventually gave a lot of weight to his laws of chemical composition, they were initially the result of theory-less, empirical weight measurements (see Lundgren 1992).

Davy, on the other hand, looked for something more profound in his chemical theories, partly as a result of his social and cultural environment. References to the 'simplicity' and 'grandeur' of nature were characteristic of the period, as Trevor Levere (1977b) has described. In nineteenth-century England, chemistry was thought of as the best science to understand, control and enhance nature. Nature was seen as unified and harmonious and chemistry was expected to trace its design in a systematic way. This required the identification of patterns in experimental results, for which analogical reasoning was the

conséquent que la plupart de nos connaissances se sont vérifiées. […] – Mes preuves de la composition de l'azote sont fort simples ; c'est à dire, j'ai fait voir que si l'azote ne contient point d'oxygène, il y a des combinaisons dont la composition quantitative est contraire aux lois des proportions chimiques ; et comme de tels [cas] ne peuvent point exister, l'azote doit être un oxyde".

perfect method (see also Ruston 2019). However, an irony that has been noted by Levere and others is that the search for such a harmonious system of chemistry led to the discovery of numerous new substances, many of which could not be decomposed. This "fecundity of Nature" (Levere 1977b, 197) motivated speculations on the internal complexity of elements throughout the nineteenth century.

While Berzelius felt more and more certain on the subject, Davy was gradually abandoning his ideas on the nature of ammonia. It seems Davy never truly felt he resolved the question, and he never characterized any view of ammonia as more than "probable". Throughout these years, Davy made sure to never appear too certain of his various hypotheses. In his *Elements of Chemical Philosophy*, Davy (1812, 475) stated that the subject of the nature of the ammonium amalgam was "still obscure and mysterious, and the true theory of the experiment [could] only be developed in consequence of new facts." He treated the ammonium amalgam in the chapter dedicated to bodies whose nature was still unknown and explained he brought up the phlogistic speculations "merely for the sake of pointing out a promising path of enquiry" (*ibid*., 483). This may have been a strategy to avoid criticism: the less he committed to a theory, the harder it was to attack him.[117]

Davy's later distrust of analogical inferences is often taken to represent his general attitude and views of chemistry. Russell (1963a, 120) has described Davy's "dislike of clear-cut conceptual models, sometimes expressed as a simple reluctance to commit himself to a theory". Siegfried (1959, 196) has likewise characterized Davy as "deeply suspicious of all theoretical attempts to give unity and coherence to the science of chemistry". While I do not want to argue that these descriptions are completely wrong, I hope to have shown in this section that Davy's views were changing and his approach cannot be characterized without taking into account when exactly he made certain statements. We cannot take for granted that his ideas from 1807 reflect the same underlying attitude about nature, chemistry and theories as his ideas from 1814.

When it comes to analogical reasoning, it seems that some development took place around 1812/13 that caused Davy to take on this cautious attitude. Perhaps there was a link

[117] As Brooke has pointed out: "Davy certainly found a thrusting eclecticism the best form of defence" (Brooke 1980, 129).

to his marriage and departure from the Royal institution, but this is difficult to ascertain. In his final reply to Berzelius from 19 October 1813, Davy explained his reservations as follows:

> "(…) having been myself deceived by analogies I am resolved to trust nothing but facts and to call no body a compound of which the elements are not objects of physical sensation" (Berzelius 1912b, 64).

He did not elaborate on the exact deception he had suffered from trusting analogies but it is possible that this was a reference to his work investigating the question of ammonia, which he felt did not have a satisfactory outcome. It must have been disappointing for Davy not to have found a solution to this question, especially seeing the efforts he made to investigate it. In the words of his brother John:

> "Persons not acquainted with the labours of original research, and the perseverance requisite to solve obscure problems experimentally, would have difficulty in imagining even, the pains he took, the time he spent, the vast number of experiments he made to resolve his doubts, on the question of the nature of ammonia; the details which he published (…) give but an imperfect idea of the varied, numerous, and laborious experiments he engaged in on this very curious, important and difficult subject (…)" (Davy 1839, V:98).[118]

When Davy explained his deception in analogical reasoning, he had recently stopped lecturing at the Royal Institution; he would spend most of the following seven years travelling around Europe with his wife (see Golinski 2019). Davy and Berzelius would not speak again until 1821, but they did engage with each other's views in a public debate on the nature of chlorine, which will be discussed in the next chapter. By that time, their ideas on the role of theory and analogy in chemistry had become completely opposed.

# Conclusion

Between 1807 and 1813, Davy and Berzelius often changed their interpretations of ammonia in order to make their hypotheses more coherent with experimental results. Because they changed their mind so many times, their reasoning can be quite difficult to

[118] John Davy explained this in a footnote in Humphry Davy's *Collected Works*, of which he was the editor.

follow; their successive views can be summarized as follows. Davy initially assumed, like many of his colleagues, that all alkalis would be compounds of nitrogen. When his decomposition of the fixed alkalis showed that they were oxides that did not contain nitrogen, he reversed his analogical inference and predicted that there might be some previously undetected oxygen in ammonia as well: oxygen would then be the cause of alkalinity as well as acidity. Berzelius' observation that it was possible to form an amalgam from ammonia caused him to adapt his interpretation once again: it now appeared plausible that ammonia was a metallic oxide like potash and soda. Both Davy and Berzelius, as well as some of their contemporaries, identified ammonia as ammonium oxide around 1808.

However, both the isolation of metallic ammonium and the experimental confirmation of the oxygen content in ammonia remained impossible. Moreover, the fact that the decomposition of ammonia as well as the decomposition of its amalgam produced only hydrogen and nitrogen contradicted the hypothesis of ammonium oxide: how could ammonia behave as a metallic oxide while also being composed of nitrogen and hydrogen? Davy proposed that nitrogen and hydrogen might themselves be oxides of ammonium, which would explain why no 'free' oxygen could be detected in ammonia. Berzelius not only adopted this idea but thoroughly investigated it through the establishment of laws of composition that enabled him to calculate the oxygen content in nitrogen and hydrogen. The further development of his theory of composition led him to change his view of nitrogen again, interpreting it not as the oxide of ammonium but of a new radical called 'nitric'. He did not accept the elementary nature of nitrogen until the early 1820s.

Meanwhile, Davy had moved on to yet another interpretation of the phenomena: from late 1809 to 1812, he believed that ammonia became metallic by combining with hydrogen. This existence of the compound metal ammonium became a key argument in favour of his theory that all metals were compounds of hydrogen, with hydrogen playing a phlogiston-like role as the cause of metallic properties. Davy investigated these ideas for years until he eventually came to abandon them and the idea of principle-like causes of properties altogether. Around 1813, he also lost his previous faith in the use of analogy to identify the internal composition of indecomposable bodies and became very committed to a strict characterization of chemical elements as indecomposable substances.

The way in which Davy and Berzelius adjusted their views and hypotheses over the course of these years shows how they dealt with contradictions between different kinds of evidence: they attempted to make their experimental results coherent with analogical inferences. Both Davy and Berzelius were reluctant to admit the possibility that one of the alkalis was not a metallic oxide like the two others. Davy did eventually accept this idea but only because it enabled him to argue that all metals had a similar composition instead. Berzelius took a much longer time to accept that ammonia did not contain oxygen, and only did so when there was a new way to fit nitrogen compounds in his view of composition during the early 1820s. Even more so than the acceptance of aluminium, the investigation of ammonia shows that these chemists relied on the consilience of different types of evidence in order to study chemical composition.

Likewise, this conclusion points towards an additional parallel with Hasok Chang's (2004) study of the development of temperature scales. Chang has interpreted the corrections that physicists made to their measurements of temperature not as the approaching of some pre-existing 'real' or correct value, but rather as an iterative process through which the correct value was itself gradually established which he has called 'epistemic iteration'. The process of epistemic iteration starts with some existing system of knowledge, which is not necessarily justified or proven in itself – scientists simply have to start somewhere. Starting from their existing knowledge, practitioners investigate a phenomenon until their findings come to contradict their existing ideas and they have to adjust their system of knowledge. This process can continue through any number of iterations, with each stage of knowledge building on the previous one, while also correcting it. This view implies a "progressive coherentism", a view of scientific knowledge as progressing even though it is not resting on an underlying foundation; rather, at each stage the different types of evidence mutually justify each other by their coherence (Chang 2007).

The prediction of the existence of aluminium did not necessarily seem to follow such a pattern because convergence happened so quickly: experimental results, analogical inference and previous knowledge all pointed towards the conclusion that alumina was the oxide of a metal called aluminium. The case of ammonia, on the contrary, provides us with an example of how practitioners progress from one hypothesis to another when they are

trying to understand a phenomenon. In cases like these, scientists do not even know what it is they are truly looking for because the expected outcome changes as hypotheses, methods and experimental setups are adjusted. The only thing they can do in order to get closer to a successful outcome is "to carry on with the iteration until [they] are pragmatically satisfied that a convergence seems destined to happen" (Chang 2004, 215). With regards to Berzelius' work, the stages of epistemic iterations continued long after the period discussed here, as the application of his system to organic compounds was so fruitful that it eventually came to contradict his dualistic view of composition (Brooke 1969; Klein 2003).

In progressing from one stage to the next, Davy and Berzelius relied on analogical inferences in the formulation of their working hypotheses as well as the design of their experimental procedures. This shows how Fisher's (2018) account of the role of analogy in the formulation of hypotheses fits within a view of scientific inquiry as progressing via epistemic iterations. Moreover, analogical inferences were more than just a heuristic to formulate new hypotheses. Like in the case of aluminium, analogies could function as a type of evidence in themselves as Davy and Berzelius relied on their knowledge of the composition of the alkalis in studying the composition of the analogous substance ammonia. Their attempts to eliminate exceptions show how incredibly attached they were to the correlation between properties and composition. For Berzelius especially, this correlation took the form of a central aim in itself, as he was trying to establish a systematic account applicable to all chemical composition.

The example of ammonia also illustrates that the identification of chemical elements happened on the basis of this rule. Contradictions between analogical inferences and failed decomposition attempts could be resolved by relying on the distinction between the apparent simplicity of bodies and their actual simplicity. Investigations of the inner complexity of indecomposable bodies was therefore not limited to metaphysical speculations; these were serious research questions and their investigation was necessary in order to identify chemical elements. Even bodies such as nitrogen which behaved like simple bodies could not be seen as simple if the general analogy of chemistry pointed to a different conclusion.

The story of ammonium, the supposed metallic constituent of ammonia, did not end in 1813 even though it was no longer argued to be a chemical element. Berzelius continued to name it as one of the metals in his textbook because it behaved like an organic metal (Berzelius 1845). During the 1830s and -40s, ammonium became a standard example of a compound radical, as a compound body that persisted throughout a number of compounds in analogy to simple bodies. This in turn motivated renewed speculations on the inner complexity of simple bodies (see Farrar 1965). The behaviour of ammonium continued to puzzle scientists even into the twentieth century, as they wondered whether something like a compound metal could exist (see for example McCoy 1911; Stevenson 1975). Much of this history is still unknown and a lot more could still be learned from the ways in which scientists tried to make sense of ammonium and the 'curious exception among the alkalis'.

Meanwhile, after 1813 Davy and Berzelius continued to drift apart as they opposed each other in a debate on the nature of a different substance: oxymuriatic acid, also known as chlorine. The question of whether or not this substance could be seen as a chemical element divided the European chemical community between approximately 1810 and 1816. This debate provides a different kind of example of a contradiction between existing chemical knowledge and new experimental results: chlorine appeared to be an indecomposable substance, but this conclusion was incoherent with existing views of the composition of acids and salts. The debate on the nature of chlorine will be the topic of the next chapter.

# CHAPTER 3 - "The Just Logic of Chemistry": The Debate on the Nature of Chlorine (1809-1816)

In his *Elements of Chemistry*, Davy argued:

> "(…) till [chlorine] is decompounded, it must be regarded, according to the just logic of chemistry, as an elementary substance" (H. Davy 1812, 241).

It might seem like Davy was simply stating the obvious. Seeing as elementary substances were commonly defined by their provisional indecomposability at the time, it would seem logical for all chemists to agree with Davy on this point. And yet, this was a highly controversial statement, published at the height of a debate on the nature of chlorine that lasted between 1810 and 1816. Among Davy's critics were a number of Europe's most famous chemists: Thomas Thomson, William Hyde Wollaston and John Dalton in Great Britain; Claude Louis Berthollet, Louis Jacques Thenard and Nicolas Vauquelin in France and Jöns Jacob Berzelius in Sweden.[119] They were reluctant to admit that chlorine was a chemical element, not because they disagreed with the idea that all simple substances should be provisionally seen as elementary – rather, they disagreed on the question of whether or not chlorine had been decomposed.

As a chemical substance, chlorine had been known since 1774, when it was first isolated and studied (see Ashbee 2007). Scheele identified it as *muriatic acid* (HCl) that had lost its phlogiston, and therefore named it *dephlogisticated muriatic acid* (Scheele 1774; 1901, 69–70). In 1785, Berthollet proposed – in accordance with Lavoisier's new system of chemistry – that it should be renamed "*oxygenated muriatic acid"* (Weeks 1956, 730–31). Most chemists working in the Lavoisian system adopted this new identification, which they sometimes shortened to *oxymuriatic acid*. In 1809, Gay-Lussac and Thenard realized that it was impossible to extract the oxygen from oxymuriatic acid using white hot charcoal. Davy confirmed this in 1810 and also found that it was impossible using the

[119] Most of these will be discussed in more detail below with the exception of Wollaston and Dalton. Dalton did not include chlorine in his table of atomic weights (see Rocke 1984, 80–82). Rocke reports that Wollaston remained unconvinced of the elementary nature of chlorine as late as 1816 (*ibid*., 62).

voltaic pile. Since it could not be decomposed using even the strongest means available, Davy defended the hypothesis that oxymuriatic acid was a simple body named 'chlorine'. Many chemists opposed his interpretation because they argued his experimental results could be explained on the basis of compound oxymuriatic acid.

One of the main issues in the debate was that the two sides disagreed on which reactions to view as decompositions and which as combinations. The reaction of chlorine/oxymuriatic acid with hydrogen could be viewed as a combination producing hydrochloric acid, or as a decomposition producing muriatic acid and water. In this case, weight measurements could not solve the debate because both sides proposed hypotheses that were coherent with the conservation of mass. Thus, two possible hypotheses could explain the facts, and principles like theoretical coherence and simplicity had be taken into consideration in order to choose the most likely explanation. Chemical analogies and the classifications based on them were of key importance: which interpretation enabled the formulation of the most coherent and useful classifications? Not only the new simple body, but also the new views of its compounds had to be accounted for and made coherent with the rest of chemical knowledge. It wasn't until after the discovery of iodine, which was analogous to chlorine, that most of Davy's opponents accepted to view chlorine as a chemical element.

Out of the different case studies that make up this thesis, the debate on the nature of chlorine is the most well-known. The debate on the nature of chlorine has been studied by Jan Golinski (1992), Hugues Chabot (2006) and Tamsin Gray, Rosemary Coates, and Mårten Åkesson (2007), but I will complete these existing works with a study of primary sources including correspondence, textbooks and scientific papers. The existing studies all show the role of the discovery of iodine in the resolution of the debate thanks to its analogy to chlorine. While this chapter will confirm their results, it will also elaborate on what exactly this analogy consisted of and why it was required in order to chlorine to become generally accepted. I will show how chemists relied on these analogies in order to ensure the coherence of their classifications and the correct interpretation of experimental results. Building on the previous two chapters, I will argue that analogical evidence was required in order for substances to be accepted as provisionally simple.

I will first describe the observations that gave Davy reason to think that chlorine might be a simple substance and argue that his opponents found themselves perfectly capable of explaining them without doing away with oxymuriatic acid. Since both sides were capable of explaining the facts, I will then show why the opponents of chlorine preferred a seemingly more complex explanation. The chapter will end with a discussion of the ways in which the discovery of iodine opened up the possibility for the elementary nature of chlorine to be accepted. Only when their compounds found a place in the general system of chemical knowledge, were the two new substance accepted as chemical elements.

# Two explanations for the impossibility of reducing oxymuriatic acid

## The old hypothesis and the new hypothesis

In february 1809, Gay-Lussac and Thenard presented their research on muriatic acid at the Institut National. They had tried to take some oxygen out of oxygenated muriatic acid in an effort to obtain dry muriatic acid. According to Lavoisier's theory, the acidity of a substance depended on the quantity of oxygen it contained: a radical would be turned into an oxide, acid or oxygenated acid when it was respectively in the first, second or third, and fourth degree of oxygenation. At the beginning of the nineteenth century, there was still much to be learned about the muriatic oxides. According to this view, muriatic acid would consist of oxygen and an unknown muriatic radical. This radical had not yet been isolated, nor had its lower degrees of oxygenation, muriatous and muriatic oxide. Lavoisier (1790, 187) proposed that this was probably due to the fact that the radical had a very high affinity for oxygen. In order to do reduce oxymuriatic acid, Gay-Lussac and Thenard therefore searched for a combustible body that would react with part of its oxygen.

However, they were unable to find a body that had enough affinity for oxygen. Gay-Lussac and Thenard tested metals, as well as sulphur and phosphorous, but all of these substances directly combined with the oxygenated muriatic acid without extracting any oxygen from it. They therefore decided to try their strongest method for extracting the oxygen out of a compound: white hot charcoal. They were able to produce oxymuriatic acid using this method but only when the charcoal was slightly moist; nothing happened when completely dry charcoal was used (Gay-Lussac and Thenard 1809). A year later,

Davy (1810b) repeated the experiments of Gay-Lussac and Thenard and confirmed their results. Besides white hot charcoal, he also his voltaic pile, and even stronger instrument for reduction. Neither of these methods could extract any oxygen from oxymuriatic acid.

The fact that none of the usual reduction methods worked caused Davy to doubt the presence of oxygen in oxymuriatic acid, and he therefore attempt to detect the oxygen using indirect methods. Among other experiments, he tried to reproduce one of Fourcroy's experiments, who had been able to form water by combining ammonia and oxygenated muriatic acid in 1802. This result had been explained, for example by Berthollet, by the idea that hydrogen from the ammonia had combined with the oxygen from oxymuriatic acid (see Gray, Coates, and Åkesson 2007, 59). Despite multiple attempts, Davy was unable to obtain the same results as Fourcroy. For Davy, the idea that oxymuriatic acid contained oxygen could no longer be seen as proven. From this moment on, he started to defend a new hypothesis according to which oxymuriatic acid was an elementary substance. Although he did not definitively rule out the possibility that it might contain oxygen, Davy argued that the name 'oxygenated muriatic acid' was not accurate as long as it could not be experimentally confirmed. Instead, he proposed that a new name be adopted in order to correctly reflect the substance's composition; after all, "names should express things and not opinions; and till a body is decompounded, it should be considered as simple" (H. Davy 1811b, 33–35). Davy suggested to name the simple body "chlorine", from the Greek word 'chloros' used to describe its green colour.

Even though they had obtained similar results, Gay-Lussac and Thenard's conclusion had been different from that of Davy:

> "Indeed, oxygenated muriatic acid gas is not decomposed by charcoal, and, following this fact as well as those which are reported in this paper, it might be supposed that this gas is a simple body. The phenomena which it presents can be explained well enough using this hypothesis; we shall not seek to defend it however, because it seems to us that they are even better explained by viewing oxygenated muriatic acid as a composed body" (Gay-Lussac and Thenard 1809, 357–58).[120]

[120] "Le gaz muriatique oxigéné n'est pas, en effet, décomposé par le charbon, et on pourroit, d'après ce fait et ceux qui sont rapportés dans ce Mémoire, supposer que ce gaz est un corps simple. Les phénomènes qu'il présente s'expliquent assez bien dans cette hypothèse ; nous ne chercherons point cependant à la défendre, parce qu'il

In other words, they did not see the need to adopt a new view of oxymuriatic acid because the impossibility to reduce oxymuriatic acid was perfectly well explained by the old view. Their explanation relied on the idea that muriatic acid contained "intimately combined" water in the proportion of ¼ of its weight (Gay-Lussac and Thenard 1809, 242). By this they did not mean the components of water: they meant that water as such existed as a component of muriatic acid, in the same way that water can also be contained in hydrate salts, for example. Gay-Lussac and Thenard explained that according to this view, muriatic acid gas could not be formed without combined water in it.

The idea of combined water explained Gay-Lussac and Thenard's (1809, 329–39) finding that the only possible way to produce muriatic acid from oxygenated muriatic acid was by a reaction with hydrogen or compounds of hydrogen. Today we would interpret this reaction as the combination between hydrogen and chlorine to produce hydrochloric acid. For Gay-Lussac and Thenard however, something else happened: the oxygen was separated from the oxygenated muriatic acid and combined with hydrogen to form water. No free water was produced by the reaction, because this water remained intimately combined within the muriatic acid gas. This could also explain why muriatic acid was heavier than oxymuriatic acid even though it was supposedly simpler, and it was consistent with the impossibility of producing muriatic acid by reduction with dry charcoal. Whereas Davy argued that chlorine had never been decomposed, those who adhered to the old hypothesis saw the production of muriatic acid as the decomposition of oxymuriatic acid. In other words, according to their interpretation oxymuriatic acid was not an indecomposable substance.

To a current-day reader, this explanation on the basis of the idea of combined water may sound rather far-fetched and complicated. Why would one accept so many suppositions when it seems much simpler to accept the elementary nature of chlorine? In fact, muriatic acid was not an isolated case, because the other mineral acids also have this property: nitric and sulphuric acid only existed in solution or as hydrates, and it was experimentally impossible to produce them in a 'dry' form even in their most concentrated

nous semble qu'ils s'expliquent encore mieux en regardant l'acide muriatique oxigéné comme un corps composé."

states. It therefore made sense to many chemists to generalize this idea and assume that the production of all mineral acids required the presence of water. Indeed, many chemists at the time defended this idea of combined water and the fact that it explained the experimental results perfectly well.

The fact that there were two possible explanations of the same phenomena meant that it was impossible to decide between the two purely on the basis of experimental results. This equivalence of the two explanations becomes especially clear from the debate between John Murray and Davy's younger brother John.

## The debate between John Murray and John Davy

One of the most persistent opponents of chlorine was John Murray (1778-1820), lecturer in chemistry at the University of Edinburgh. Humphry's brother John Davy (1790-1868), who had helped research chlorine as an assistant at the Royal Institution, became a medical student in Edinburgh between 1811 and 1814 (see Lacey 2019). He entered into a two-year long discussion with Murray, which took place through publications in William Nicholson's *Journal of Natural Philosophy, Chemistry and the Arts* (for an overview, see Golinski 1992, 222–31). Davy insisted very heavily on the idea that chlorine should be seen as simple as long as it had not been decomposed – Murray, however, argued that the Davy brothers' experiments did not prove that chlorine had not been decomposed. Their main point of disagreement was on the relation between theory and fact: starting from the same experimental result, they arrived at very different conclusions.

This philosophical disagreement appears most clearly in the early papers of their debate. In February 1811, Murray published the first paper, arguing that the impossibility of reducing chlorine was perfectly explained by the idea that it contained combined water (Murray 1811b). John Davy opened his reply by reminding his readers that "it is generally admitted as a fundamental principle of modern chemistry, that all bodies not yet decompounded are to be considered simple substances" (J. Davy 1811b, 193–94). Whereas his brother's ideas were purely based on facts, he characterized Murray's ideas as speculations. To this, Murray replied that they clearly did not have the same views on the distinction between facts and theories. The facts, or theory-less observations, were: oxymuriatic acid and hydrogen produce muriatic acid; with other substances, oxymuriatic

acid forms other products. In Murray's eyes, the view of the reaction producing muriatic acid as a chemical combination was already an interpretation of the facts, rather than a simple observation. Since multiple hypotheses could explain the facts, the experiment in itself did not prove either one of them (Murray 1811c). Since purely observable facts could not help decide between either of the interpretations, Murray continued to prefer oxygenated muriatic acid because he found it more coherent with the rest of chemical theory. Davy (1811a) did reply but he did not engage with these ideas on theory.

Besides this aspect of their debate, Murray also proposed a number of experiments that provided evidence in favour of the old hypothesis. The first one consisted of transforming carbonic oxide (what we would now call carbon monoxide) into carbonic acid (carbon dioxide) using oxygenated muriatic acid and hydrogen (Murray 1811a). If this was confirmed, it meant that he successfully extracted some oxygen from oxygenated muriatic acid, thereby proving that it contained oxygen in the first place. The Davy brothers replicated all of Murray's experiments in order to show his mistakes. Murray responded to this strategy by also replicating his own experiments. He did not deny the Davys' results, but he did refute their inferences from these results. They argued back and forth like this until John Davy announced that he had identified the product of this reaction as a new gas. Murray would thus have produced this new substance (later called phosgene, ClCO) rather than carbonic acid (J. Davy 1812a). Murray (1812c) attempted to disprove this but John Davy never responded, likely because his older brother did not think Murray's paper was "worth notice".[121]

Murray (1812a) therefore attracted their attention to a different, 'crucial' experiment that might once and for all show the presence of water in muriatic acid: Fourcroy's reaction of muriatic acid with ammonia. Muriatic acid and ammonia combined to form sal ammoniac (now known as $NH_4Cl$) and Murray claimed that water was formed during this reaction. Since there was no water in ammonia, it must have come from the intimately combined water in the muriatic acid.[122] Once again they argued back and forth, repeating

[121] Humphry Davy to John Davy, 7 January 1812. http://davy-letters.org.uk/cms/search/letter.php?id=226.

[122] This time, Humphry's criticism of Murray was even worse: in a letter to John he wrote "Murray writes like a petulant child & experiments worse than a druggist Apprentice. His last paper is disgraceful". Humphry Davy to John Davy, February 1812. http://davy-letters.org.uk/cms/search/letter.php?id=231.

each other's experiments in support of opposite conclusions (J. Davy 1812b; Murray 1812b). While Humphry Davy was on his honeymoon in Scotland in October 1812, he stopped by Edinburgh and performed the reaction of muriatic acid and ammonia in the College Laboratory in the presence of chemist-geologist Sir George Mackenzie (1780-1848), mathematician and geologist John Playfair (1748-1819), the Professor of medicine and chemistry at the university of Edinburgh, Thomas Charles Hope (1766-1844), "and some other gentlemen" (J. Davy 1813, 69). Although they observed the formation of a small quantity of moisture, the amount was almost negligible and it could not be due to combined water. After this moment, the Davy brothers refused to carry on the debate, which they felt they had won. In Humphry's words, "the controversy is closed".[123]

John Murray did not share their opinion. He never became convinced of the elementary nature of chlorine, and continued to argue in favour of the old hypothesis in the fourth edition of his *System of Chemistry*, Murray (1819a, chap. VI). He still argued that "no fact has ever been produced which the old doctrine does not perfectly explain" (*ibid*., 424). If two equivalent explanations are possible, which hypothesis should be accepted? Murray had his own view on this:

> "The whole presents a series of phenomena which are capable of being explained in both views; and which of them is to be preferred must be determined, in want of more conclusive evidence, from the considerations of which affords explanations least complicated, and conformable to the strictest analogies" (*ibid*., 425).

Experimental results alone could not help to choose between the two hypotheses and other indirect arguments and epistemic values therefore had to come into play.

Murray's debate with the Davy's illustrates the impossibility of defending a strictly empirical view of chemical elements: multiple hypotheses could explain the experimental results, and any interpretation in terms of chemical composition already relied on a number of assumptions regarding the composition of the substances involved. The debate with John Murray did not do much to convince other chemists and many agreed with Murray that the old hypothesis could be used to explain the facts. Faced with this equivalence of the two hypotheses, they also relied on analogy, simplicity and coherence with existing knowledge

[123] Humphry Davy to John Davy, 25 October 1812. http://davy-letters.org.uk/cms/search/letter.php?id=291.

in order to decide which interpretation was best. Before moving on to some of the arguments of Davy's opponents, I will first explain Davy's view of chlorine in more detail in order to show how his ideas compared to the old view.

## Chlorine as a simple supporter of combustion

In order to understand the debate on the nature of chlorine, it is important to note that Davy's view of chlorine and its compounds was different from how they are viewed today. Whereas chlorine is now classified as one of the halogens, this group did not yet exist in 1810 and Davy therefore had to find another way to fit the idea of chlorine as a simple substance within the rest of chemical knowledge. According to Davy, chlorine was most analogous to oxygen: not only was it an electronegative element, it also had the capacity to combine with combustible substances, to form acids and oxide-like compounds. Although Davy did see muriatic acid as formed of hydrogen and chlorine, he did not think that hydrogen played the acidifying role of oxygen in this acid. It was in fact hydrogen that was acidified by chlorine:

> "For if, as I have said, oxymuriatic acid gas be referred to the same class of bodies as oxygene gas, then, as oxygene is not an acid, but forms acids by combining with certain inflammable bodies, so oxymuriatic acid, by uniting to similar substances, may be conceived to form either acids, which is the case when it combines with hydrogene, or compounds like acids or oxides, capable of forming neutral combinations, as in the instances of the oxymuriates of phosphorus and tin" (H. Davy 1810b, 250).

The capacity of forming acids was not the only property that chlorine had in common with oxygen. It also reacted in similar ways with combustible bodies, producing light and flames:

> "All the metals that I tried, except silver, lead, nickel, cobalt and gold, when heated, burnt in the oxymuriatic gas, and the volatile metals with flame. Arsenic, antimony, tellurium and zinc with a white flame, mercury with a red flame. Tin became ignited to whiteness, and iron and copper to redness; tungsten and manganese to dull redness; platina was scarcely acted upon at the heat of fusion of the glass" (H. Davy 1811b, 22).

Davy really saw this 'burning' in chlorine as a form of combustion. In Davy's (1812, 235–45) terms, oxygen and chlorine were both 'supporters of combustion'.

In analogy to the compounds formed by burning in oxygen, Davy viewed the compounds formed by burning in chlorine as a kind of oxide (H. Davy 1810b, 244). He saw the products of the reaction between chlorine and metals as direct compounds of chlorine with lead, potassium, silver or mercury or any other metal and thought that chlorine was capable of displacing oxygen from oxides in order to form such direct compounds. According to the old hypothesis, the products of these reactions would rather be salts composed of muriatic acid and a salifiable base. Since he no longer saw them as salts, Davy proposed a new name for these compounds using the suffix – ane. For example, Davy (1811b, 32) proposed 'argentane' as the new name for muriate of silver (silver chloride), which he viewed as a binary compound of silver and chlorine rather than a salt containing silver, oxygen and muriatic acid.

Thus, Davy did not argue against the role attributed to oxygen in Lavoisier's chemistry, but he did make it less central. In a letter to David Warden, he summed up his "principal conclusions":

> "1. That the oxymuriatic acid (as it is improperly named) is a simple body, belonging to the same class as oxygene. 2dly. That it combines with pure inflammable bodies in the same manner as oxygene; forming compounds which have properties analogous to acids and oxides, but which differ from them in being decomposable by water. 3dly. That its affinities for many bodies are stronger than those of oxygene. 4thly. That muriatic acid has for its basis hydrogene, and this gas (…) for its acidifying principle. 5thly. That phosphorus, sulphur, tin, arsenic, and many other bodies are acidified by this gas (…). The phlogistians supposed one principe of inflammability; the anti-phlogistians one principle of acidity, or solution: BUT THERE ARE CERTAINLY TWO ACIDIFYING PRINCIPLES KNOWN, AND MANY OTHERS MAY BE DISCOVERED."[124]

In 1810, Davy still viewed oxygen as a supporter of combustion and a principle of acidity, but it was no longer the *universal* principle. Oxygen was reduced to one of a series of supporters of combustion.

John Hedley Brooke (1980) has shown the complex relation between chlorine and the oxygen theory of acidity and argued against the view of Davy as a radical reformer of the

[124] Capitalization as transcribed by the Davy letters project. Davy to Warden, 7 August 1810, accessible on http://davy-letters.org.uk/cms/search/letter.php?id=1411.

acidity theory. Davy's arguments in favour of the simplicity of chlorine were not based on a correction in the views of the composition of acids and he did not replace an oxygen-theory with a hydrogen-theory. Instead, Davy himself went through a transitional period between 1810 and 1816, during which his ideas of composition and its relation to chemical properties changed. Indeed, during his years of working on chlorine, Davy's view of chemical composition shifted from a principle-based ontology, in which specific elements could be seen as the cause of properties of compounds, towards the idea that it was the arrangement of particles rather than elementary composition which caused properties. These shifting views also complicated his own vision of acidity.

In short, Davy proposed a new view of oxymuriatic acid and its compounds to replace the old hypothesis according to which it contained oxygen. Both hypotheses were capable of explaining the experimental facts. Even though Davy proposed a way to integrate his new view into the general system of chemical theory, many of his contemporaries were reluctant to accept chlorine. The next section will analyse the arguments against chlorine proposed by Berzelius and the French chemists.

# The arguments against simple chlorine

## The French chemists: authority, analogy and salts

The Parisian chemical community at the time of the debate on chlorine was marked by a hierarchical institutional structure. Gay-Lussac and Thenard's choice not to defend the idea that oxymuriatic acid was a simple body after their failure to reduce it can be explained by this context. When Gay-Lussac presented their findings at the Society of Arcueil, Berthollet advised him not to defend the new hypothesis as anything more than an unlikely possibility (Berthollet 1817). They followed his advice and did not defend such an unconventional idea at the Academy of Sciences, even though Gay-Lussac did present chlorine as an element in his courses at the Ecole Polytechnique (Gay-Lussac 1814, 98).

At the French Institut National it was particularly difficult to defend unconventional ideas because it functioned with a system that subjected all new papers to a rigor check from an expert committee. Hugues Chabot (2000; 2006) has illustrated this using the case of the French pharmacist and industrial chemist François-René Curaudau (1765 – 1813), who defended the hypothesis that oxygenated muriatic acid was a simple body in 1810,

before Davy's paper was published. His paper was rejected by the Academy based on the fact that his crucial experiment could not be repeated by the committee. In 1811, after Davy's claim, Curaudau presented his ideas again, this time claiming priority over the hypothesis. This time Curaudau's experiments were judged as insufficient and poorly executed without a replication, on the basis of previous results of expert chemists (Berthollet, Chaptal, and Vauquelin 1811). In both of these cases, Berthollet played an important role in judging the acceptability of the hypothesis of simple chlorine.

Berthollet and his colleagues did also bring up other issues besides arguments from authority. In their report on Curaudau's second paper, Berthollet, Vauquelin and Chaptal (1811) argued that the most important issue in choosing between the old and new hypothesis was to determine which hypothesis fitted in best with the existing system of chemical knowledge. According to Berthollet and his colleagues (*ibid*., p. 137), "the essence of theories is to link together facts in such a way that the phenomena can be explained without obscurity and foreseen without uncertainty".[125] Even if the old hypothesis could give rise to some doubts, they argued that it should be preserved because it linked the facts together in a more coherent way.

In his individual paper on the topic, Berthollet similarly argued that the old hypothesis was to be preferred for reasons of economy and analogy. Both hypotheses explained the facts equally well and the choice between them therefore had to be made on the basis of other considerations:

> "(…) when it comes to the nature of bodies, to the way in which they combine, and to the changes that can occur in the elements that compose them or in those that result from their decomposition, it is easy to multiply the hypotheses; but those that rely most on analogy, and which require the smallest number of suppositions in order to link together the facts so that the mind can easily grasp how they are related, should be preserved" (Berthollet 1811, 42).[126]

[125] « L'essentiel des théories est de lier les faits de manière que les phénomènes puissent être expliqués sans obscurité et prévus sans incertitude. »

[126] « (…) lorsqu'il s'agit de la nature des corps, du mode de leurs combinaisons, et des changements qui peuvent se faire dans les élémens qui viennent les composer, ou dans ceux qui résultent de leur décomposition, il est facile de multiplier les hypothèses ; mais celles qui s'appuient le plus sur l'analogie, et qui exigent le plus

Analogy was therefore an important criterion for the choice between multiple hypotheses for Berthollet. Berthollet did not specify what he meant by 'reliance on analogy', but I argue he relied on the general rule that analogous substances had a similar composition. Berthollet and his colleagues wanted to choose the theory that produced a classification of substances that was most coherent with this correlation.

In order to determine whether a hypothesis about the nature of a substance is coherent with chemical analogy in this sense, the various compounds and chemical reactions involving the substance have to be taken into account. Some accounts explain the French chemists' reluctance to accept the simple nature of chlorine because of its consequences for acidity and the composition of acids (see for example Weeks 1956, 732). Davy's idea that muriatic acid, one of the strongest acids, was composed only of hydrogen and chlorine was contradictory with the Lavoisian theory of acidity according to which all acids contained oxygen. Nevertheless, the role of acidity was much more complicated: oxygen was accepted as an important acidifying substance, but questioned as the *universal* principle of acidity, by both opponents and proponents of chlorine.

Already during Lavoisier's lifetime, it was known that there were exceptions to his view of the composition of acids. Various challenges to Lavoisier's theory were published in the *Annales de Chimie*, some of them even while Lavoisier was still the editor of this journal (Crosland 1994, 190–92). Exceptions to the oxygen theory of acidity were known since the 1780s: prussic acid (hydrogen cyanide) and sulphuretted hydrogen (hydrogen sulphide) both very clearly behaved like acids even though they did not contain oxygen. Taking into account these exceptions, Berthollet himself summarized his view as follows in his *Essai de Statique Chimique*:

> "To want to conclude from the fact that oxygen gives acidity to a large number of substances, that all acidity comes from it, even that of muriatic, fluoric and boracic acids, is to push the limits of analogy too far" (Berthollet 1803, 2:8).[127]

---

petit nombre de suppositions pour enchaîner les faits, de manière que l'esprit en saisisse facilement les rapports, doivent être maintenues, (…). »

[127] « Vouloir conclure de ce que l'oxigène donne l'acidité à un grand nombre de substances, que toute l'acidité en provient, même celle des acides muriatique, fluorique et boracique, c'est reculer trop loin les limites de l'analogie. »

The theory had also been challenged by others such as Fourcroy, Thomson, Gay-Lussac and Chenevix. Brooke (1980) has also suggested that even Lavoisier himself may have seen the presence of oxygen as necessary but not sufficient for a substance to be acidic. In itself, it was not completely inconceivable to admit another exception to the oxygen theory of acidity.

There was, however, a much more important, and not entirely unrelated, consequence of Davy's view of chlorine. This issue was the reclassification of the metallic muriates, formed by the combination of muriatic acid and metals, which Davy argued should no longer be seen as salts. The generally accepted view of salts was that they were formed by the combination of an acid and a base, and they therefore had to contain oxygen (both from the acid and from the base). Davy's view of chlorine implied that metallic muriates did not contain oxygen and therefore could no longer be seen as salts. However, this completely went against the principles of classification on the basis of analogy since some of these muriates were the most paradigmatic examples of salts there were (such as muriate of soda, now known as common kitchen salt or NaCl). Berthollet (1811, 41) therefore cited the classification of salts rather than acidity as a reason to retain the old hypothesis.

In 1810, Davy had anticipated that the classification of salts might form an obstacle to his new theory. His way of refuting the possible objection was to argue that the analogy between the metallic muriates and the salts was really not that strong:

> "It may be said, that a strong argument in favour of the hypothesis, that oxymuriatic acid consists of an acid basis united to oxygene, exists in the general analogy of the compounds of oxymuriatic acid and metals, to the common neutral salts; but this analogy when strictly investigated, will be found to be very indistinct, and even allowing it, it may be applied with as much force to support an opposite doctrine" (H. Davy 1810b, 239).

Berthollet was clearly not convinced by this argument, and he was not the only one. Nor was the issue limited to the Parisian chemical community because it was likewise raised in English journals. The editor of the *Annals of Philosophy*, Thomas Thomson, noted in his annual report for 1813:

> "It must be obvious to every chemist that Sir H. Davy's explanation of the muriates (…) constitutes the vulnerable part of his theory of chlorine. Indeed, his opinions respecting these bodies cannot be embraced without overturning all the received doctrines respecting the neutral salts, doctrines upon which every thing resembling theory in chemistry is founded" (Thomson 1814, 13–14).

For many chemists, the old hypothesis was more coherent with chemical analogy because it enabled a view of all salt-like substances as a single class of substances that shared a similar composition. A similar view, though in a much more complicated form, was defended by Berzelius.

## Berzelius' laws of composition

Berzelius was one of the most active opponents of chlorine and among the last to accept its elementary nature. He brought up many different arguments against chlorine, some of which were more conventional and others more unique to his own view of chemical composition. Like many of the other opponents of chlorine, he argued that any experimental results that Davy cited in favour of chlorine could be explained just as well using the old hypothesis (Berzelius 1813b). Although Davy's explanation might seem simpler, Berzelius assured his readers that "the most simple explanation is not always the most accurate" (Berzelius 1813b, 256). Rather, in order for an explanation to be accurate, Berzelius considered the most important factor its relation with the general theory of chemistry. Berzelius, more than anyone, had a very clear idea of what the general theory of chemistry looked like – at least according to his own view, as I have discussed in the previous chapter as well.

Indeed, the muriatic radical fit very well into Berzelius' patterns of oxidation, especially after Davy identified a new compound of oxymuriatic acid and oxygen. Davy (1811a) first identified what he called 'euchlorine' as a compound of (simple) chlorine and oxygen, but for Berzelius this compound provided the missing degree of oxidation in order for the muriatic acid radical to follow his law of oxidation. Berzelius was convinced that this discovery would help Davy realize his own mistakes, and he thanked him for providing a confirmation of his ideas. However, Davy did not change his mind and continued to see Berzelius' view as "contrary to all analogy"

(Berzelius 1912b, 28–29).[128] Berzelius (1816, 276) did not change his mind either and continued to see the muriatic radical as an example of his successful theory: it combined with two, three, four and eight volumes of oxygen to respectively form muriatic acid, oxygenated muriatic acid, euchlorine, and hyperoxygenated muriatic acid. According to the new hypothesis, chlorine would only have two degrees of oxidation: euchlorine (with one volume of oxygen) and chloric acid (with five volumes of oxygen). This leap from one to five was unheard of and completely contradictory with Berzelius' patterns of oxidation.

Similarly, the old hypothesis was consistent with Berzelius' view of salts. For Berzelius, the very fact that oxymuriatic acid formed salts proved that it had to contain oxygen. Furthermore, he claimed he was able to calculate the inaccuracy of the new view using his laws of composition. According to one of these laws, the quantity of oxygen in the combined water of a hydrate salt was always equal to the amount of oxygen contained in the metallic oxide of the salt. This rule was confirmed when viewing submuriate salts according to the old hypothesis, but not in the new hypothesis (Berzelius 1815). He therefore concluded that either Davy's ideas, or this rule regarding the composition of salts had to be inaccurate – and the latter seemed unlikely to him. Like in the case of ammonia, Berzelius was very reluctant to admit exceptions and very confident that his theory was true.

Furthermore, the new hypothesis did not fit in with Berzelius' electrochemical ideas. In 1816, Berzelius (1816) published a long article comparing the old and new hypotheses, of which the largest part was dedicated to disproving Davy's experiments with a peculiar detonating substance. Davy had learned of this oily substance from the French polymath André-Marie Ampère (1775-1836) and his studies showed that it was composed of three volumes of chlorine and one volume of nitrogen (H. Davy 1813a; 1813c). When ignited, the oil produced chlorine and nitrogen in an extremely violent explosion.[129] Berzelius (1816, 429–41) took this as a sign that chlorine could not be a simple body.

[128] Berzelius to Davy, June 1811 on the topic of euchlorine: "(…) je suis sûr que cette confirmation de mes idées, faite par vous, (…) m'épargnera au moins une partie de la controverse." (Berzelius 1912b, 28–29).

[129] Davy had identified trichloramide ($NCl_3$), a compound that looks like olive oil but has an extremely pungent smell. The experiments with the oil "nearly deprived [him] of an eye" and he was unable to work for months. Davy to Ampère, 6 March 1813, available at http://davy-letters.org.uk/cms/search/letter.php?id=315.

According to his electrochemical theory, any fire and heat emitted during a reaction resulted from the combination of opposite electrochemically charged bodies and the resulting neutralization of their electrochemical force. The production of simple bodies could never produce any heat or light, since there was no combination of oppositely charged bodies. Therefore, seeing as the detonation of Davy's oil was almost explosive in its emission of heat and light, no simple bodies could be produced during this reaction.

Davy did not engage with any of these arguments and barely made the effort to acknowledge Berzelius' publications. Berzelius (1815, 213) was very annoyed by Davy's dismissal of his ideas and he did not feel he was taken seriously:

> "Sir H. Davy, in speaking of my objections to his thesis, says, 'I cannot regard these arguments as having any weight'; 'and there is no general canon with respect to the multiples of the proportions in which different bodies combine.' I do not think that this manner of refuting is admissible in the sciences. This celebrated chemist has taken advantage of his great superiority, and has predisposed the reader to believe that six years of my part to find and establish by numerous experiments the law, which he says does not exist, have been lost without fruit. I suppose, however, that he will one day do me the justice to take the trouble to prove by experiment that I have deceived myself if he finds that I am in the wrong."

Despite the fact that this statement was published in English in the *Annals of Philosophy*, Davy did not respond to it.[130] A year later, Berzelius (1816, 209) cited the same dismissal of his argument by Davy, stating: "This I call wishing to prove a thing by authority. But while I acknowledge the authority with respect, I must firmly dispute its force as a scientific proof". Berzelius (1816, 274) himself, meanwhile, ensured his readers that his theory was "much cultivated" and "fully established".

Unfortunately for Berzelius, Davy's remark that his chemical theory was not commonly admitted appears to have been true since Berzelius' ideas on muriatic acid did not receive much attention from the chemical community. Gray et al. (2007, pp. 64–65) propose two reasons why Berzelius' ideas on oxymuriatic acid were not really picked up.

[130] It is possible that Davy never read the article, since he wrote that same year: "I do not read Thompsons [sic] journal or look at any thing that has the name of his malignant Co. attached to it (…)". Davy to Children, 30 August 1816, accessible on http://www.davy-letters.org.uk/cms/search/letter.php?id=368.

They suggest that the geographical distance between Sweden and the rest of Europe may have played a role in creating this theoretical distance. Although Berzelius was indeed relatively far away from many of his peers, this explanation seems unlikely. While he was no longer in contact with Davy himself, Berzelius had a rich correspondence with many other chemists in France as well as England. Though there are indeed signs of unreliable postage to and from Sweden, this often appears to be linked to the Napoleonic wars which complicated correspondence between other European countries as well. Despite these difficulties, Berzelius regularly published in English, German and French journals and summaries of his works were regularly written by journal editors (Beckman 2016).

The second reason suggested by Gray et al. is more plausible: it appears that even at the time, very few people really understood Berzelius' arguments. Berzelius had a very intricate theoretical system on which he had been working for years, and to debate with him on this topic would require a deep knowledge of his system. This is confirmed, for example, by a letter from the Swiss-born physician Alexander Marcet (1770-1822), whom Berzelius had befriended on his 1812 trip to London where Marcet lived. In 1813, Marcet explained in quite a euphemistic way that he was unable to understand Berzelius' writings:

> "You have all of chemistry as a picture before your eyes; every little fact reminds you of a theory, and every theoretical idea reminds you of a host of facts. The result is a richness in your writings that dazzles ordinary philosophers. You should perhaps put yourself a little more within the reach of ordinary minds" (Berzelius 1913, 43).[131]

The fact that Berzelius took this remark as a compliment (*ibid*., 55) says much about the role he attributed to theory in his chemistry. On the subject of chlorine, Berzelius was not so much engaged in a debate with other chemists as simply publishing his views from time to time without receiving a clear response.

One of his arguments, however, was more widely shared by the chemical community: the idea that the choice of hypothesis should be made on the basis of simplicity, analogy

[131] "Vous avez toute la chimie comme un tableau devant vos yeux; chaque petit fait vous rappelle une théorie, et chaque idée théorétique vous rappelle une foule de faits. Il en résulte une richesse dans vos écrits qui éblouit les philosophes d'une trempe ordinaire. Vous devriez peut-être vous mettre un peu plus à la portée des esprits ordinaires." By "ordinary philosophers", Marcet meant himself.

and existing knowledge. The acceptance of chlorine as a chemical element required too many adjustments of chemical theory to be feasible. In the *Annals of Philosophy*, Berzelius summarized why the identification of chemical elements required this way of proceeding:

> "(…) can we with propriety affirm that we can make no further progress in this subject, and that our posterity never will be able to reduce these bodies by methods at present unknown to us? I do not believe that any philosophical chemist is of this opinion" (Berzelius 1816, 263–64).

In other words, how could any chemist be sure that the impossibility of decomposing a substance (such as oxymuriatic acid) really was a sign of its simplicity? There was no way of knowing for sure whether it might become possible in the future to decompose bodies that had never been decomposed before, and that is why the impossibility of decomposing a substance in itself did not prove anything. Analogy was a way to overcome this difficulty. Yet, when Berzelius published this statement he was one of the only remaining opponents of chlorine. The other chemists who accepted chlorine had not abandoned the principle of analogy, but a new discovery had been made that added to the analogies in favour of chlorine: the new substance iodine, which appeared to be chemically analogous to chlorine. I will describe this shift towards the acceptance of chlorine in the next section.

# The end of the debate

## The discovery of iodine and the acceptance of chlorine

In late 1811, Bernard Courtois (1777-1838), the owner of a factory that produced soda from seaweed ash, added sulphuric acid to a partly evaporated liquor of algae and noticed that it produced a violet vapour. The vapour crystallized into a solid substance that almost looked metallic. In 1812 he gave a sample of the substance to Nicolas Clément (1779-1841), professor of chemistry at the Conservatoire des Arts et Metiers in Paris, who presented it with his close friend Bernard Desormes (1777-1862) to the French Academy on 29 November 1813. They described the substance, its compounds with phosphorous, the alkalis and metals, and ammonia. The new substance also formed an acid with hydrogen that was so similar to muriatic acid that it was mistaken for it at first. Davy – who was in Paris at the time – and Gay-Lussac were both given a sample of the new substance at the

end of November. In December, they both argued that it was a chemical element analogous to chlorine: iodine (for a summary of early works on iodine see Partington 1964, 4:85–90; Weeks 1956, 736–41). Gay-Lussac and Davy each claimed priority for this discovery (Ruston 2019; Crosland 1978, 80–87; Fullmer 1975).

Gay-Lussac relied on the analogies between iodine and chlorine in order to argue that both were simple substances. Seeing the similarity between the new acid and muriatic acid, there were two explanations possible: either the new substance was the oxide of an unknown base and its acid a combination of that base with water, or iodine was a simple substance and the acid a compound of hydrogen and iodine. Gay-Lussac (1813; 1814) insisted on the probability of the latter explanation. The fact that these bodies were so similar made both of their elementary natures more likely. Gay-Lussac proposed the name *iode* in analogy to the French *chlore*, and in reference to its purple colour (from the ancient Greek for 'violet').

Davy provided a similar argumentation. He wrote a paper about iodine in December 1813 which he read to the Royal Society in January 1814 upon his return to England (H. Davy 1814a). He highlighted the many similarities between iodine and chlorine, including the fact that some of iodine's compounds even smelled similar to chlorine compounds (specifically those formed with phosphorous). He also attempted to decompose iodine using both the voltaic pile and white hot charcoal in order to potentially extract oxygen from it. He noted that it was relatively electronegative (though less so than chlorine) and that it had a strong affinity for metals, with the possibility of producing a combustion-like reaction with potassium. Davy likewise chose the English name 'iodine' to resemble the terms 'chlorine' and 'fluorine'.

Fluorine, though it had never been isolated, had been named a year earlier by Davy (H. Davy 1813b). Like the radicals of the other inorganic acids, the radical of fluoric acid had already been postulated by Lavoisier. When Davy argued that chlorine was a simple body, he received a suggestion from Ampère about the nature of fluorine. Based on the resemblance between muriatic and fluoric acid, Ampère proposed that fluoric acid might contain a simple body analogous to chlorine in 1813 (see H. Davy 1816b; 1813b). Despite the impossibility to decompose fluoric acid and isolate fluorine until 1886, the element

appeared in most classifications of simple substances from the 1810s onwards.[132] The analogies between muriatic and fluoric acid sufficed in order for fluorine to be accepted as an element (see also Banks 1986).[133]

The discovery of iodine, and the new analogies that came with it, made the existence of simple chlorine a lot more likely and the elementary nature of chlorine came to be accepted rapidly thereafter. In 1814, both Gay-Lussac (1814, 98) and Davy noted that the new hypothesis had become generally accepted in France.[134] Gay-Lussac and Thenard publicly announced acceptance of elementary chlorine following the discovery of iodine. However, it appears they had already been defending this view in their teaching and they had succeeded in convincing Ampère and Dulong (Berthollet 1817, 604).[135] Vauquelin reportedly accepted chlorine after the discovery of iodine as well (Berzelius 1816, 257). Eventually, even Berthollet (1817) announced that he had changed his mind.

Thomson's annual reports of the progress of chemistry for the years 1813 to 1816 likewise report a shift in the chemical community. In 1813, both oxygenated muriatic acid and chlorine coexisted in chemists' views, as Thomson (1814, 13–14) described:

> "The two opposite hypotheses of chlorine and oxymuriatic acid are liable each to objections, which in the present state of our knowledge it is almost impossible to obviate."

However, a few years later, he reported that chlorine had become generally accepted as an element:

[132] For example, Dumas (1828, 107) provided a detailed explanation of why he accepted the existence of fluorine on the basis of the analogy between fluoric and muriatic acid.

[133] Paneth (1931, 115) has also famously mentioned fluorine as an element that was known to exist before it was isolated.

[134] Humphry Davy to John Davy, 18 March 1814. http://davy-letters.org.uk/cms/search/letter.php?id=375.

[135] This was the case at least for Gay-Lussac (1814, 97), who claimed priority over the discovery of chlorine for Thenard and himself. Berthollet (1817, 604) only mentions Gay-Lussac as a defender of chlorine, so for Thenard it is not clear whether or not he defended chlorine as an element in his daily life. In his 1813 textbook, he defended the old hypothesis (Thenard 1813, 562), whereas in the 4th volume he did name chlorine as a simple body (Thenard 1817, 215).

> "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" (Thomson 1816, 27).[136]

By 1816, chlorine had been accepted as one of the chemical elements. Murray and Berzelius were the only two chemists who still refused to admit chlorine as a simple body after the discovery of iodine, though both of them noted that they were its last opponents (Berzelius 1816, 257; Murray 1819a, 426). Murray (1819b) continued to publish works on muriatic acid until just before he died in 1820, and it seems he was never convinced of the existence of chlorine. Berzelius would eventually come to change his mind around 1820, as I will discuss at the end of this section.

## Iodine, classification and acidity

The discovery of iodine as an additional simple body increased the likelihood that chlorine was simple as well; nevertheless, this discovery did not change the fact that the accommodation of these bodies and their compounds into chemical theories of composition required a significant adjustment of classifications. Gay-Lussac and Davy each had their own view on the way in which classifications of chemical substances should be rearranged in order to create a place for iodine and chlorine. In order to show how they should be classified, they both highlighted specific analogies of iodine and its compounds to other bodies.

Gay-Lussac argued that iodine was analogous to chlorine and sulphur because it formed an acid with hydrogen. In analogy to chlorine, Gay-Lussac predicted that iodine would also form an acid with oxygen that would be analogous to the oxyacid of chlorine. In order to separate between these various acids, he proposed to call them chloric acid and iodic acid on the one hand, and hydrochloric and hydroiodic acid on the other hand. Gay-Lussac coined the term 'hydracids' for the group of acids that contained only hydrogen and no oxygen (as distinct from the 'true acids' that did). The group of hydracids initially consisted of hydroiodic, hydrochloric and hydrosulphuric acid, but prussic acid was also known not to contain any oxygen. In 1815, Gay-Lussac therefore set out to find the radical

[136] As is noted by Gray et al. (2007): when this report was published, Murray also remained unconvinced of the existence of chlorine. It seems Thomson did not think of him as a "chemist of eminence".

of this acid, which he renamed hydrocyanic acid, expecting it to be a simple substance in the chlorine-iodine family (see Crosland 1978, 129–31). He found that the acid was composed of one volume of hydrogen and one volume of cyanogen, a radical composed of carbon and nitrogen. Cyanogen would later become a key example of a compound that behaves analogously to a simple body.

These findings showed that there was an entire group of acids which all had a similar chemical behaviour and a similar composition. Gay-Lussac (1814, 117–18) did not use this in order to argue for a new theory of acidity, and he was open to the possibility that many other bodies could form acids as well. He preferred to stick to a very empirical definition of acidity:

> "For me, for a long time now, an acid, considering the word in its biggest generality, has been nothing more than a body that may or may not contain oxygen and which neutralizes alkalinity, and an alkali similarly is any body which neutralizes acidity" (Gay-Lussac 1814, 145).[137]

This was quite a typical statement for Gay-Lussac, who did not easily express his support for any claims that were too bold (see Crosland 1980). In 1815, Gay-Lussac explained acidic properties on the basis of both arrangement and composition (Crosland 1978, 131–34). The phenomenon of acidity remained too complex to capture in a single theory, but at least now there was a place for iodine in a group of bodies that formed hydracids.

Gay-Lussac did not propose a new view of salts in order to accommodate the compounds of chlorine and iodine with metals. He viewed the compounds of iodine and chlorine with oxygen and with metals as analogous to sulphates, nitrates and phosphates. In 1815, Pierre Louis Dulong (1785-1838) proposed that all acids might be analogous to the hydracids and all salts analogous to metallic chlorides: in other words, he argued that oxygen did not play a role in acidity nor in salt formation (Partington 1964, 4:275). Gay-Lussac (1816) did not agree with this view and explicitly distinguished between salts

[137] "Un acide n'est depuis longtems pour moi, en considérant ce mot dans sa plus grande généralité, qu'un corps, renfermant de l'oxigène ou non, qui neutralise l'alcalinité, et un alcali n'est également qu'un corps quelconque qui neutralise l'acidité."

and metallic compounds of chlorine and iodine. In his view, the term 'salt' should be reserved for the compounds of acids and alkalis. His explanation for why potassium chloride seemed similar to a neutral salt was that whenever it was dissolved in water, it reacted with the water to form a neutral salt. Gay-Lussac argued that instead of using the salt suffix –ate, these compounds of iodine and chlorine should be named 'iodure' and 'chlorure' in analogy to 'sulfure'.[138]

Davy, meanwhile, had completely changed his mind on both acidity and salt formation. Although he had originally proposed to classify iodine with oxygen and chlorine as the three acidifying substances, Davy gradually rejected the view according to which properties such as acidity could be caused by any one element (Brooke 1980). In 1816, Davy argued against the idea of a principle of acidity altogether, a view which he (wrongly) ascribed to Gay-Lussac. For Davy (1816a, 285), this kind of view had become dismissible as "an attempt to introduce into chemistry a doctrine of occult qualities, and to refer to some mysterious and inexplicable energy what must depend upon a peculiar copuscular arrangement".[139] Instead, he proposed that acidic properties were due only to the arrangement of particles in a substance. Davy also suggested that the idea of neutral salts should be revised, as it started to become clear to him that very few of the common salts actually contained the acid and base in their entirety. Acids and bases could indeed be reproduced from them, but only using water or other compounds of hydrogen. The only exceptions of salts containing oxygen were phosphates and carbonates, but in reality these were much less saline than muriate of lime (calcium chloride), for example (H. Davy 1816a, 287). More generally, Davy proposed a way to fit iodine into a classification of the simple bodies that fit with his new view of chemical composition.

[138] Today we would translate these French terms as iodide, chloride and sulphide, but Gay-Lussac argued against these names because the suffix –ide implied an analogy to oxides.

[139] According to Levere (1980, 10), Davy's harsh criticism of Gay-Lussac here was in part motivated by a note on ammonia added to Gay-Lussac's 1814 paper on chlorine.

## Davy's changing views of analogy and composition

Between 1814 and 1816, Davy once again revised his fundamental view of chemical composition. Whereas he previously admitted the existence of a family of acidifying substances, he started to reject his previous view of certain elements as the causes of properties in favour of an explanation based only on the arrangement of particles. By 1816, he had even abandoned the link between properties and composition altogether:

> "It is impossible to infer what will be the qualities of a compound from the qualities of its constituents; (…). When certain properties are found belonging to a compound, we have no right to attribute these properties to any of its elements to the exclusion of the rest, but they must be regarded as the result of combination" (H. Davy 1816a, 286).

The most striking example for Davy were the compounds of hydrogen and oxygen: whereas both were present in very strong acids, they combined together to form the perfectly neutral substance water. Therefore, they could not be seen as always passive or always active, and they sometimes acted as an acidifier and sometimes as a base.

Davy's work on the diamond likely played a role in his changing views of the relation between chemical properties and composition. Studies of the composition of the diamond continued to point towards the fact that it was composed only of carbon, including Davy's own experiments (summarized in Siegfried 1966). This was of course very puzzling: if the difference in properties between charcoal and diamond did not come from a difference in composition, it would have to come from the arrangement of their constituents. In 1814, Davy still thought this was impossible and that some substance other than carbon would be found in the diamond, perhaps a very light and almost undetectable substance:

> "It seems reasonable to expect, that a very refined or perfect chemistry will confirm the analogies of nature, and shew that bodies cannot be exactly the same in composition or chemical nature, and yet totally different in all their physical properties" (H. Davy 1814b, 73).

During the following two years, Davy changed his mind as it remained impossible to detect another substance in the diamond. Without explicitly referencing this work in 1816, he had clearly come to choose the arrangement-hypothesis. This had led him to doubt one of his

most fundamental convictions: the idea that analogy in properties indicated analogy in composition.

Davy's new view did not allow for the explanation of acidity by the presence of any kind of principle of acidity. He instead proposed an entirely different way of incorporating iodine into a classification of the simple bodies that arranged them into a continuous chain rather than into separate families. Davy had first mentioned a "chain of resemblances" as a way of ordering the metals in his 1807 Bakerian lecture (H. Davy 1808b, 41). In his textbook, Davy (1812, 478–79) expanded on this idea and described the properties according to which the metals could be placed in a chain in more detail. Rather than consisting of distinct families, each element would be linked to the next via a gradual change in properties, thus forming a continuous series. Though the extremities of the chain might differ from each other, each element would be closely related to the next – this way, even the very dissimilar bodies were connected to each other. In 1816 he expanded the idea of a chain of analogy beyond the metals, developing it into an entire 'system of analogy' (H. Davy 1816a, 283).

In Davy's system, there were no longer any distinct families because all bodies were connected to one another. Thus, for example, chlorine was still placed next to oxygen but they were no longer classified as a family of acidifying substances. The newly discovered iodine provided new analogies that connected chlorine to sulphur, as well as connecting the non-metals to the metals with which iodine shared the properties of high density, metallic lustre in its solid state, and opacity. Iodine was mostly similar to tellurium because they both produced acids with hydrogen. This was Davy's own way of arguing that iodine had its place in a classification of simple bodies, without placing it in a specific family. He highlighted his capacity to view beyond such classes and show the entire network of analogies that existed among the simple bodies.

Davy's system of analogy was linked to his horizontal ontology in which there were no more active and passive substances, each was similar to all the others. There is a clear continuity with his changing views during 1812 and 1813, and Davy had settled very far from his original views about 'true' elements. By 1816, he exclusively referred to chemical elements as 'undecompounded bodies'. After defending a variety of different views of the nature of elements, Davy eventually became more strictly Lavoisian than Lavoisier

himself. Davy did not provide any visual representation of his system of classification, but I have attempted to produce one (see Figure 5).

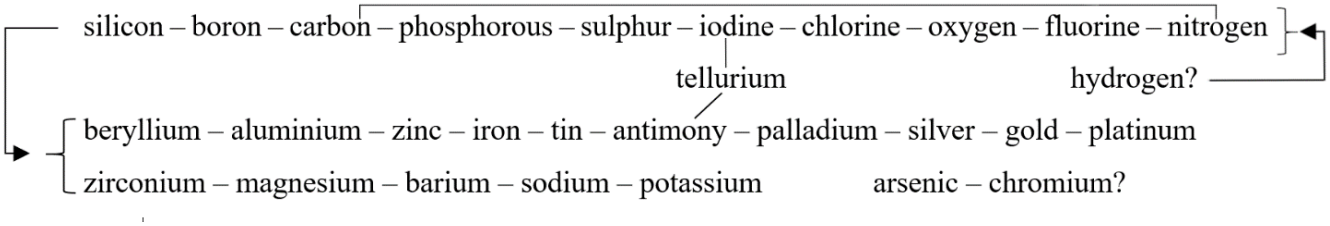



*FIGURE 5 - An attempt at representing Davy's (1812; 1816a) system of analogy. Simple bodies followed by a question mark were not explicitly placed anywhere by Davy.*

Davy's friend Ampère likewise dismissed the separation into different groups of simple substances on the basis of a single property as artificial (see Knight 1978, 150–53). In his essay on classification, Ampère (1816a) proposed to compare all simple substances with each other: only classifications that took *all* analogies into account could uncover the true natural order of things. The resulting classification similarly took the form of a 'chain of analogies': "a system in which every body clings to neighbouring bodies by analogies on either side", so that they formed a circular chain in which it was impossible to establish a separation between any two neighbouring substances (Ampère 1816a, 306). In Ampère's system, the metals were ordered in a double series from tin and antimony to the "acidifiable infusible metals" (tungsten, chrome, columbium and molybdenum). The acidifiable metals were connected to the non-metallic bodies via carbon and boron, whereas tin and antimony were placed next to phosphorous and arsenic. Each element closely resembling the next, the series passed through all different degrees of affinity for oxygen, and the corresponding oxides through all different degrees of acidity and alkalinity.[140]

[140] In the second part of his article, Ampère replaced his chain of analogies with a system of natural groupings inspired by Linnaeus. He proposed groups called gazolytes, leucolytes and chroïcolytes, which were distinguished primarily by their melting point. This proposition was not very successful. According to David Knight (1992b, 131), "the criteria which he used must strike most chemists as odd, and seem to have done so in his own time".

The idea of a chain of analogies echoed the natural historical chain of being, a classification of all beings that placed God at the top and descended through a hierarchy of humans, animals and plants down to minerals. Rather than consisting of classes in which all members shared a certain property, such a classification constituted a network of relations of similarity and difference between all entities. This use of analogy surpassed analogical reasoning: according to Philippe Descola (2005, chap. 9), chains of being are characteristic of *analogism*, an analogy-based ontology. Faced with a world constituted of heterogeneous entities, analogism accentuates similarities rather than differences in order to classify them. Likewise, since they were faced with a multitude of substances that were all different from the next, Davy and Ampère chose to highlight analogies to create order. By arranging the individuals according to slight gradations of difference, they could give the appearance of constituting a continuous chain rather than a chaotic multiplicity. This way of highlighting all the different analogies among the 'undecompounded' bodies was also a way of portraying himself as a 'true philosopher', someone who saw the relations between all the phenomena in nature. Sharon Ruston (2019) has shown how Davy adopted this attitude in his priority dispute against Gay-Lussac in order to show his superiority. Even though Gay-Lussac himself had relied on the chemical analogy between chlorine and iodine in arguing their simple nature, Davy accused him of relying only on facts without understanding how they were connected.

Thus, the ideal view of a classification as representing the most possible analogies between the elements was consensual during the nineteenth century. Even though it was criticized, Ampère's publication motivated the pursuit of natural classifications that developed over the course of the next decades in France (Bertomeu-Sánchez, Garcia-Belmar, and Bensaude-Vincent 2002; Bensaude-Vincent and García-Belmar 2015). During the 1820s, this 'natural' approach was still overshadowed by a more mainstream artificial classification under the influence of Thenard's textbook, in which elements were classed on the basis of their affinity for oxygen. The proponents of artificial classifications generally chose them for pragmatic and pedagogical reasons, rather than because they believed the artificial approach to be superior. The following decade, French chemists showed a renewed interest in natural classifications but these attempts were often criticized for being imperfect: even when taking a maximum of similarities into account, some

choices had to be made in prioritizing certain analogies over others and therefore these classifications too were therefore in a sense artificial. Eventually, a hybrid approach combining artificial and natural groupings within a single classification became dominant in France, from the middle of the nineteenth century until the early twentieth century.

## Berzelius' adjustment of his chemical system

After Murray's death in 1820, Berzelius was the last remaining opponent of chlorine. Sometime between 1820 and 1822, he finally admitted its elementary nature. He had already declared that "the obstinacy with which many philosophers adhere to old opinions is owing to their incapacity of perceiving the force of the arguments which are used against them" (Berzelius 1816, 273). Gray et al. (2007, 66) therefore argue that Berzelius simply changed his mind because the rest of the chemical community did. On the contrary, I argue there were specific reasons why he was able to accept simple chlorine and iodine around that time, which had to do with the ways in which iodine and chlorine compounds started to fit into his theory of composition.

When iodine was discovered, Berzelius viewed it as the superoxide of a new radical, which we might call 'oxygenated iodic acid', because this fit better with his theory of definite proportions (following a similar argumentation as in the case of oxymuriatic acid). Berzelius was more attached to the oxygen theory of acidity than most chemists but by 1816 he did already admit the existence sulphuretted hydrogen (hydrogen sulphide) and telluretted hydrogen (hydrogen telluride) as two exceptions to this theory (Partington 1964, 4:167–68). Nevertheless, he argued that muriatic and iodic acid were more similar to oxygen acids, because of their strength, action on vegetable colours and their ability to produce salts (Berzelius 1816). Indeed, the most important reason for Berzelius to be attached to the idea that oxymuriatic acid and oxyiodic acid contained oxygen was because they formed salts, and the idea that salts contained oxygen was central to Berzelius' laws of composition.

Berzelius' new interpretation of salts gradually emerged from 1819 when he investigated cyanide salts and found that they did not contain oxygen.[141] He also found that

[141] Jorpes (1970) links Berzelius' acceptance of chlorine to his stay in Paris during 1818-19 where he discussed the matter with Dulong.

the sulphuretted alkalis (potassium and sodium sulphides) did not contain oxygen either. This resulted in him admitting a new type of salt that did not contain oxygen, which were composed only of the radicals of the acids and bases. This in turn increased the likelihood that muriates were similarly composed, and muriatic acid was perhaps similar to sulphuretted hydrogen and prussic acid. When Heidelberg Professor Leopold Gmelin (1788-1853) identified red prussiate of potash (ferricyanide) and the colour was similar to that of a muriate salt (ferric chloride), this provided a final analogy in favour of the new view of chlorine. There was now a series of bodies that all reacted in a similar way, forming acids and salts without oxygen (Partington 1964, 4:167–68; Söderbaum 1899, 116–18).

Between 1819 and 1822, Berzelius gradually became more and more convinced that there could be acids and salts without oxygen. The fact that entire groups of such bodies existed resolved all his reservations and tipped the scale in favour of chlorine. In his 1825 textbook, Berzelius identified a peculiar class ("ganz eigentümlichen Klasse") of simple bodies that included fluorine, iodine and chlorine. They were distinct because of the reactions they could undergo with other bodies, the strong acids that they formed with hydrogen and the salts they formed by direct combination with metals. Because of this last property he called them "halogens", meaning "saltbuilders" (Berzelius 1821, 262).[142] Like all the other chemists who eventually came to accept the elementary nature of chlorine and iodine, he had found a way to incorporate these substances into his chemical system in a way that reflected the chemical analogies among various bodies.

## Conclusion

From 1810 onwards, Davy argued that chlorine should be seen as a simple substance because it could not be decomposed using the most powerful means available. However, his various opponents believed that this result did not justify the new view of chlorine as a simple substance. The old view, they argued, explained the experiments just as well. Moreover, even though Davy had tried to provide a way to fit chlorine into the existing

[142] During the 1830s, chlorine would once again become problematic for Berzelius as his dualistic theory of the constitution of organic substances came to be contradicted by the finding that chlorine (an electronegative element) could substitute hydrogen (an electropositive element) in acetic acid (see Brooke 1969, chap. 5; Rocke 1984, 191–200; Klein 2001b).

knowledge as a simple supporter of combustion, his opponents found his explanation less coherent with their existing knowledge than their own. They argued that, since oxymuriatic acid was known to form acids and especially salts, it had to contain oxygen. It was only when iodine was identified (and, not long thereafter, cyanogen and fluorine) that they started to accept chlorine as an elementary substance. This created the possibility of fitting in a family of substances that formed hydracids and salt-like substances without oxygen. Briefly put, chlorine was no longer an exception.

During the debate on chlorine, the opposition between Davy and Berzelius became especially clear. Davy and his brother repeatedly insisted on the Lavoisian definition of the chemical element, and Davy's strict use of the term 'undecompounded body' went beyond Lavoisier's own views of simplicity. Davy's appeal to "the just logic of chemistry" was not unusual; however, it was quite exceptional to place the definition of chemical elements as indecomposable bodies at the centre of this logic. Berzelius, on the other extremity of the debate, instead asked for the logic of chemistry to follow his view of salts.[143] Most other chemists had a more nuanced view of the relation between theory and experiment than Davy and Berzelius did at this time. Despite individual differences of opinion, the general shift in the chemical community that took place after the discovery of iodine shows that there was a shared wish for hypotheses to be coherent with analogy-based classifications and existing theories of composition.

This debate also illustrates why such coherence was needed in order to ensure that the most plausible explanation was chosen. As Murray argued, the fact that hydrogen and oxymuriatic acid reacted to form muriatic acid did not prove anything without the appeal to additional hypotheses. Likewise, Berzelius recalled that the impossibility to reduce oxymuriatic acid did not prove that it was simple. Chlorine was identified as a chemical element once analogical inference and experiments converged in this direction. Like in the cases of aluminium and ammonia, analogy could help chemists choose the most plausible interpretation of their experimental results. This conclusion also shows that no chemical

[143] Reacting to Davy's suggestion that metallic muriates were analogous to oxides rather than salts, he wrote: "I now ask, can any man hold out such opinions as correct chemical philosophy? And is this *the just logic of chemistry*, which the chemists of the new doctrine have been under the necessity of adopting?" (Berzelius 1816, 202).

substance, simple or compound, could be studied in isolation from all the others. In order to characterize it, its reactions and similarities with other substances had to be taken into account. Without such information, experimental results could not be interpreted in the first place – in other words, no simple substances could be identified without a pre-existing knowledge of composition.

# Conclusion to Part I

In the three chapters that made up this first part of the thesis, I discussed three rather puzzling examples of investigations into the elementary nature of specific substances in the early nineteenth century. The first chapter focused on the identification of aluminium as a chemical element, over fifteen years before it was isolated. At the turn of the nineteenth century, textbooks like those of Fourcroy and Thomson characterized alumina as an indecomposable body, but not a chemical element. Around 1810, the status of alumina (aluminium oxide) changed from an indecomposable body to a compound and its metallic constituent 'aluminium' started to appear on lists of elements. I have argued that this was the result of Davy's decomposition of the alkaline earths which showed that they were compounds of metals and oxygen. On the basis of the similarities between alumina and the alkaline earths, Davy could argue that they likely all had the same composition. Although he could not directly prove this using experimental decomposition, chemical analogy provided him with the additional evidence in favour of this claim. His contemporaries followed his reasoning and accepted aluminium as an element. I finished the chapter showing how Davy's contributions were retrospectively erased in favour of a history of aluminium that focused on its production as a metal.

In the case of aluminium, the analogical inference of its existence was coherent with experimental results and even though aluminium itself could not be isolated, there were no signs contradicting its existence. However, Davy also made a much more controversial prediction, namely that of the existence of the metal ammonium. In chapter two I described Davy and Berzelius' attempts to make sense of the composition of the compound ammonia, and the results of these investigations for their view of the elementary nature of ammonium, hydrogen, nitrogen and nitric between 1807 and 1813. Davy and Berzelius each proposed a number of interpretations of the composition of ammonia, continuously adapting their hypotheses in order to make them coherent with experimental results. I have argued that this development might be best described as a process of epistemic iteration, with each stage of their work building on their previous knowledge while also correcting it. The way in which Davy and Berzelius adapted their hypotheses and experiments to each new finding shows that they were incredibly attached to the idea that analogous substances had a similar

composition: especially Berzelius was very reluctant to admit that ammonia behaved like a salifiable substance but was not composed as one. Davy eventually gave up the study of ammonia in 1812 and vowed not to trust analogical inference again, whereas Berzelius increasingly became convinced of the idea that nitrogen was an oxide.

By the time of the debate on chlorine, Davy had developed a very strict identification of chemical elements on the basis of the negative-empirical criterion, stricter even than Lavoisier himself. Yet, despite his emphasis on the argument that chlorine was indecomposable, his contemporaries were reluctant to admit its elementary nature. Chapter three summarized the arguments in favour of and against the elementary nature of chlorine, focusing on the period between 1810 and 1816. The opponents of chlorine argued that Davy's results could be explained perfectly well on the basis of the idea that chlorine was a compound called oxymuriatic acid. Moreover, they preferred this explanation because it was more coherent with existing views of the composition of a number of substances, most notably the idea that salts and acids contained oxygen. After the discovery of iodine in 1813, the opinion of the European chemical community started to shift. Gay-Lussac and Davy insisted on the analogies between chlorine and iodine in order to argue that they were both chemical elements, and the fact that chlorine was no longer just an exception motivated chemists to adapt their views. They adjusted their ideas of the composition of salts and acids and created space for a new family of chemical elements in their classifications.

It is possible to identify a shared characterization of chemical elements in the early nineteenth century on the basis of these three stories. This group of chemists was generally working with a (mostly implicit) distinction between indecomposable substances, chemical elements and 'true' elements, just like Lavoisier had done. For example, Davy's identification of oxygen and later hydrogen as true elements differed from his characterization of bodies like aluminium and chlorine as 'insignificant' chemical elements. The former was a matter of metaphysical speculation on the ultimate nature of matter, which happened independently of the provisional identification of chemical elements. The identification of chemical elements, on the other hand, was fundamentally based on the distinction between provisionally simple substances and those that were merely impossible to decompose. Alumina, for example, was viewed by many as an

indecomposable substance but not as a chemical element. Another example was Davy and Berzelius' prediction that nitrogen was a compound, even though it behaved like a simple substance. The negative-empirical criterion for elementary nature could not be used in order to make this distinction between indecomposable substances and chemical elements because experimental results could be interpreted in a variety of ways. Early nineteenth-century chemists therefore relied on chemical analogy as additional evidence of chemical composition, which helped them interpret and explain their experimental results. They established their knowledge of chemical composition on the basis of the consilience of experimental and analogical evidence.

The inference of composition on the basis of analogy relied on chemical analogy as a principle of classification: if a substance had enough relevant similarities in its behaviour to be categorized as a certain kind of substance, it could be inferred that it would be composed in the same way as all members of that kind. The central assumption in all of these inferences was that analogies in chemical properties were somehow linked to analogies in composition, in other words that the same kinds of substances generally contained the same kinds of elements.

In these three chapters, I have only briefly touched upon questions regarding the justification of this use of analogy. In the philosophical literature on analogical reasoning in science, the question of whether and how analogical arguments warrant their conclusion is of central importance. Unlike deductive arguments, the conclusion of analogical inferences does not logically follow from their premises. Yet, this is a very fruitful form of reasoning which often works well.[144] One approach to studying this question has been to develop a formal method for the evaluation of analogical arguments in general, such as those proposed by Paul Bartha (2010) and Mary Hesse (1966). Others have argued that analogical arguments cannot be captured by a logical argumentative structure and their validity can only be evaluated within a specific context. For instance, John Norton (2022) has recently defended a view of analogical inferences as relying on a 'fact of the analogy' which expresses when two systems are similar in a way that can be fruitfully explored and

[144] The same could be said about induction, and analogy has indeed been characterized as a certain kind of induction in some accounts. The identification of a set of specificities that set apart analogical reasoning is a complex question that cannot be treated here.

which is completely context-dependent. However, Norton does not specify what in turn warrants the warranting fact, because in his view there can be no general evaluation beyond purely local inferences. While Norton approaches this question from an external point of view, other authors who argue against logical justification have been able to alleviate the issue of justification by studying analogical reasoning from within specific kinds of scientific practice (for example Wylie 1988; Currie 2016).

The view of analogical inferences that I have defended in this part of the thesis points towards a similar, practice-based solution of the question of justification. I suggest that early nineteenth-century chemists' use of analogical inference was pragmatically justified: their conclusions were warranted simply because they seemed to work well for them, through a kind of operational coherence (see Chang 2022). As the story of ammonia shows, whenever inferences led to incoherence, chemists either revised their experimental protocols, their view of the composition of certain substances, or their classifications. At each stage of epistemic iteration, the different types of evidence mutually justified each other through convergence, similar to Chang's (2004) 'progressive coherentism'. This may appear to be a rather circular justification, but the main idea is that in these cases, analogical inferences did not justify a conclusion by themselves.[145] Early nineteenth-century chemists did not aim at formulating analogical inferences as such; these inferences were merely among their tools to achieve the goals of understanding, transformation, producing and classifying chemical substances. As a part of chemical practice, analogical inferences were integrated with a variety of other methods by which to study chemical composition.

So far, these first three chapters have only addressed a few examples of identifications of elementary nature, involving a relatively small group of actors. The context in which they were working was rather exceptional in that they were dealing with new phenomena, such as electricity, or new types of chemical substances, such as the halogens, and they had to figure out how to integrate these discoveries into existing chemical knowledge. In order to arrive at a more general conclusion regarding the characterizing of chemical elements

[145] The question of justification of an analogical inference in isolation might perhaps be more relevant for cases like analogue experiments, in which analogical inferences are the only way to warrant a conclusion. On that topic, see (Dardashti, Thebault, and Winsberg 2015; Crowther, Linnemann, and Wuthrich 2019) and the forthcoming PhD thesis of Grace Field (University of Cambridge).

between 1770 and 1870, more case studies are therefore needed. Other types of nineteenth-century chemical practice were less spectacular, in the sense that they were not dominated by Davy-like figures who presented their numerous discoveries in front of captivated audiences. One such practice was analytical chemistry, of which the history has been relatively little studied. Yet, the chemical analysis of minerals consistently led to the most discoveries of new elements during the eighteenth- and nineteenth centuries. In the next part of this thesis, I will describe the identification of new chemical elements in nineteenth-century mineral analysis and compare the argumentation to those used in the cases of aluminium, chlorine and ammonia.

# PART II - "A Substance Sui Generis": The Identification of Metals in Nineteenth-Century Analytical Chemistry

The rapid increase in the number of elements during the late eighteenth and nineteenth century is often associated with the development of novel techniques such as electrolysis and spectroscopy, each of which led to a number of new discoveries. In the first part of this thesis, I have discussed some of the relatively famous discoveries of elements that were made in part thanks to the development of the voltaic pile as a new instrument for the study of chemical composition. However, most of the discoveries of elements that were claimed during the eighteenth and nineteenth centuries were based on the results of mineral analyses (see Pérez-Bustamante 1997). Already before the chemical revolution, the characterization of mineral substances on the basis of their chemical composition led to the identification of many previously unknown constituents and this continued throughout the nineteenth century.

Indeed, while plant and animal substances are mostly composed of the same small number of elements, minerals often contain traces of many different metallic oxides and earths that have extremely similar chemical behaviours. During the eighteenth and nineteenth centuries, the struggle to separate similar constituents was one of the key motivations for the refinement of analytical procedures. The development of new techniques in turn often led to the discovery of new elements. For example, Charlotte Abney Salomon (2019) has shown how the ubiquitous use of the blowpipe facilitated the discovery of a large number of elements by Swedish mineralogists in the eighteenth century. The history of the discovery of chemical elements is therefore completely intertwined with the development of analytical procedures. The link between the identification of new elements and the efforts to separate the often almost indistinguishable

constituents of minerals has been illustrated in the case of the rare earths, but the similar case of the tantalum metals has so far largely escaped the notice of historians.[146]

Between 1801 and 1866, the number of metals in the tantalum family remained open for debate. Of this group of metals, only tantalum and niobium are still recognized as chemical elements today; the discovery claims of columbium, pelopium, ilmenium and dianium were all retracted or refuted. The controversy surrounding this family of elements is contained in a rich collection of primary sources in which chemists explicitly argued in favour of and against the elementary nature of each of the tantalum metals. In this part of the thesis, I will analyse these arguments in order to investigate the identification of chemical elements through the chemical analysis of minerals during the early-to-mid nineteenth century.

Chemical analysis is the study of chemical composition using a number of techniques that could vary according to historical and practical contexts. Analytical methods originated in various arts and crafts and even after the institutionalization of chemistry, they remained important outside of the academic laboratories, for example in quality control, medicine and industry. In these three chapters I will focus on the chemical analysis of mineral substances because of the strong link between this practice and the identification of new chemical elements.

I have selected the sources and therefore actors for this part by starting from the identification of the tantalum metals – they are therefore either mentioned because they contributed to this endeavour or because they developed new analytical methods otherwise. These were not isolated authors: most of the chemists that were known for their analytical work were connected by a network of teacher-student relationships (see Figure 6). Until around 1830, most of these skills were acquired through individual apprenticeships; later in the nineteenth century, more large-scale practical education was provided in teaching laboratories where multiple students could carry out the same experiments simultaneously (see for example Brock 2003; Homburg 1999). In both of these institutional contexts,

[146] For the history of the rare earths, see Evans (1996). Niobium, columbium and tantalum are described in Weeks (1956) whereas pelopium, ilmenium, dianium have been discussed by Fontani, Costa, and Orna (2015). With the exception of my own work on the topic, to my knowledge no studies were aimed at the group of elements as a whole (Hijmans 2022b).

practical education was a key part of transmitting the largely tacit skills needed for chemical analysis.

Indeed, analytical chemistry was centred on experimental practice and did not lead to any grand theories of chemical composition. It could even be seen as a type of exploratory experimentation where the main aim was to classify the reactions of specific substances to specific tests (Steinle 2016). At stake in these experiments was the identification of the composition of specific minerals, as well as the development of new practical tests for the presence of certain constituents, both of which happened mostly independently of chemical theories. This very problem-oriented nature of mineral analysis, the fact that its publications were rarely more general than the results of specific analyses, might be one of the reasons why its history has been very little studied. This is especially true for the history of nineteenth-century analytical chemistry, because of the increasing importance of organic chemistry during this period.

In the three chapters that make up this second part of the thesis, the controversies surrounding the tantalum metals will provide insight into the ways in which analytical practice changed during the early and mid-nineteenth century. This part relies on various secondary sources on the history of analytical chemistry, but the story of the tantalum metals is an original case study of relatively unknown primary sources. On the basis of scientific publications on this topic, I will argue that in claiming the discovery of a new metal and establishing its identity, the central question was not whether the metal could be isolated in the form of a simple substance (that is, as a metal), but rather the chemical properties of its compounds.

This argument contradicts the common idea that the discovery of new elements was a matter of isolating a new indecomposable substance. Chemists implicitly based their identification of metals on a similar inference as used in the case of aluminium: if a new substance behaved like a metallic oxide, chemist predicted that it contained a metal. When chemical atomism became more widespread, it even became possible to predict chemical formulae on the basis of analogy. However, whereas Davy and his colleagues reflected on their uses of analogy, as I have highlighted in the previous three chapters, practitioners of analytical chemistry did not provide the same reflections. Only on very rare occasions did

they make it clear that they also believed in the general rule that similar substances shared a similar composition.

The question of the simplicity of metals – whether they were chemically indecomposable – was therefore only of secondary importance in identifying them. Instead, the history of the tantalum metals points towards a continuous tradition in the identification of metals tracing back to the eighteenth century. Long before they were seen as simple substances, metals and metal-like substances were identified as a distinct class of substances because of their economic value and usefulness. Ursula Klein (2014) and Hjalmar Fors (2015; 2014) have argued that this happened independently of theoretical views about their internal composition: for the classification of metals as such, it made little difference whether one ultimately saw them as simple or complex bodies. This part of the thesis will extend the scope of their argument to include the nineteenth century and the tantalum metals. Indeed, although Lavoisier changed the theoretical conception of the composition of metals, the methods used to identify them remained largely the same.

After a relatively standardized methodology combining 'dry' and 'wet' methods emerged at the end of the eighteenth century, the procedures used in chemical analysis remained largely unchanged during the nineteenth century (see Hudson 2005). Wet analysis, the study of minerals in solution, consisted in separating out the components of a mineral substance by consecutive steps of solution in different solvents, precipitation with various reagents, and evaporation. Dry analysis consisted of metallurgical assaying procedures such as fusion, calcination or vitrification, which required a high temperature. While these were traditionally carried out in furnaces, the blowpipe provided a portable, quick and affordable tool for performing dry analysis on a small scale (Oldroyd 1974). I argue that these methods were more concerned with identifying compounds than with decomposing them into their simpler components.[147] For example, reagents such as prussiate of potash (potassium ferrocyanide) and tincture of gall (an extract produced from abnormal growth on plants) could be used to detect different metals in solution by the production of coloured precipitates. Likewise, although the blowpipe could in some cases produce a metal, it generally did not decompose the substances under study.

[147] Chang (2011a) has also defended this view of analysis.

As Ferenc Szabadváry (1966, 174–85) has described, even quantitative analysis proceeded by forming new compounds rather than the production of simple bodies. My argument therefore also contradicts a common view of 'analysis' as being synonymous with 'decomposition'.

In this part of the thesis I will divide the history of the tantalum metals in two parts. First I will explain in more detail what I mean by saying that analytical chemists identified metals primarily on the basis of the reactions of their compounds. I will do so in chapter 5, which focuses on the first decade of the nineteenth century and takes the identification of tantalum and columbium and their consequent retraction as a starting point. In chapter 6, I will focus on the debates on the so-called 'tantalum metals' that took place during the middle of the nineteenth century. In order to grasp the ways in which new chemical elements could be found in mineral sources, it is important to understand the analytical procedures that chemists could rely on. I will therefore begin by describing the methods of analytical chemistry and their origins in chapter four.

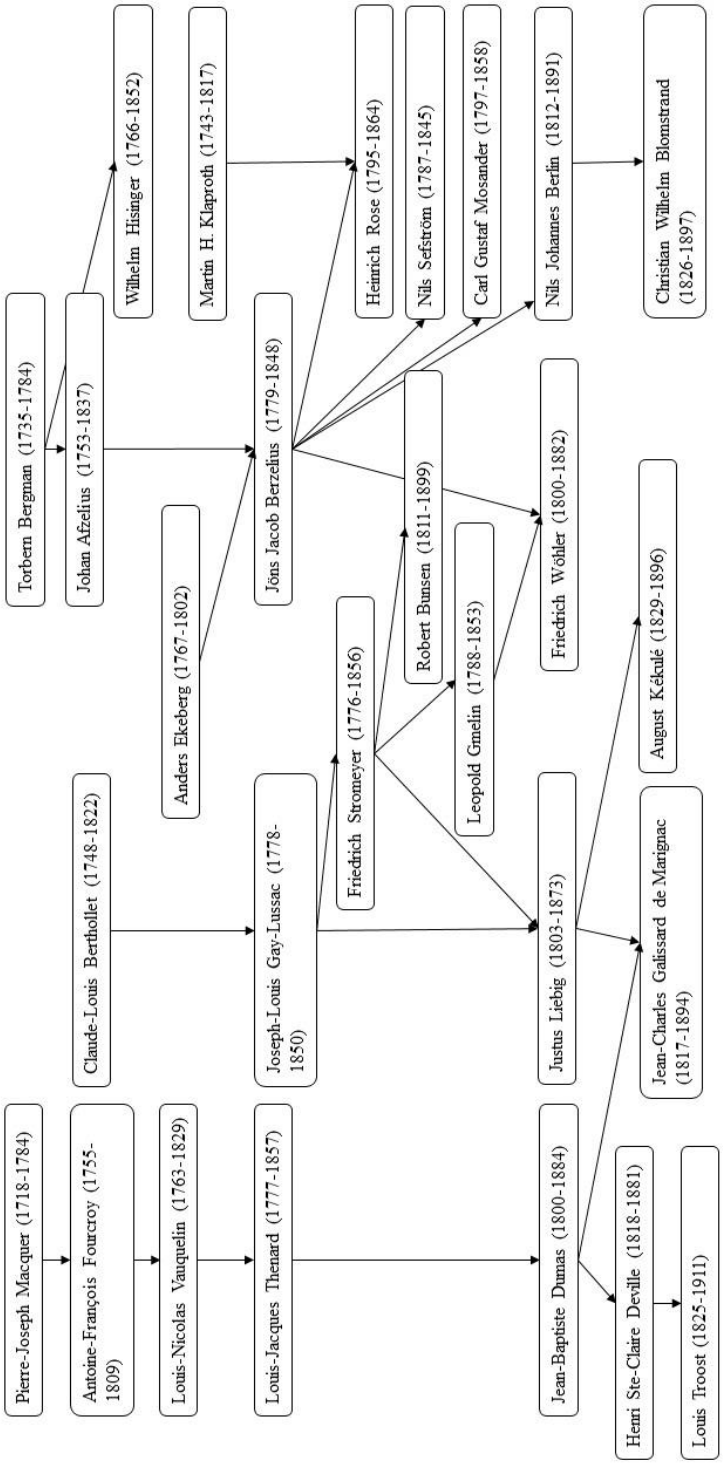



*FIGURE 6 - Schematic representation showing how most of the actors mentioned in this part of the thesis were connected. Arrows represent a teacher-student relationship. This figure is inspired by a similar figure in Perez-Bustamente (1997) but adapted with information from Homburg (1993), Partington (1962a; 1964), Szabadvary (1966) and individual biographical descriptions.*

# CHAPTER 4 - The Methods of Mineral Analysis

The terms ‘analytical chemistry’ and ‘chemical analysis’ date from the last few decades of the eighteenth century, and it was around that time that a relatively standardized methodology of chemical analysis was established (Homburg 1993, chap. 8). As will become clear in the next two chapters, these different analytical procedures continued in use throughout the nineteenth century. It is therefore important to understand what they consisted of in order to grasp the debates of the first half of the nineteenth century.

Generally, a full analysis consisted of both ‘dry’ and ‘wet’ methods, referring respectively to the procedures of assaying carried out at high temperatures, and the study of minerals in solution by combining of different types of solvents and reagents, in order to test a sample for the presence of different kinds of earths and oxides. Besides being useful for resolving specific practical questions (such as quality control of food, drinks and medication), analysis was one of the essential elements of chemical research as a method for the study of chemical composition. The distinction between the ‘wet’ and ‘dry’ ways of studying chemical composition was first represented in affinity tables in the early eighteenth century (see Duncan 1996). These tables and the different reactions presented in them resulted from the (joint) development of metallurgy and pharmacy, which were the main fields of chemical theory and practice during the sixteenth and seventeenth centuries. Metallurgy led to new methods and concepts surrounding the identification and extraction of metals, such as the use of *aqua fortis* (nitric acid) for the separation between gold and silver. This method became the prototype for the separation of metallic substances by precipitation, a method that spread extensively in seventeenth century pharmacy. By the early eighteenth century, chemists were able to identify and classify salts, alloys and aqueous solutions based on their composition (Szabadváry 1966, chap. 3; Klein and Lefèvre 2007, chap. 8).

This brief summary of the origins of chemical analysis already suffices to show that this practice largely developed at the intersection of many of the chemical arts. Indeed, one cannot write its history without acknowledging the overlap between the history of science, technology, industry and crafts: the development of early analytical chemistry is rooted in

arts and crafts as much as it is in the study of nature. Most of the substances that were studied by early-to-mid-eighteenth century chemists were products known in mining, metallurgy, distilleries and apothecary shops. Likewise, the networks of chemical practitioners show a shared material culture: chemistry was not restricted to institutions of learned inquiries, but also practiced at different kinds of non-academic sites and sites of commercial production (Klein and Lefèvre 2007, chap. 1; Klein 2008b).[148] Around 1800, when the first generally applicable methods of chemical analysis were established, chemistry "was in the process of crystallizing out into a modern scientific discipline quite distinct from its dependent arts, such as pharmacy or mineralogy to name but two" (Simon 2017, 152).

In this chapter, I will provide a summary of the different analytical methods and the way in which these influences came together to establish analysis as a chemical method at the end of the eighteenth century, mostly on the basis of secondary sources. Although various forms of analysis were used in different aspects of chemistry, I will focus on the analysis of mineral substances because these were the methods that generally led to discoveries of new chemical elements (as opposed to the analysis of organic materials, for example). I will describe the different influences on wet and dry analysis as well as their main procedures, before ending the chapter with a description of the different steps and goals of the generally applicable analytical methodology that emerged at the end of the eighteenth century.

## Mineral analysis and metallurgical assaying: the influence of various industries on the development of analytical methods

Between the late seventeenth and late eighteenth century, chemical analysis fruitfully developed, largely thanks to its close links with industry (Szabadváry 1966, 42). As Europe started to industrialize, state officials became interested in such materials and funded not only industry itself, but also additional research in mineralogy and geology

[148] For the locations of chemical practice, see also the project *Sites of Chemistry, 1600-2000* which led to the publication of two special issues of *Ambix* in 2013 and 2014. For the eighteenth century, see Perkins (2013).

(Laudan 1987, 47–56; Klein 2020). Chemical mineralogy benefitted from the creation of mining schools and other teaching institutions throughout Europe, which provided mineralogists with a secure position and the possibility to make a career in mineralogy. This stimulated chemistry in many different ways throughout Europe, most notably thanks to the importance of mineralogical assaying and analysis for the mining industry. Important contributions to methods of chemical analysis came from Sweden, France and German states such as Saxony and Prussia. These different communities were not at all separated from each other, as translation and other exchanges were continuously happening. The political-industrial context was also similar in these countries: their governments funded industry and the corresponding research in the domains of metallurgy, porcelain, glass and even the production of sugar. This section will consist of a summary of the development of mineral analysis in these contexts.

## Mineralogy, chemistry and classification in eighteenth-century Sweden

Because of its important mining industry, Sweden was "the centre of metallurgical analysis" throughout the eighteenth and well into the nineteenth century (Szabadváry 1966, 43). The town of Uppsala and Stockholm and the nearby Bergslagen region formed not only a lucrative mining region but also the home of many internationally renowned chemists. Swedish mineralogy, geology and chemistry largely benefitted from the 'Era of Liberty' (1718-1772) preceding the realm of Gustav III, which was characterized by mercantilist and utilitarian ideals, and during which new paid positions were created for chemists. During this time, chemistry was practiced both in the mining industry and at the university, and there was a close collaboration between these two groups (Lundgren 1988).[149] The community of chemical mineralogists greatly contributed to the development of two of the main methods of chemical analysis: the blowpipe and mineral water analysis.

[149] The famous Swedish chemists Carl Wilhelm Scheele (1742-1786) constitutes an exception, as he was neither an academic chemist nor employed by the Board of Mines: in 1775, he became the first apothecary assistant to become a member of the Swedish Academy of Sciences (see Partington 1962a, 3:205–34). Moreover, Swedish nationality was not required in order to participate in this methodological community, as the example of the brothers Elhuyar, Juan José (1754-1796) and Fausto (1755-1833), shows.

At the Board of Mines, which had controlled and regulated all aspects of the Swedish mining industry since 1630, two technical sections were dedicated to chemistry: the Chamber of Assaying and the *Laboratorium Chymicum*. During the eighteenth century, both of these sections were focused on testing the quality of metals produced and assessing new mineralogical specimens. Many of Sweden's well-known chemists held positions at the Board of Mines and did not occupy any academic positions: this was the case, for example, for Axel Fredrik Cronstedt (1702-1765), Petter Jacob Hjelm (1746-1813) and Johann Gottlieb Gahn (1745-1818) (Partington 1962a, 3:173, 201, 236). However, even at the university, Swedish chemistry was characterized by its dependence on the mining industry: chemical works concentrated on metallurgy, mineralogy and assaying. The first chair in chemistry outside of a medical faculty was created at Uppsala university in 1750, and held successively by Johan Gotschalk Wallerius (1709-1785) and Torbern Olof Bergman (1735-1784, professor at Uppsala from 1767).

During this time, mineralogy and chemistry grew together as minerals came to be classified based on chemical composition. As Rachel Laudan (1987, chap. 4) explains, eighteenth-century taxonomy had been dominated by Linnaeus (1707-1778) and his *Systema Naturae* of 1735, in which he proposed a mineralogical classification inspired by botany. Very few mineralogists accepted his mineralogical classification as it was, but his methods were so successful in botany that for the next fifty years, mineral taxonomists' theory and practice was shaped by their reaction to Linnaeus' system. The most important reaction, especially in Sweden, was to refute classifications based on external characteristics. Such a system was first published by Cronstedt and later expanded by Bergman,[150] who both thought that the identities of minerals were determined by their chemical composition rather than characteristics such as shape and colour. As opposed to Linnaeus, they did not see the mineral realm as a continuation of plants and animals, and they thought they should be classified according to separate, chemical principles. The classification of minerals on the basis of chemical composition united natural history

[150] Outside of Sweden, in Freiberg, Abraham Gottlob Werner (1749-1817) also defended a chemical system of mineralogy.

with the more practical considerations of assaying (Fors 2014). As a result, assayers at the Bureau of Mines and mineralogists now had the same goal: to characterize mineral substances on the basis of their chemical composition.

## The blowpipe: a new method of dry analysis

The classification of minerals on the basis of chemical composition promoted the discovery of new substances because it required researchers to identify their composition. One of the methods the Swedish mineralogists adopted for this purpose was the blowpipe. As its name implies, the blowpipe consisted of a pipe through which one could blow air into a flame in order to direct it and increase its heat. The instrument had been used by goldsmiths since antiquity, and in the seventeenth century it was widely used by glassblowers who used it to melt small quantities of glass. The instrument was commonly used to study minerals in Prussia and Sweden from the 1740s, where it provided chemical mineralogists with a portable, quick and affordable way of performing chemical analysis, of which the results could easily be shared and replicated (Szabadváry 1966, 50–55).

Although there were individual variations in design depending on personal preferences, the basic shape of the blowpipe remained fairly stable: it consisted a brass or silver tube of about 30 cm, with a diameter of 0.5 cm, tapering to a nozzle with a pinhole-sized opening. Most of them also had a bend or a separate chamber to trap moisture. Despite this quite simple design, it was very complicated to correctly operate the instrument for qualitative analysis and it was almost impossible to master from a textual description alone (see Dolan 2003). In the English translation of Cronstedt's 1758 mineralogical treatise, Gustav von Engeström (1788) described how to carry out a blowpipe analysis. On the basis of this explanation, David Oldroyd (1974) has provided a summary of the different steps to be followed in a blowpipe analysis:

1. Examine the sample with a magnifying glass so as to discover any heterogeneous parts;
2. Test its hardness;
3. Test the effect of the heat of a blowpipe flame on a sample placed on a charcoal block;
4. Likewise, with a flux of soda;
5. Likewise, with a flux of borax;
6. Likewise, with a flux of 'microcosmic salt' (sodium ammonium phosphate).

Depending on the way mineral samples responded to the heat of the blowpipe (see Table 2), mineralogists could detect the presence of one or more components. The use of fluxes was another method that chemists had learned from metallurgists and glass makers: when a sample had too high a fusion point to be directly melted, these different salts could be added in order to lower the fusion point (Newcomb 2009, 43–45). In some cases, the blowpipe could be used to directly produce metals from their ores.

The blowpipe had many advantages as a tool for mineral analysis (Abney Salomon 2019). A full chemical analysis consisted of both wet and dry methods, but traditional dry analysis required the use of large furnaces, which were not only expensive and cumbersome but also required large samples to function. The blowpipe enabled assayers to replace this large-scale procedure with the analysis of a small sample, which could be done in a shorter amount of time using only a candle, a blowpipe and a block of charcoal. The fact that it required less resources made this method accessible: since it was affordable, small-scale and quick, this meant that chemists and mineralogists were now able to carry out a full analysis outside of the laboratory, at home or in the field. Another advantage was that the reactions could be viewed in real time, which was not the case in a furnace. This new method did not completely replace the furnace, which was often still needed for decompositions or quantitative analysis, but in combination with wet analysis it provided an excellent tool for the determination of the composition of substances, that was sufficient for the majority of qualitative results.

Charlotte Abney Salomon (2019) has argued that the large number of Swedish element discoveries of the late eighteenth century could be explained by the ubiquitous use of the blowpipe in this community. The shared use of the blowpipe meant that almost every Swedish mineralogist had access to the same analytical methods and their results could easily be exchanged: mineralogists would send small samples to their colleagues so that they could replicate each other's analyses. Later, preliminary blowpipe results would be published so that the investigations could be carried on by colleagues or successors. Most often, the first characterisation of a newly found mineralogical sample was done by assayers from the Bureau of Mines, but the universal use of the blowpipe meant that anyone could then continue the investigation. Thus, claims to element discovery in eighteenth-century Sweden resulted from multiple analyses, consisting in part of replications of earlier

(published) blowpipe results. Abney Salomon's examples of elements discovered using such a "blowpipe-facilitated" processes include manganese, barytes, molybdenum, yttrium, tantalum, tungsten and cerium (*ibid*., 19-21). Other discoveries could be added to this list, such as nickel and native antimony, which took place around 1750 (see Partington 1962a, 3:173). In the next two chapters it will become clear that this use of the blowpipe for new discoveries was not limited to the Swedish mineralogical community: discoveries made elsewhere were also facilitated by the use of this instrument.

| **Substance under study (on charcoal block)** | **Reaction to the action of heat** |
|---|---|
| Calcareous substances | They become friable but do not melt. On cooling and washing with water, they produce considerable heat. |
| Siliceous substances | They become brittle but do not melt; sometimes they lose their colour. |
| Garnets | They melt and produce a black slag. |
| Mica and 'asbestus' | They become hard and brittle. They are mostly resistant to heating but they can be some signs of fusion. |
| 'Fluores' | They emit light and melt, producing a white and opaque slag. |
| Zeolites | They foam and form a frothy slag |
| Iron ores | They can become magnetic, but do not fuse. |
| Ores containing sulphur or arsenic | They produce fumes and smell of burning sulphur or garlic. |
| Lead ores | Production of metallic lead. |
| Some copper ores | Production of metallic copper. |
| Antimony ores | They volatilize and give off a characteristic smell. |
| Zinc ores | They produce white flowers of zinc. Sometimes metallic zinc is formed, in that case it burns with a blue flame. |

*Table 2 - The responses of various substances to heat of the blowpipe, based on a summary by Oldroyd (1974, 511).*

## Mineralogy, mining and other industries in France

Similar to the Swedish context, the growing French interest in mineralogy was also linked to the country's industrialization.[151] As opposed to Sweden, where mining had already been the most fruitful industry for centuries, France had traditionally been a mostly agricultural country. After a more difficult period, the French economy became stable from around 1730 and its industry grew quickly, in the metropole as well as the colonies. Different types of industry, such as faïence, glass, steel and textile profited from the economic growth, and since this growth in production required increasing amounts of fuel, coal mines developed as well. Besides coal, other mineral species were mined because of their usefulness or economic (and aesthetic) value. Though mines could be owned and operated by private people, French industry was also heavily controlled and promoted by the state. The state wanted to centralise quality control and advise mining supervisors on technique and installation of mines, but there was a lack of technological expertise. Following the examples of Prussia and Saxony, the French state therefore founded special schools dedicated to the education of scientific-technological experts. These schools provided training in chemical analysis and assaying. This linked the tradition of assaying, often named 'docimasie', to chemistry and the study of minerals.

During the 1750s, the translation of Swedish mineralogical works played an important role in the development of French mineralogy, because no French mineralogical treatises were written during the first half of the eighteenth century. Paul-Henri Thiry, Baron d'Holbach (1723 – 1789) initiated the diffusion of foreign mineralogy in France, starting with a translation of the German edition of Wallerius' mineralogical treatise. Another key figure for the introduction of Swedish mineralogy in France was Louis-Bernard Guyton de Morveau (1737-1816) who started translating Bergman's work in 1780. De Morveau also set up the 'bureau de traduction' of the Academy of Dijon, where a collective translation effort made many Swedish mineralogical works available to French readers (see Bret 2016). Following his translation of Bergman's work on the topic, de Morveau also started to teach blowpipe analysis during his chemistry courses (*Ibid*., 140).

[151] My summary of developments in eighteenth-century French mineralogy is based on works by Arthur Birembaut (1953; 1986).

Whereas Swedish mineralogy was mainly concerned with metals, French natural history focused more so on gems, which were the main minerals to interest the amateur elite (Bycroft forthcoming). As opposed to ores, these were mainly described based on external characteristics like colour and shape rather than chemical composition. In 1773, a year after the translation of Cronstedt's mineralogical treatise into French, Jean-Baptiste Romé de l'Isle (1736-1790) proposed a mineral classification based on geometrical shape. As opposed to Cronstedt, who encouraged a fusion of chemical and mineralogical interests, Romé de l'Isle saw the two as separate disciplines. This style of reasoning continued in the works of René Just Haüy (1743-1822) who published his famous treatises in 1784 and 1801. The question of how to reconcile natural history and chemical mineralogy persisted until the end of the century, when they came together in crystallography.[152]

Since there was no tradition of assaying gems, the question of how to identify their chemical composition spurred the development of new analytical methods. As Michael Bycroft (forthcoming) argues, the analysis of gems led to the amalgamation of assaying traditions from Sweden and Germany with French natural history and methods from different types of (chemical) crafts: diamond-cutting, glass-blowing, porcelain production, and drug-making. Thus, many other influences played a role in the development of mineral analysis besides the Swedish and German mining industries.

Likewise, industries other than mining were important in the development of analytical methods in France: especially dye-works and porcelain manufactories required the study of different soil components and coloured precipitates. The project for making hard-paste porcelain motivated several groups of chemists to systematically investigate the reactions of different types of earths and stones. Some of the country's most well-known chemists were also supervisors of this type of industry: for example, Pierre-Joseph Macquer (1718-1784), a Parisian medical doctor and member of the French Academy, was both a chemistry professor at the *jardin du roi* and a supervisor of the royal manufactories of tapestries at Gobelins and porcelain at Sèvres which required him to examine many different soil samples (Lehman 2012). Macquer also worked on analytical methods with

[152] The coming together of chemical mineralogy and natural history can be illustrated by the collaboration between Vauquelin and Haüy at the Ecole des Mines (Bycroft forthcoming, 27–32). See also below on Vauquelin.

his colleague and collaborator Antoine Baumé (1728-1804), who had a manufacturing laboratory where they both carried out chemical tests. Baumé investigated affinities in the dry and wet way, and therefore studied a different number of precipitation reactions that could be used as chemical tests (Partington 1962a, 3:90–95).

Thus, in France as in Sweden, technological and scientific advances went hand-in-hand. These are the two examples that I have discussed more in detail, but other European countries were similarly beneficial for the development of chemical arts and crafts. In her recent book on technoscience, Ursula Klein (2020) has provided a detailed discussed of the Prussian context, where a similar government stimulation of various industries took place. Like in the other contexts, chemical analytical methods were developed in porcelain manufactories, pharmaceutical workshop and at Academies of Sciences. The influence of this state funding for chemical mineralogy becomes especially clear by comparing these countries to the British context, where such state funding was lacking and the development of mineralogy was mainly dependent on the leisure time of professionals or the individual works done by wealthy people (Laudan 1987, 47–56). Nevertheless, Swedish mineralogy also spread to Britain, where by the beginning of the nineteenth century various chemical practitioners had adopted the blowpipe (Golinski 1992, 236–88).[153] Thus we see how new methods of chemical analysis, even if they were developed in a specific context, could circulate and spread to other countries. All throughout Europe, the economically motivated aim of characterizing substances in terms of their composition led to the fruitful development of analytical methods.

[153] A few British chemists had travelled to Sweden in order to learn the technique directly from their Swedish colleagues (Dolan 2003). These chemists later defended the legitimacy of the method against criticism from Davy and others (Dolan 1998).

# Mineral water analysis: the influence of pharmacy on the development of analytical methods

Besides metallurgy and different types of industry, pharmacy has been one of the most important influences on the development of chemical analysis. In both France and Germany, there were no clear distinctions between pharmacy and chemistry: most chemical practitioners were pharmacists and chemical education was mainly part of medical training (Homburg 1993, chap. 3; Simon 2017; Klein 2020, chap. 3). In these two countries, as opposed to Sweden, chemistry was not institutionalized separately from pharmacy until the last decades of the eighteenth century. Although pharmacists used various analytical methods for the study of plant and animal matter, here I will focus only on the pharmaceutical analysis of mineral substances because it is more closely linked to the identifications of new chemical elements that I will discuss in the next two chapters.[154] Pharmacists and doctors analysed mineral substances mainly in the form of naturally occurring mineral waters, which had all kinds of medical uses.

The development of wet analysis, the study of mineral substances in solution, was closely linked to pharmacy from its origins. Early modern Paracelsians used mineral analysis for the development of chemical remedies, and they adopted precipitation methods from metallurgy for the identification of minerals in solution. A number of systematic investigations of the different reactions of reagents with metals were published during the sixteenth and seventeenth centuries (Szabadváry 1966, 26–40). During the eighteenth century, this use of reagents developed into a transferable methodology that could be applied to many different substances. This systematization occurred in Sweden thanks to the works of Torbern Bergman, but it was applied and further refined throughout the rest of Europe.

[154] For the history of the analysis of plant and animal matter during the eighteenth century, see Simon (2017), Klein (2005), Holmes (1989). For its history between 1785 and 1835, see Tomic (2010). On the method of fire analysis traditionally used to analyse these substances see Debus (1967) or Holmes (1971).

## Bergman's method of mineral water analysis

Torbern Bergman was the professor of chemistry and pharmacy at Uppsala university between 1767 and 1780 and a member of the Swedish Academy. His work mainly focused on mineralogy and he was known as an experienced user of the blowpipe.[155] However, Bergman's main contributions to analysis lay in the development of systematic chemical tests for detecting the presence of different metallic substances. He used indicators such as litmus, brazil wood and turmeric and a large number of reagents as well as alcohol to distinguish between salts (see Table 3). Bergman also practiced quantitative analysis by weighing the precipitates and using them to deduce how much of their components had been present in the original sample (Partington 1962a, 3:185–87).

Besides simply adding new chemical tests, Bergman also made the analysis of mineral waters more systematic. Earlier in the century, the different processes that made up chemical analysis were only described as they occurred in specific studies. As more and more chemical substances became known, there was an increasing need for a systematic method to identify them. Though Bergman's work consisted mainly of records of his own analyses, Szabadváry has argued it contained the first "methodical summary of the processes of analytical chemistry grouped according to the nature of the substance analysed" (Szabadváry 1966, 71). His method, as summarized by Oldroyd (1973), consisted of grinding the mineral down to a powder and dissolving it. Then he produced precipitates and separated them from the solution until all constituents of the mineral were separated out. Bergman's 1778 paper "De Analysi Aquarum" improved, simplified and standardized a number of existing analytical techniques into a single system which could be transferred to different contexts and replicated by anyone. Thus, whereas analysis was an individual practice or art before, it became a single comprehensive methodology that could be applied in many different areas.

[155] Bergman had learned the use of the blowpipe from Gahn, who had been his assistant before moving to Fahlun to become a mining supervisor. Gahn himself was known as an extremely skilled blowpipe user, who introduced the 'cobalt-pearl' test (heating alumina with cobalt nitrate to form a blue globule). Though Gahn himself barely published anything, Bergman summarized the existing knowledge on the blowpipe and its methods in 1779 (Partington 1962a, 3:201; Szabadváry 1966, 53–54).

| Reagent | Reaction |
|---|---|
| Prussiate of potash (potassium ferrocyanide) | Blue precipitate with iron |
| | Brown precipitate with copper |
| | White precipitate with manganese |
| Sulphuric acid | Precipitate with barytes |
| | Effervescence with carbonates |
| Nitric acid | Precipitate (of sulphur) when added to sulphides |
| White arsenic | Yellow precipitate with sulphuretted hydrogen |
| Fixed and caustic alkalis | Precipitate with all metals |

*Table 3 - Examples of reagents used by Bergman. Based on Partington (1962, 186).*

## Pharmacy and mineral waters in France

Bergman's method immediately found its application outside of Sweden, for example in France, where the use of mineral waters as remedies became more widely spread in the eighteenth century (see Cornu 2022). Whereas waters were originally classified by the (medicinal) effects they procured, they gradually came to be characterized based on the quantities and types of minerals they contained (Cornu 2019). The *Société Royale de Médecine* (founded in 1778), which controlled the sales of all mineral waters in France, frequently hired chemists to carry out the quality control of these waters using chemical analysis. However, the waters were very difficult to analyse: they only contained trace amounts of minerals and they were chemically instable (over time, samples could change in temperature for example, or the gases they contained could slowly evaporate). Chemists were therefore forced to improve their methods, and Bergman's approach to wet analysis was a welcome innovation. It provided a clear and detailed methodology that could be applied to any kind of (mineral) solution sample. By the end of the eighteenth century, Bergman's method was widely adopted among French chemists.

For Jonathan Simon (2017, 110), the development of mineral water analysis is characteristic of a shift in the relationship between pharmacy and chemistry at the end of the eighteenth century. His main argument is that two revolutions enabled chemistry to separate itself from its traditional association with pharmacy in France: the chemical revolution and the French revolution. Lavoisier's system of chemistry installed a new

'philosophical' chemistry which forced the community of chemists to rethink its relationship to pharmacy. Pharmacy itself, meanwhile, was established as a separate field, thanks to the formation of the *Collège de Pharmacie* in 1777 and the subsequent reforms it went through during the French revolution and under Napoleon's reign.

Following this shift, a new mode of chemical analysis emerged, which followed the Lavoisian approach of characterizing substances in terms of their composition rather than by their medicinal effects, as had traditionally been the case in pharmacy or medicine.[156] The new view of analysis was part of a wish to make pharmacy more 'scientific' by completely basing pharmaceutical knowledge on chemical classifications and systems. One of the figures who actively encouraged this establishment of scientific pharmacy in France was Antoine-François Fourcroy (1755-1809), a medical doctor, teacher and statesman (Simon 2017, chap. 4). As one of the collaborators of Lavoisier, he promoted the new system of chemistry and its application to pharmacy. For Fourcroy, analysis was such a key part of chemistry that he defined the discipline based on it: "Chemistry… is a science the object of which is to examine the nature and the properties of all the substances by their analyses and their combinations" (Fourcroy 1782, 2; cited by Newcomb 2009, 88).

For Jonathan Simon, analysis was so closely tied to the artisanal practice of pharmacy that he refers to it as 'pharmaceutical chemistry' (following some authors of the time, see Simon 2017, 141–45). As chemistry separated itself from pharmacy, analysis came to be placed under the heading of the new science. However, one could make the same argument regarding mineralogical influences: the new discipline of chemistry adopted traditional assaying methods as a central part of its research practice. Here I want to emphasize the ways in which pharmacy and mineralogy came together in the development of chemical analysis, rather than treating either field in isolation.

[156] These two modes of analysis corresponded to the difference between 'immediate principles' and 'ultimate principles'. These two traditions continued to develop, and Sacha Tomic (2010) has interpreted the birth of organic chemistry in the nineteenth century as the hybridization of the pharmacists' immediate analysis and chemists' elementary analysis.

# Analytical chemistry at the end of the eighteenth century

Between 1790 and 1810, chemical analysis was one of the main concerns of chemists throughout Europe, and an important part of any chemical investigation (Szabadváry 1966, 114). Bergman had provided a methodology of mineral analysis that could be applied in many different contexts, which his successors continued to refine. The different influences from mineralogy, pharmacy and other crafts came together in a single chemical methodology which was standardized around 1800. This section will consist of a description of this methodology, its main aims and the relation to the chemical revolution.

## The method of chemical analysis: the examples of Klaproth and Vauquelin

In order to reconstitute the procedure of chemical analysis around the turn of the nineteenth century, I will base myself on the work of two of the most famous chemists of the time: Martin Heinrich Klaproth (1743-1817) and Louis Nicolas Vauquelin (1763-1829).[157] Klaproth's and Vauquelin's career exemplify the way in which mineralogical and pharmaceutical influences came together at the end of the eighteenth century. Working respectively in Prussia and France, both of these men had completed apprenticeships and practiced as apothecaries. However, both of them turned towards the rapidly developing field of chemical mineralogy and published most of their works on mineral analysis. As opposed to their predecessors, who taught mainly private courses in their shops, they taught at state-funded Academies for the training of scientific-technological experts, such as the Prussian and French mining academies, as well as to students of pharmacy and medicine (in Vauquelin's case). Although they both came from relatively humble backgrounds, their career enabled them to rise to become a part of the elite.[158]

[157] For the life and works of Klaproth and Vauquelin, see Klein (2014; 2020, chap. 2), Simon (2017, chap. 5), Partington (1962a, 3:551–57) and Szabadvary (1966, chap. VI.1). For a detailed description of a typical chemical laboratory of this period, including its instruments, see Tomic (2010, chap. 1).

[158] Klaproth was the son of a tailor and became the director of the laboratory of the Prussian Academy, as well as a member of the inner circle of mining administration and professor at the University of Berlin.

The bulk of Klaproth and Vauquelin's publications consist in analyses of specific substances. Whereas Vauquelin published a manual of metallurgical assaying (Vauquelin 1812), Klaproth did not publish a general analytical scheme and followed complex methods which are generally hard to summarize. Multiple authors have therefore decided to study specific analyses published by Klaproth in order to understand how he proceeded: Klein (2014) has focused on pitchblende, Newcomb (2009, 98–99) on leucite, Szabadvary (1966, 119–21) on zoisite and Oldroyd (1973) on sapphire. Using these studies and comparing them to the method used by Vauquelin (summarized by Oldroyd 1973), I will summarize here what the relatively standardized methodology of chemical analysis consisted of at the very end of the eighteenth century.

These chemists began their analyses with a preliminary description of the sample, its colour, shape and any other remarkable characteristics such as texture or taste. Following this description, the sample was analysed using the 'dry' and 'wet' ways. Dry procedures of assaying consisted for example of fusion, vitrification, reduction, amalgamation, sublimation, cementation, roasting, calcination, eliquation, and precipitation under fusion. Klaproth had access to the furnaces of the Royal Prussian porcelain manufactory, where he could carry out dry analyses, but he also used a blowpipe to characterize his samples.

In order to carry out a wet analysis, one first had to dissolve the mineral sample. Depending on the species, this could be quite difficult because solubility varied. There were different methods to increase the solubility of mineral samples: for example, Bergman had introduced the glass manufacturers' method of heating a sample with alkalis into chemical analysis. Klaproth and Vauquelin similarly ground their samples and heated them with alkalis or alkaline solutions. Alternatively, various types of salts could be used as fluxes and sometimes resulted in the production of soluble globules. Once the sample was dissolved, it could be identified with the help of a large number of reagents (see Newcomb 2009). These reagents were mainly different kinds of acids and bases, of which the reactions were well known by the end of the eighteenth century, and which were used for the solution of mineral ores as well as for forming salts with different types of

However, the contrast was especially strong in the case of Vauquelin, who had very poor origins but became the most important pharmacist-administrator of his time, in part thanks to the influence of his master Fourcroy.

metals and earths. Various salts such as nitrates or acetates could also be used, for example in order to carry out precipitation reactions.

The steps of wet analysis consisted of separating out different precipitates by combination of different types of solvents and reagents, and (sometimes) by evaporating until a residue was left behind. This way, the substance could be tested for the presence of different kinds of earths and oxides, which would be separated out and weighed. These procedures built on the basic scheme established by Bergman, which was gradually expanded as more and more different steps were added in order to identify additional species. At various stages of the analysis, chemists also relied on indicators, which were mainly used to test for acidity and which were often made of plant material: rose infusion, violet syrup, turmeric solution, ground galls, berry juices, different types of wood, litmus (made from a plant lychen), sunflower solution and more.

Following Bergman's example, Vauquelin started with the separation of silica out of the mineral sample, because large amounts of silica were often present in minerals. In order to do so, he evaporated an acidic solution of the mineral sample to dryness and extracted the residue with water. This left behind a precipitate of siliceous earth which could be filtered out of the solution. A possible next step was the addition of a caustic alkaline solution to the remaining aqueous solution: this caused iron oxide, magnesia and lime to precipitate, whereas alumina and glucina (beryllium oxide) remained in the solution. Alumina could be separated out from the solution by adding sal ammoniac (ammonium chloride), whereas glucina was left behind after as a residue evaporation. Following a similar pattern of dissolution, precipitation, evaporation and filtration, different constituents could thus be separated out. By weighing each precipitate, he could then calculate the proportion of the constituents in the original sample. Klaproth's methods generally consisted of similar steps but not necessarily carried out in the same order.

## The goals and stakes of mineral analysis

I have described the steps that made up a standard mineral analysis, but these do not tell us anything about the goals with which such analyses were carried out. An important and immediate goal of each chemical analysis was the investigation of the composition of the substance under study, which enabled their identification as a species, their naming and their classification. Around the end of the eighteenth century, each mineral species was

characterized by the presence of a specific component in a certain proportion, which was thought to be responsible for some of its properties like weight and shininess. The mineralogical goal of classifying the naturally occurring "raw" minerals led to a chemical one, which was "the experimental isolation of the distinct chemical component, determination of its proportion, and its identification" (Klein 2014, 29). This was part of the process of characterizing and identifying the mineral. This double aim of decomposition and identification was clearly summarized in the *Encyclopédie*, where Venel (1755) defined *docimasie* (metallurgical and mineralogical assaying) as "the art of examining a composed mineral substance of any kind by chemical operations, in order to know exactly the species & the proportion of the different substances of which it is composed, & to determine to the most advantageous ways of separating them."[159]

Because of such references to separating constituents, 'analysis' is often seen as synonymous with 'decomposition'. According to David Oldroyd (1974) for instance, "genuine chemical analyses" consist of "chemical decompositions and separations" or "resolutions into simpler substances". Thus, for example, he has excluded the blowpipe as a true analytical method because it did not break down mineral into their constituents: as I have described, the presence of certain metals could be detected based on the way the substance reacted in the blowpipe, without any decomposition taking place. In Oldroyd's view, the blowpipe did not belong to chemistry but to natural history, providing the natural historian with an extra set of characteristics by which a substance could be identified. Following Oldroyd, Klein (2014) also excludes blowpipe procedures from genuine chemical analysis.

However, I argue that analysis should not be seen as synonymous to decomposition, at least not when it comes to the chemical analysis of mineral substances. The blowpipe was not the only analytical method that enabled a characterization of substances without decomposing them: as I have described in this chapter so far, chemists and mineralogists also relied on various indicators in order to characterize their substances. Likewise, during (quantitative) wet analysis, even though they separated out various precipitates from the

[159] "L'art d'examiner par des opérations chimiques une matiere minérale composée quelconque, afin de connoître exactement l'espece & la proportion des différentes substances dont elle est composée, & de déterminer les moyens les plus avantageux de les séparer."

solution, these precipitates were not necessarily the constituents of the original mineral substance. Various reagents reacted with the substance in solution in order to form an insoluble compound. This way of separating the elements from each other was simply easier than isolating indecomposable bodies, as Friedrich Accum (1769-1838) would later explain:[160]

> "For the great object of acquiring a knowledge of the chemical nature of bodies consists in separating analytically their component parts; this, however, is seldom practical without, at the same time, uniting them to another body, and it is this that leads to the object in view, namely, the knowledge of the composition of the substance under examination" (Accum 1818, 50).

Analytical procedures therefore should not be characterized as a process of progressive decomposition, even when it comes to gravimetric analysis. Although a full decomposition was generally attempted, this was not always possible, and on the other hand it was possible to identify a compound's chemical composition without (completely) decomposing it.

It is true that chemists themselves often characterized analysis as aimed at decomposition. For instance, the dictionaries of Nicholson (1795, 244) and the Aikin brothers (1807, 70) both defined analysis as the "separation of any substance into its constituent parts, with a view of ascertaining their nature, relative proportion, and mode of union". Lavoisier and his colleagues also clearly thought of analysis as decomposition. Fourcroy (1782, 2–5) distinguished between "real or simple" and "false or complicated" analysis. Real analysis, according to Fourcroy, produced the unaltered principles of composed bodies, and it could be identified by the possibility to recompose a compound after its constituents had been separated from each other. False analysis, on the other hand, could be recognized by the fact that it produced bodies that could not recompose the initial substance; this implied that its products were not the constituents of the compound but altered bodies, artefacts that didn't exist as such in the analysed substance. According to Fourcroy, one should not trust this second type of analysis for identifying the composition

[160] Friedrich Accum was born in Hannover but ran a laboratory and chemical supply shop in London between 1800 and 1820, besides lecturing at various institutions. Ursula Klein (2020, 219–21) has described his career as an example of a scientific-technological expert.

of substances, and synthesis was therefore more trustworthy as a proof of composition.[161] Lavoisier himself meanwhile literally characterized analysis as the production of simple bodies, by defining simple substances as "the last point which analysis is capable of reaching" (Lavoisier 1790, xxiv).

How can we reconcile these different views of analysis – the fact that chemists aimed for 'real analysis' but still relied on various methods that did not decompose the substances under study? I argue that this view of analysis as the production of simple constituents is an idealization from analytical practice. In reality, only very few experiments could qualify as true analysis according to Fourcroy's terminology. Firstly, no organic analyses could qualify as 'true', because resynthesis of the plant and animal matter was impossible. Secondly, though resynthesis was possible for a number of mineral species (Fourcroy named the example of cinnabar), many naturally occurring mineral substances were too complex to be synthesized (T. M. Porter 1981, 568–69). Perhaps, the requirement was not so much the strict necessity to always completely break down a substance and build it up again, but the possibility of tracing a constituent through various chemical transformations, being able to extract it from certain compounds and reform them again without necessarily literally in the form of a simple substance.

Likewise, it is important to note that characterizing a substance in terms of (elementary) composition is not the same thing as literally decomposing the substance in question. An example that might illustrate this is Lavoisier's analysis of plant substances. In order to know the elementary composition of sugar, he did not decompose it and isolate carbon, hydrogen and oxygen; rather, he calculated its elementary composition from the products of its fermentation (carbonic acid and water) (see F. L. Holmes 1985). Similarly, Lavoisier performed an analysis by combustion of many different organic substances (described in Simon 2002): he burned different kinds of inflammable substances and calculated their original elementary composition based on the products of combustion (water and carbonic acid). Although he did break the substances down and he did characterize them in terms of elementary composition, Lavoisier did not actually produce any simple substances with

[161] Similarly, Lavoisier (1790, 33) states that "chemistry affords two general methods of determining the constituent principles of bodies, the method of analysis, and that of synthesis. (...) and in general it ought to be considered as a principle in chemical science, never to rest satisfied without both these species of proofs".

these analytical experiments. Similarly, we might conclude that the direct aim of analytical procedures was to characterize the substance under study rather than to decompose it.

Another aim of analytical procedures was the improvement of the methods themselves. One of the central problems of inorganic chemistry, especially mineral analysis, during the late eighteenth and for most of the nineteenth century, was that the exact composition of minerals was extremely difficult to determine: they often contained traces of many different metals and earths, between which even the most skilled experimenters could not always distinguish because they were so similar, and it was impossible to say how many elements were contained in a mineral species, as many of them were unknown.[162] The struggle to separate similar elements was one of the key motivations for the developments in this field.

The results of individual analyses were published in the newly founded journals of the late eighteenth century, but in general, little technical information was provided, and it was rarely explained why a certain reagent or (unexpected) technique was chosen.[163] Each of the methods of analysis was elaborated and refined in the study of particular substances. There were no systematic treatises of chemical analysis until later in the nineteenth century, and though some ideas for reagents could be gotten from affinity tables, much of this development was simply trial and error: chemists could try out new reagents or change some of their methods simply to see what would happen. This required systematic experimentation with different reagents, vessels, temperatures, solvents and modes of precipitation, in order to establish a classification of different reactions.

## Conclusion

In this chapter, I have described the origins of analytical chemistry, and the different steps that mineral analysis consisted of. These methods mainly developed with chemical arts and crafts and as part of mining and other forms of industry. During the widespread government-stimulated industrialization in various European countries, there was an

[162] These difficulties are remarked by Ursula Klein (2014, 30–31) and Sally Newcomb (2009, 96) as well.

[163] As is remarked by Klein (2014, 31), this is an issue for historians as well, because it is very difficult to know why a chemist employed a certain method.

increasing need for the chemical study of all kinds of substances. This enabled the systematic characterization of the way in which various substances reacted to chemical tests so that they could then be detected by them. Methods of dry analysis found their origins in metallurgy and mineralogy, and the development of the blowpipe as a tool for chemical analysis especially provided a new and accessible way to perform dry analysis in the field. Wet analysis meanwhile mainly originated in pharmacists' and physicians' study of mineral waters. The systematic use of reagents to characterize substances in solution resulted mainly from Bergman's work but his method found an application for all types of analysis throughout Europe. By the end of the eighteenth century, all of these methods had come together into a relatively standardized, widely applicable method that enabled the study of the chemical composition of mineral substances. I have argued that, besides the improvement of the methods themselves, the main aim of these procedures was not to decompose the substances under study. Rather, chemists wanted to characterize substances in terms of their composition, which could be done indirectly without breaking them down and isolation each of the constituents. Despite Lavoisier's definition of chemical elements as 'the last point which analysis is capable of reaching' we should therefore not see analysis as proceeding only via decomposition.

This chapter has only provided preliminary information to the study of the identification of new chemical elements using mineral analysis. Here I have described the methods that chemists used to identify the composition of mineral substances, but the procedure in order to characterize a new substance was different from a routine analysis. At the end of a quantitative analysis, if the final proportions did not add up to 100%, there were two possible explanations: either there had been a mistake in the analysis or an unknown substance had escaped the attention of the chemist because there was no established way to separate it out in the form of a precipitate. In the latter case, a systematic series of tests with different reagents was carried out in order to characterize the new substance. These tests consisted of the same procedures described in this chapter, but used in a more systematic and exploratory way in order to characterize the reaction of the new substance to each procedure. In the next two chapters, I will investigate the identification of new (metallic) elements using the methods of mineral analysis.

# CHAPTER 5 - Tantalum, Columbium and the Importance of Characteristic Reactions (1801-1810)

In late 1801, Charles Hatchett (1765-1847), a wealthy London chemist and Fellow of the Royal Society, claimed the discovery of a new metal called columbium.[164] During the next year, the assistant professor of the university of Uppsala Anders Ekeberg (1767-1813) published his discovery of a new metal called 'tantalum' in a Finnish sample of the mineral yttria.[165] Although these new elements were announced separately and had been found in separate mineral sources, they were so similar that the two metals were argued to be identical in 1809 by the famous English chemist and natural philosopher William Hyde Wollaston (1766-1828).[166] Starting from this episode, this chapter will study the arguments on the basis of which the discovery of new metals could be claimed during the first decade of the nineteenth century. How were the methods that I described in the previous chapter applied for the identification of new substances? How did chemists know what kind of substance they were handling and whether or not it was elementary? What were the arguments on the basis of which the existence of new chemical elements could be refuted? This chapter will be aimed at answering those questions.

Tantalum and columbium were both metals. Metals are fairly easy to recognize and anyone probably knows how to identify metals around them in daily life. Besides their characteristic opaqueness, shine and relatively high density, they conduct heat and electricity. They also have a number of properties that make them useful materials, such as elasticity and strength. They are solid at room temperature except for mercury, and they have a more or less distinctly metallic taste. However, as I will argue in this chapter, new

[164] For biographical information on Hatchett, see Griffith and Morris (2003), Partington (1962a, 3:705–6) or Weeks (1956, chap. 14).

[165] Ekeberg analysed a sample of yttria, but because of the large quantity of tantalum he found in it, he renamed this particular mineral yttrotantalite (Ekeberg 1802). For Ekeberg's biography, see Partington (1962a, 3:236). For Ekeberg's place in the Swedish chemical community and his role in the diffusion of Lavoisian chemistry in Sweden, see Lundgren (1988).

[166] For biographical information on Wollaston, see Usselman (2015).

metals were rarely identified in the form of isolated metals in the nineteenth century. Rather, they were characterized as the constituents of more complex (generally mineral) substances. In order to detect metals in this way, chemists had to rely on their chemical properties, which are less evident in everyday interactions with metals.

A very important property was the metals' tendency of producing oxides which in turn could form salts by combining with acids. The Aikin brothers, Charles (1775-1847) and Arthur (1773-1854) even defined metals on the basis of this property in their mineralogical dictionary:

> "(…) if a metal be defined, *a combustible or oxydable substance capable when in the state of oxyd of uniting with acids and forming with them chemical salts*, we shall be in possession of a character applicable to all metals and to no other class of bodies, and yet still not have mentioned one of those properties which doubtless first led to the discovery of metals" (Aikin and Aikin 1807, 94).

Early nineteenth-century chemists made use of this property when identifying the presence of (previously unknown) metals in minerals. They used the methods of mineral water analysis to produce various types of salts by adding reagents to a solution of the mineral substance; these often had very specific ranges of colours that could be used to identify constituents.

In using these methods, early nineteenth century chemists relied on an existing tradition of the study of mineral substances that I discussed in the previous chapter. Metals were especially important and well-studied because of their economic value and usefulness and their central place in different types of mining industry. Despite changing theoretical conceptions about their internal composition, they were continually recognized as a distinct class of substances since antiquity. Until the late eighteenth century, metal ores as well as metals proper were classified in the same category of 'metallic substances' (Laudan 1987, 21–28). As will become clear from various examples in this chapter, this close link between metals and their simplest compounds continued to exist into the nineteenth century, as metals were still studied on the basis of their compounds.

In the standard procedures of dry and wet analysis, the goal was to detect (and where possible, isolate) known constituents of a mineral so that its composition could be identified. These routine procedures could not be used in exactly the same way to detect

an unknown constituent, because there was no way to detect and identify it yet. Once an unidentifiable substance was left over at the end of a quantitative analytical procedure, a systematic study of its different reactions to the blowpipe and various chemical tests had to be recorded to see whether it corresponded to anything known or whether these were completely new properties. I will call this series of reactions to chemical tests that characterized a metal 'characteristic reactions'. Once the substance was described in this way, in case it was identified as a metallic oxide, a reduction was attempted. Ideally, chemists aimed to isolate any new metal that they identified, but I argue this was not required in order to claim a new discovery. A new metallic oxide by definition contained a new metal and the identification of a previously unknown oxide could therefore suffice.

When claiming a discovery, it was important to clearly identify a series of replicable characteristic reactions because otherwise the claim might be refuted. Wollaston's refutation of tantalum and columbium as two separate discoveries was not unique. Especially during the early nineteenth century, when many chemists felt a general discomfort regarding the rapidly increasing number of chemical elements, such debates surrounding the existence of specific elements were not uncommon. Motivated by the uncertainty regarding the true simplicity of substances, many chemists speculated on their inner composition. Some chemists aimed to reduce the number of elements where possible, for example via speculations on the complexity of the elements or attempts at reduction to a smaller number of true elements, as Davy did (see Farrar 1965; Brock 1985). However, as I have argued in previous chapters, besides the metaphysical uncertainty there was also the procedural difficulty of identifying substances as simple in practice. It was not always possible to know whether a newly claimed discovery was correct or whether there was another explanation, and discovery announcements were therefore often questioned. Without necessarily turning towards metaphysical speculations, many chemists also questioned the existence of specific elements: they thought it might be possible for some of the many discoveries of the early nineteenth century to be mistakes rather than genuine additions to the list of simple substances. Such controversies forced chemists to explicitly state why they thought a specific element did or did not exist, and they are therefore extremely useful sources for the study of the criteria for the discovery of a new chemical element.

In this chapter, I will focus on the first decade of the nineteenth century. I will refer not only to the publications of Hatchett, Ekeberg and Wollaston but also compare the cases of tantalum and columbium to those of cerium, palladium and erythronium in order to make more general claims about the arguments needed for the identification of a new metal. First I will analyse the different arguments on which discovery claims were based, and then I will study controversies and retractions in order to find out what the most important questions were if one wanted to establish the existence of a new metal.

## Metals, metallic oxides and the procedures by which they were identified

In this section I will go over the steps used to identify new substances and show that it was not uncommon for chemists to claim the discovery of a new metal on the basis of the identification of a new oxide. This type of experiment differed from the standard wet analysis method in which the different constituents are separated: here the main aim was to establish a number of characteristic reactions by which the new substance could be characterized. This series of reactions was essential for the identification of a new metallic substance because it could tell chemists whether the substance was metallic and whether it differed from those previously known.

### The different steps in the analysis of a new mineral substance

Ekeberg (1802) made his discovery claim on the basis of the identification of a substance that appeared to be a new metallic oxide. The mineral substance he analysed was characterized by its insolubility in all acids: it became soluble in water only after fusion with caustic alkali. The addition of an acid led to the production of a white precipitate, which could be melted in the blowpipe and did not colour the different fluxes. When mixed with charcoal in a crucible and subjected to high heat, it formed a metal regulus. Though it resembled the oxides of tin, tungsten and titanium, Ekeberg listed the properties by which his white precipitate could be distinguished from these other substances. Seeing as his substance was not any of the known metallic oxides, he concluded it contained a previously unknown metal: tantalum.

Ekeberg had two reasons to believe his white substance was a metallic oxide: the density and the possibility to reduce it into a metal regulus using charcoal.[167] Weight was a common indicator that a mineral might contain a metal, especially before the discovery of the very light metals potassium and sodium. For most of the first decade of the century, high density was still seen as a shared property of metals. Hatchett identified columbium in a "small specimen of a dark-coloured heavy substance" that attracted his attention when he was organizing the mineral collection of the British Museum (Hatchett 1802).[168] However, the possibility of reducing the substance set Ekeberg's white precipitate apart from that of Hatchett. In a postscript to his article he mentioned that "a complete reduction of [the new metallic oxide] is still far from being easily effected" (*ibid.*, 180). Hatchett therefore claimed the discovery of columbium purely on the basis of his identification of his white precipitate as a new metallic oxide and inferring that it would contain a new metal.

The identification of the metal columbium on the basis of its oxide was not unusual, as the example of cerium illustrates. The Swedish mine owner and mineralogist Wilhelm Hisinger (1766-1852) collaborated with the newly graduated Jöns Jacob Berzelius (1772-1848) on different chemical questions such as the effects of the voltaic pile on different types of earths (see Jorpes 1970, 23–24). In 1803 they studied the composition of a sample of Bastnäs tungsten, a type of stone that intrigued mineralogists because of its high density ('tungsten' meaning 'heavy stone' in Swedish). When they tried to detect yttria in their samples, they found some unexpected results, and further study indicated that they might be dealing with a new metallic oxide. The way in which it reacted with acids and precipitating agents distinguished it from known metallic oxides, which meant that it had to be a new discovery. Hisinger and Berzelius (1804) therefore concluded that they had probably discovered a new metallic substance, for which they chose the name cerium (after the planet Ceres). Despite many attempts at reducing the oxide, cerium was not

[167] Klaproth (1810) questioned the possibility to reduce the substance, and argued it was an earth rather than a metallic oxide, see below. Berzelius and Eggert later confirmed Klaproth's conclusion that the substance could not be reduced using coal, see Berzelius (1827b, 2:369).

[168] The mineral had been gifted to the museum from America. Hatchett proposed the name 'columbium' in honour of its origin.

obtained in metallic form until 1875; nevertheless, in the words of Jan Trofast (1996, 26), Berzelius and Hisinger's experiments "fully satisfied the criteria of a new element".

In other words, I argue that in order to claim discovery of a new metallic element, it sufficed to identify a new metallic oxide and clearly distinguish it from all previously known metallic oxides. By definition, a metallic oxide was composed of a metal and oxygen, and the identification of a previously unknown metallic oxide therefore logically implied the presence of a previously unknown metal. Moreover, once an (inferred) new constituent was classed as a metal, there was no need to test whether it was decomposable because it was automatically seen as a simple substance. According to the Aikin brothers:

> "Metals are simple substances, at least if they are not absolutely so, yet there is no instance of any one of them having been hitherto decomposed, notwithstanding the almost innumerable processes to which they have been subjected for this very purpose" (Aikin and Aikin 1807, 97).

Regardless of the existing speculations regarding the true nature of metals throughout the nineteenth century, the entire class was provisionally accepted as chemical elements. Once a newly identified constituent was classed as a metal it was therefore automatically seen as a chemical element and isolation of the metal itself was therefore not necessary. This implied making the same analogical inferences as I discussed in the first part of this thesis: if a substance behaved enough like a metallic oxide in order to be classified as one, it probably also contained the same elements. However, in this case the analogies were not explicitly referred to, and this is a sign that chemists agreed that this inference generally worked. Needless to say, this raises many more questions regarding these early nineteenth-century discovery claims: what does it mean to 'behave like a metallic oxide'? How could chemists be sure they were dealing with a metallic oxide? How did they distinguish it from known metallic oxides in order to claim a new discovery? The rest of this section will answer those questions.

## Recognizing metallic oxides

It should not be underestimated how difficult it was to perform a qualitative analysis and characterize a new substance. Even very experienced chemists could not always distinguish between a mixture of known metallic compounds and a single previously

unidentified metallic compound. Likewise, it was not easy to know whether something was a metallic oxide in the first place and a lot of carefully repeated analyses were therefore required. This is why a new discovery could generally not be accepted until it had been confirmed by multiple well-known chemists. For example, Hisinger and Berzelius sent samples of their cerium oxide to their colleagues at the Board of Mines and at the university, in order for them to replicate their analytical results. Moreover, especially those at the Board of Mines had access to large furnaces in which they could attempt the reduction of metallic cerium.

The difficulty of recognizing a metallic oxide becomes clear from the fact that different chemists did not always agree on the identification of a single compound. Ekeberg and his colleague in Uppsala Johan Afzelius (1753-1837) first thought the new substance might be a mixture of manganiferous yttria and glucina, two earths, rather than a new metal. This quite annoyed Berzelius who ensured that they had been very careful about comparing all of its properties to known earths and oxides (see Trofast 1996, 23–24). Another chemist who questioned the metallic nature of cerium was Klaproth. When Adolph Ferdinand Gehlen (1775-1815) informed Berzelius and Hisinger that their paper would be published in his *Journal der Chemie*, he also warned them that Klaproth already had a paper in print about a discovery of a new earth in Bastnäs tungsten. This new earth, called 'ochroite', was characterised by the same ochre colour as cerium oxide. Klaproth thought ochroite was an earth because of the colour it took in a flame, and because of its density. Hisinger and Berzelius on the other hand argued that they were dealing with a metallic oxide because of the yellow colour of the substance and the possibility to pass through different oxidation states. For the same reasons, Vauquelin and Gehlen eventually sided with Berzelius and Hisinger. Vauquelin also replicated the analysis of the substance in late 1804 and confirmed Berzelius' and Hisinger's results.

In the case of tantalum, Klaproth made a similar point when he argued that tantalum oxide was in fact an earth and should be renamed tantalea. In an addition to the German translation of Wollaston's 1809 work on tantalum and columbium, the editor of the *Annalen der Physik* Ludwig Wilhelm Gilbert (1769-1824) evaluated this claim (Gilbert 1811). From these papers, it becomes clear that there were two criteria for the distinction between metallic oxides and earths during the first decade of the nineteenth

century: metallic oxides exhibited colour changes when heated and could pass through multiple stages of reduction and oxidation. The distinction between earths and oxides remained relevant until around 1810, when it became a consensus that all simple earths should be reclassified as (difficulty reducible) metallic oxides.[169]

Thus the identification of a substance as a metallic oxide was not an easy judgement and it was largely a question of personal skill and careful experimentation. Experience in analytical chemistry was necessary in order to recognize substances that contained metals on the basis of subtleties in colour shades. However, even very experienced analysts did not always agree on how to classify a new substance. This explains why even as the methods of analytical chemistry became increasingly standardized, individual skill continued to play an essential role in this practice.

## Characterizing metallic oxides with the help of chemical tests

The identification of a substance as a metallic oxide alone was of course not enough to claim the discovery of a new metal: one also had to show that this metallic oxide was different from the ones that were already known, because only in that case would it contain a new metal. In order to show this, chemists relied on a number of characteristic properties to show that their substance could be clearly identified and distinguished from all others. These characteristic properties were established on the basis of systematic series of chemical tests, consisting mostly of the same procedures as standard wet and dry analysis but with the goal of testing the reaction of the new substance to each procedure.

When a new substance was isolated, the first step consisted in an external description of the texture and colour of the precipitate, its taste and reaction to indicators such as the litmus test or other measures of acidity. Then, chemists would try out various dry analytical procedures such as heating, annealing or calcination and study the substance under the blowpipe. They would not only record the reaction of the substance itself but also add various fluxes (carbonates, phosphates and alkalis) to see if any fusion occurred and whether any coloured or soluble globules were produced. The subsequent wet analysis required a solution of the substance, which therefore had to be tested for solubility in

[169] This reclassification happened as a consequence of Davy's work on the decomposition of the earths, see part I of this thesis.

(warm) water and different acid or alkaline solutions. Once it was dissolved, they added different types of reagents (acids, alkalis, salts and specific reagents) one by one in order to see if any (coloured) precipitates could be formed. As opposed to a quantitative wet analysis, the goal was therefore not to separate out these precipitates but rather to describe them. Each of the outcomes of these different tests was recorded and together they formed a unique set of characteristic properties.

Hatchett's characterization of columbium oxide might provide a helpful illustration. First he produced a precipitate from his mineral by separating it from the other metallic compounds (in this case, only iron oxide). The precipitate was white, flocculent, and flavourless. It coloured litmus red, which meant it had to be a metallic acid – according to the commonly admitted ideas at the time, this meant it contained oxygen. He then performed a dry and wet analysis which convinced him that it was a metallic oxide:

> "This substance is proved to be of a metallic nature, by the coloured precipitates which it forms with prussiate of potash, and with tincture of galls; by the effects which zinc produces, when immersed in the acid solutions; and by the colour which it communicates to phosphate of ammonia, or rather to concrete phosphoric acid, when melted with it" (Hatchett 1802, 177).

Nevertheless, there was a specific series of characteristic reactions that made it possible to distinguish this new substance from other metallic compounds. He provided eight characteristic properties of the oxide (*ibid*., 177-178):

1. It was not affected by digestion with nitric acid;
2. it was soluble in sulphuric and muriatic acid solution, and could be precipitated from them in the form of a white precipitate by the addition of zinc or alkalis;
3. it produced a "copious and beautiful olive-green precipitate" with prussiate of potash;
4. it produced a deep yellow or orange precipitate with tincture of galls;
5. it did not combine with ammonia to form a salt, unlike most metallic acids;
6. it did not combine with sulphur;
7. under the action of the blowpipe, the only flux it coloured was phosphoric acid;
8. when dissolved with potash, it could be precipitated by adding a solution of other potash or ammonia salts.

It is rather remarkable that Hatchett here did not distinguish between the properties of the white precipitate and those of columbium itself. Ekeberg followed a very similar procedure for the identification of tantalum. So did Berzelius and Hisinger: they provided a precise description of the salts that the oxide formed with fourteen different acids, so as to distinguish it from all known metallic oxides and characterize the new metal.[170] During the early nineteenth century, these studies were all carried out with a compound precipitate rather than with a metal, even though the results were recorded as properties of the metal. There was no clear distinction between the characterization of the metallic oxide and that of the metal itself. In the next section, I will rely on debates and retractions to show that this list of characteristic reactions was really the main point in establishing the nature of a new substance.

## The role of characteristic reactions in debates on elementary nature

Hatchett concluded his announcement of columbium as follows:

> "I am much inclined to believe, that the time is perhaps not very distant, when some of the newly discovered metals, and other substances, which are now considered as simple, primitive and distinct bodies, will be found to be compounds. Yet I only entertain and state this opinion as a probability; for, until an advanced state of chemical knowledge shall enable us to (…) decompose, these bodies, each must be classed and denominated as a substance *sui generis*. Considering, therefore, that the metal which has been examined is so very different from those hitherto discovered, it appeared proper that it should be distinguished by a peculiar name; and (…) I have been induced to give it the name of Columbium" (Hatchett 1802, 179–80).

In this paragraph, Hatchett almost seemed to apologise for adding a new metal to the list of known simple substances. His wording is representative of the metaphysical discomfort that many chemists of the early nineteenth century felt regarding the rapidly growing

[170] The acids used were nitric, phosphoric, arsenic, molybdic, oxalic, tartaric, carbonic, benzoic, citric, acetic, succinic, gallic, muriatic (hydrogen chloride) and prussic (hydrogen cyanide) acids. See Hisinger and Berzelius (1804).

number of chemical elements.[171] This caused chemists such as Hatchett to apologise for adding to the ever-growing number of simple substances. It could also motivate others to question the nature of specific chemical elements or to refute new discovery claims. Unfortunately for Hatchett, this is exactly what happened in the case of columbium, which was eventually retracted from lists of chemical elements.

In this final section of the chapter I will compare the retraction of columbium with the controversies on erythronium and palladium and argue that characteristic reactions were the most important factor in establishing elementary nature. In the controversies cited above, Klaproth did not question that a new discovery had taken place, but rather argued against the proposed identification of the new substances as metallic oxides. This section will show that the recognition of having discovered a new chemical element was in danger only when the new substance could not be clearly distinguished from those that were already known.

## Wollaston's characterization of palladium and columbium

In 1809, Wollaston performed a comparative analysis of columbium and tantalum minerals in order to find out whether they really contained two distinct metals.[172] Neither Ekeberg nor Hatchett had provided a way to distinguish between their two metals and he therefore suspected that there might not be any differences. After carrying out the analysis, Wollaston concluded that there were "so many points of agreement in the modes by which each of these bodies can or cannot be dissolved or precipitated, as to prove very satisfactorily that these American and Swedish specimens in fact contain the same metal" (Wollaston 1809, 247). According to Wollaston, the most important similarity lay in the solubility of the oxides: while they were both insoluble in the three mineral acids (muriatic, nitric and sulphuric acid), they could be dissolved in organic acids (oxalic, tartaric and citric acid) and after evaporation of this solution, the residue could only be dissolved again

[171] See for example the conclusion of Johan Gadolin's publication announcing the discovery of yttria, where he also reflected on the likelihood that all simple substances might turn out to be compounds (Gadolin 1794; see also Evans 1996, 1–12).

[172] Wollaston was not the first to question the existence of tantalum. Johan Gottlieb Gahn (1745-1818) had already questioned the existence of tantalum in 1807, suggesting that it might be identical to tin (see Berzelius 1807).

after a second fusion with potash. Although he did notice a remarkable difference in density between the two minerals, he did not consider this enough of an issue so as to disprove his comparative results, because it could be explained either by cavities in the mineral or differences in degree of oxidation.

In light of the criteria for the discovery of a new metal that I discussed in the previous section, it is not surprising that Wollaston's comparison of tantalum and columbium did not involve a study of the metals themselves. His argument that they were identical was made on the basis of the impossibility to distinguish between their compounds, rather than the impossibility of isolating metallic columbium. This argumentation is consistent with the reception of Hatchett's and Wollaston's results by other chemists. For example, the Scottish chemist Thomas Thomson listed columbium as one of the metallic elements in his *System of Chemistry* (Thomson 1810, 71), explaining that the properties of the metal itself were unknown because all efforts to isolate it had been unsuccessful. Berzelius (1827b, 2:368-369) later suggested that Hatchett may have been misled by the presence of tungsten impurities. Neither of them cited the lack of isolation of the metal as a problem for its elementary nature. It seems Ekeberg and Hatchett were unable to react to Wollaston's claim and show how their elements were distinct: Ekeberg died in 1813 and Hatchett gave up chemistry after inheriting his father's coach-making business (Weeks 1956, 387).[173] Wollaston's results were widely accepted and chemists concluded that the minerals tantalite and columbite contained only one and the same element, for which the name 'tantalum' was generally chosen.[174]

Thus, the elementary nature of these metals was not determined via their isolation in the form of simple substances. Moreover, even if a metal could be isolated, this did not necessarily suffice as proof of its elementary nature, as is shown by the well-known

[173] Ekeberg's last publication dated from 1807. Hatchett published three papers between 1809 and 1821, none of which were reactions to Wollaston's paper (Royal Society 1868 vol.2, 474 and vol. 3, 214)

[174] This choice depended somewhat on geographic location. No article in the *Comptes Rendus de l'Académie des Sciences* mentioned columbium between 1835 and 1880, whereas ten were published on tantalum and its compounds, according to the *Table Générale des Comptes Rendus de l'Académie des Sciences* (Académie des Sciences 1853). However, 'columbium' was still mostly used in England, according to Connell (1854).

controversy on the nature of palladium between 1803 and 1805 (Usselman 1978). This debate also involved Wollaston and opposed him to the Irish chemist Richard Chenevix (1774-1830), another well-known analyst and Fellow of the Royal Society. Wollaston anonymously sold metallic palladium in London and Chenevix questioned that this was a chemical element. Chenevix argued that although palladium appeared to be metallic, it might be an alloy from which it was impossible to separate the constituent metals. Wollaston's defence of palladium therefore mainly relied on the fact that it formed a series of distinct metallic compounds that set it apart from all other metals, rather than on the impossibility of decomposing palladium itself (Wollaston 1805). Even in this debate, the most important argument in favour of the existence of the new metal was the series of characteristic reactions by which the metallic oxide could be distinguished from all others.

## Erythronium and vanadium

As a further illustration of the importance of characteristic reactions in proving elementary nature in the early nineteenth century, I will finish this chapter by discussing the case of erythronium, a metal that was questioned by multiple European chemists and eventually retracted because it could not be clearly distinguished from chromium.[175] Erythronium was named by Andrés Manuel del Rio (1764-1849), a Spanish chemist and professor of oryctognosy (mineralogy, geognosy and palaeontology) at the College of Mines in Mexico City. He identified it as a new metal in a sample of brown lead or from a mine near Zimapán in 1801 (see Caswell 2003). The metal formed a number of very coloured salts and oxides, some of which turned red when heated and he therefore named it 'erythronium' after the Greek word for red. Although a short notice was published in a Spanish journal in 1802, Del Rio was unable to publish a full paper on the discovery because the manuscript which he addressed to the French Academy of Sciences was lost in a shipwreck on its way to Paris. He described his experiments in a footnote of a translation of a mineralogical textbook (Karsten 1804, 61–62).

From 1803 to 1804, the German naturalist (and fellow student of the Freiberg mining academy) Alexander von Humboldt (1769-1859) spent a year in Mexico during his South American expedition. Del Rio showed Humboldt his samples of erythronium, but

[175] Vanadium and erythronium are discussed by Weeks (1956, 352–61 and 391–403).

Humboldt was sceptical of the discovery because of the close resemblance between the new element and chromium. Louis-Nicolas Vauquelin had announced the discovery of chromium in France in 1797 but his publication did not reach Mexico City until the end of 1803. When Humboldt told his friend that the red coloration of erythronium compounds was not unique, Del Rio lost confidence in his new metal and concluded his ore must have been a lead chromate. Nevertheless, he gave Humboldt a paper detailing his findings as well as a sample of the brown lead ore, which Humboldt passed on to Victor Collet-Descotils (1753-1815) for analysis when he arrived back in Paris. Descotils (1805) published an analysis of the ore and concluded that it contained "nothing of a new metal". He did notice some unusual colours in the sample, but he dismissed this as an irregularity of the reagents. By this time, Del Rio had already publicly retracted his discovery, and when he learned of Descotils' paper he was quite annoyed by the idea that his friend trusted the results of French chemists over his. As he recalled in 1822:

> "Mr. Des-Cotils has published this result in Paris in 1805, I however did so a year earlier in Mexico (…). Then again, who reads Spanish mineralogy as a pastime? Mr. Humboldt (…) doesn't seem to have deemed the *Annales de Ciencias Naturales* (…) worthy of reading even once; for otherwise he would have found that in number 19 of the year 1804 I explicitly stated (…) that brown lead ore is (…) a hypo-chromate of lead. The matter was then already concluded, yet Mr. Humboldt wanted this discovery to be a foreign monopoly by all means, with the exclusion of the poor Spanish."[176]

Del Rio's suspicion that his conclusions were ignored because they were published in Spanish was likely correct: as the editor Gilbert added in a note to this paper, the *Annales de Ciencias Naturales* were unavailable in Paris.

[176] "Hr. Des-Costils [sic] hat sie öffentlich zu Paris im Jahre 1805, ich aber habe sie zu Mexico schon ein Jahr zuvor bekannt gemacht, (…). Allein wer liest zum Zeitvertreibe Spanische Mineralogien? Hr. von Humboldt (…) scheint nicht einmal die Annales de Ciencias naturales (...) zu lesen gewürdigt zu haben; denn sonst würde er in der Nummer 19 vom Jahr 1804 gefunden haben, dass ich dort ausdrücklich, obschon mit der nöthigen Bescheidenheit, sagte: "ich glaubte, das Braun-Bleierz sey (…) ein sous-chromate de plomb". Die Sache war also damals schon ganz ausgemacht, und doch wollte Hr. von Humboldt durchaus, dass diese Entdeckungen ein fremdes Monopol mit Ausschluss des armen Spanier seyen"(Del Rio 1822, 8–9).

Twenty-five years later, Berzelius (1830, 332) announced the discovery of "a substance with properties that differ from those of all the bodies we know so far" in Sweden. His colleague Nils Sefström (1787-1845), director of the school of mining in Fahlun, had investigated a type of iron that was extremely malleable and detected a new metal which he named 'vanadium' after the Scandinavian deity Vanadis (also known as Freya). In his article, Sefström (1831b) warned that vanadium could easily be confused with chromium; yet, through a series of comparative tests on the oxides of these substances, he was able to show the ways in which his new element was unique. Vanadium and chromium are indeed very similar, and besides some differences in shade and solubility, they could only be separated by the fact that chromium compounds can be heated to a red vapour whereas vanadium compounds lose their red colour when subjected to too much heat.

It immediately became clear that vanadium was identical to Del Rio's erythronium. In Germany, Friedrich Wöhler (1800-1882) had analysed Humboldt's sample of brown lead ore and showed that it contained vanadium. When Del Rio heard about the rediscovery of his element, he expressed his frustration. He felt the situation could have been avoided, if only Humboldt had placed more trust in him:

> "When [Humboldt] left Mexico, I (…) gave him a copy in French of my experiments so he could publish them: if he had judged them worthy of public light, they would have excited the curiosity of the chemists, and *the discovery of the new metal would not have been delayed for thirty years* (…)" (Del Rio 1832, 484–85).[177]

At the time of publication of Sefström's paper, the editors of the influential journals *Annales de Chimie* and the *Annalen der Physik* (Poggendorff, Gay-Lussac and Arago) had already been informed that vanadium was identical to Del Rio's erythronium. For the editors, this did not diminish Sefström's credit in any way, as they stated in a supplement to the publication:

[177] "A su salida de México le di sin embargo una copia en francés de mis experimentos para que los publicase: si los hubiese juzgado dignos de la luz pública, habrian excitado la curiosidad de los químicos, y *no hubiera tardado treinta años en descubrirse el metal nuevo*, que es la objeción que me hacen ahora sin culpa ninguna mia." Emphasis original.

> "Mr. Sefström has (…) rendered an even bigger service to science, by discovering his metal under far more difficult conditions in a mineral product of European origin, and by being the first to prove its existence beyond any doubt."[178]

Del Rio rightly suspected his disadvantage as a Spanish chemist living in Mexico. Alhough he had a similar academic background to many of his European colleagues (he was trained by outstanding European chemists and mineralogists, and spoke German, French and English besides his native Spanish), Del Rio had trouble inserting himself into the European scientific circles. In France and Germany, few people read publications in Spanish. Moreover, he depended on a slow and fragile transatlantic communication meaning works could take years to arrive – if they were not lost at sea.

Besides providing an interesting illustration of the ways in which scientific knowledge circulated in the early nineteenth century, this story also illustrates the importance of characteristic reactions. Once again, the identities of these metals were not established on the basis of their properties as simple substances, but rather by the behaviour of their compounds. Only when a distinct series of characteristic reactions could be established was the identity of the new metal accepted by the chemical community.

## Conclusion

In the first section of this chapter, I described how chemists during the first decade of the nineteenth century reacted to finding an unrecognized constituent in a mineral sample. They first tested it to see if it had any of the properties of known substances, and if it did not they systematically tested its reaction to as many analytical procedures as possible. If they found the substance behaved like a metallic oxide they would attempt a reduction in order to isolate the metal. However, cases like that of columbium and cerium show that it was possible to claim discovery of a new metal even if the metal itself could not be produced. The identification of a new metallic oxide sufficed in order to infer the existence of a previously unknown metal. Metallic oxides could be recognized on the basis of a few properties, most notably their colours (and the colours of their salts) and the possibility to modify their degree of oxidation. The most important properties, however, were the series

[178] The same statement is made in German and French, see Sefström (1831b; 1831a).

of characteristic reactions of the oxide to a number of chemical tests that enabled its identification. In the second section of this chapter, I relied on the debates on the nature of tantalum, columbium, palladium and erythronium to argue that these characteristic reactions were the most important factor in establishing the nature of new metal. From their first identification, metals were therefore characterized on the basis of the compounds they formed and there was no clear distinction between the properties of the metals themselves and those of their compounds.

This method presupposed an implicit analogical inference very similar to the ones I analysed in the first part of this thesis. In these cases, metallic oxides were assumed to be compounds of metals and oxides before they were actually decomposed, and it was not necessary for the metal to exist in the form of a simple body. In short, if a substance behaved like a metallic oxide, it likely contained a metal. Yet, although they often did refer to chemical analogies between newly discovered metals and other chemical elements, the chemists in these cases did not make their analogical inferences explicit. They took for granted the idea that they could recognize the 'metallic nature' of a substance from the types of compounds it formed. This lack of reflection on the question of whether they were making the correct inferences, and whether they had enough evidence to do so, suggests that these inferences were not subject to any controversy. This can be explained by the longstanding history of the study of metals. Whereas the identification of aluminium and chlorine, for example, required the use of new techniques and the recognition of new families of elements, metals had been successfully studied since antiquity. There was no need to specify the inferences chemists were making because they could be fairly confident that they knew how to identify metallic substances.

Indeed, the methods used by Hatchett, Ekeberg, Wollaston and their colleagues show a direct continuity with the actors I discussed in the previous chapter. In her study of Klaproth's discovery of uranium in 1789, Klein (2014) has described very similar methods. Klaproth's analysis consisted on the same steps and he likewise provided a list of characteristic reactions by which uranium and its calxes could be identified. This may seem fairly unremarkable: only two decades separate Klaproth's publication from that of Wollaston, and Klaproth himself was still active in the early nineteenth century. However, during those two decades, important theoretical changes had taken place in chemistry.

In 1789, Klaproth still viewed metals as compounds compounds of phlogiston. Yet, despite viewing calxes as the simpler substances, Klaproth emphasized the discovery of a new metal. Klein has therefore argued that the robust class of metals was independent of theoretical considerations about composition:

> "In the context of mineralogical-chemical classification it made no difference whether you accepted the theory of phlogiston or Lavoisier's theory. The mineralogists defined metals as natural kinds and simple mineral species and so did the eighteenth-century 'chemical mineralogists'. Their theoretical differences (…) had no impact on their mineralogical classification" (Klein 2014, 40).

The examples I discussed in this chapter confirm this conclusion, and show that the adoption of the Lavoisian definition changed very little in the practice of chemical analysis. New metals were identified in the same way, regardless of the views of their inner composition.[179]

When it came to the identity of tantalum and columbium, Wollaston's results were commonly accepted and it became a consensus that tantalite and columbite minerals contained only one kind of tantalum. This remained the case until 1844, when the Prussian chemist Heinrich Rose (1795-1864) announced that he had identified niobium in columbite minerals. His findings motivated various other chemists to analyse minerals as well, and a number of other 'tantalum metals' were argued to exist in columbite and tantalite samples. In the next chapter, I will discuss the debates on the nature of these metals and their resolution during the middle of the nineteenth century.

[179] One thing that does set apart the publications I analysed here from Klaproth's work is that Klaproth insisted on the resynthesis of pitchblende as proof that he had not produced artefacts with his analytical methods. For example, while Hatchett also mentioned that he was able to reproduce the original ore by mixing his white precipitate with iron oxide, he did not insist on this result in order to argue in favour of his discovery. The synthesis did show that he had correctly identified the white precipitate as a constituent of the mineral, but it could not tell him anything about the nature of the precipitate or the fact that it contained a new metal.

# CHAPTER 6 - The 'Tantalum Metals': Debates on Niobium, Ilmenium, Pelopium and Dianium (1844-1866)

Wollaston's conclusion that the different tantalite minerals contained only one metal (tantalum) remained the consensus until 1844, when the Prussian chemist Heinrich Rose (1795-1864) announced the discovery of "the oxide of a metal that differentiates itself from those previously known" (Rose 1844, 335).[180] Rose named his new metal 'niobium' and it was added to the list of known simple substances without giving rise to any debate. Following this announcement, the Saxon chemist and mineral water salesman Hans Rudolph Hermann (1805-1879) analysed a number of tantalum minerals from Siberia and confirmed the presence of niobium in them. In addition to niobium, Rose, Hermann and others also announced the discoveries of pelopium, ilmenium and dianium as additional 'tantalum metals', which were all eventually rejected as chemical elements. Ilmenium and dianium especially were the topic of various publications arguing in favour and against their existence as metals. During the middle of the 1860s, these debates were finally resolved, largely because of the contributions of Jean-Charles Galissard de Marignac (1817-1894) and Christian Wilhelm Blomstrand (1826-1897). They determined the composition of various niobium and tantalum compounds and were able to show that neither ilmenium nor dianium were elements.

In this chapter, I will analyse the publications on niobium and the other tantalum metals that were published between 1844 and 1866 in order to determine which arguments were brought forward in favour and against elementary nature. The controversies took place via publications in scientific journals, which were generally translated and widely circulated across Europe. During this period, chemistry as a whole underwent important theoretical and institutional changes. On the one hand, a new understanding of the

[180] "(…) das Oxyd eines Metalls, das sich von den bisher bekannten unterscheidet". Rose named niobium after Niobé, the daughter of Tantalus in Greek mythology. This relation between their names gives a new sense to the idea that they were a 'family' of elements. For biographical information on Rose, see Partington (1964, 4:185–90) and Rammelsberg (1866).

constitution of molecules was developing in the growing field of organic chemistry; on the other, analytical training acquired an increasingly important place in university education, and teaching laboratories emerged throughout the German-speaking lands from the 1820s onwards. Despite these changes, the publications on the tantalum metals point towards a continuity in the identification of metals. Until the end of this period, chemists continued to rely on the same types of analytical methods as their predecessors, which enabled the identification of metals on the basis of the behaviour of their compounds. Only during the middle of the 1860s did the recent theoretical reforms change the way in which chemists characterized chemical elements. This chapter is divided in two parts. First I will focus on the work of Heinrich Rose and the various debates in which he took part, from his announcement of niobium until his last publication on the topic. Then I will study the contributions of Marignac and Blomstrand in order to show how they were able to resolve the controversy.

# Heinrich Rose and the debates on niobium, ilmenium and dianium (1844-1863)

In 1844, Heinrich Rose, professor at the University of Berlin, announced his discovery of niobium in tantalite minerals from Bodenmais (Bavaria). However, this wasn't the only proposed addition to the tantalum family and Rose was involved in multiple controversies surrounding similar discovery claims until the end of his life. Using the discovery of niobium and the debates on the existence of ilmenium and dianium, this section will identify the criteria for the discovery of an element using mineral analysis in the middle of the nineteenth century.

## A 'second tantalum': the distinction between tantalum and niobium

One of the possible reasons that Rose's niobium was accepted immediately relates to the existing suspicion that there might be multiple tantalum metals. Since Wollaston's identification of columbium and tantalum, various analyses of tantalite minerals had shown a puzzling difference in crystal structure and in specific weight between samples from different geographical origins (see Rose 1844 for a summary). Berzelius and his previous

student Friedrich Wöhler (1800-1882) came especially close to identifying a second tantalum metal, as their correspondence shows. Wöhler isolated a substance "X" from the mineral pyrochlore and investigated it in order to know whether it was a new metal. He sent a sample to Berzelius who tried to investigate it as well:

> "Enclosed I return your X, whom I asked as many questions as I could, but from whom I received only evasive answers. Are you titanium? I asked. It replied: Wöhler has told you that I am not. I realized the same. – Are you zirconia? No, it answered; [when heated under the blowpipe] I fuse with soda to form an enamel-white glass that does not penetrate into the charcoal, which zirconia does not do. Are you tin? I contain tin, but only very little. Are you tantalum? I am related to it, it answered, but I am gradually, though slowly, dissolved in hydrothyonkali [potassium sulphide] and I come out of it as a yellow-brown precipitate. Well, what kind of satanic thing are you then? I asked. Then it seemed to reply to me: I have not yet been given a name. However, I am not quite sure whether I heard it properly, for it was on my right side, and I hear very badly in my right ear. Since your hearing is probably much better than mine, I send the rascal back to you for a new interrogation."[181]

Wöhler and Berzelius' exchange on this topic is interesting because it provides an insight into the process by which new constituents were identified: through careful and repeated comparison of all the characteristic reactions of the new substance to those of similar, known substances. A few months later, Wöhler concluded that X was simply tantalic acid, because it had the same properties as tantalic acid from Bodenmais tantalite. He did notice

[181] Berzelius to Wöhler, 18 June 1839 (Berzelius and Wöhler 1901, 120). "Ich sende Dir anbei Dein X zurück, das ich so viel ich konnte gefragt, von dem ich aber nur evasive Antworten erhalten habe. Bist Du Titan? fragte ich. Es antwortete: Wöhler hat Dir gesagt, dass ich es nicht bin. Dasselbe fand ich auch. – Bist Du Zirkon? Nein, antwortete es; ich werde ja in Soda zu einen emailleweissen, in die Kohle nicht einkriechenden Glas gelöst, was die Zirkonerde nicht thut. Bist Du Zinn? Ich enthalte Zinn, aber nur sehr wenig. Bist Du Tantalum? Ich bin damit verwandt, antwortete es, aber ich werde in Hydrothyonkali allmählich gelöst, obgleich es langsam geht, und werde gelbbraun daraus gefällt. Nun, was bist Du denn für ein Satansding? fragte ich. Da schien es mir zu antworten: Einen Namen hat man mir noch nicht gegeben. Indessen bin ich nicht recht sicher, ob ich recht gehört habe, denn es war auf meiner rechten Seite, und ich höre sehr slecht auf dem rechten Ohr, und da Dein Gehör vermutlich viel besser als meines ist, so schicke ich Dir den Schlingel wieder zurück, um ein neues Verhör mit ihm anzustellen."

a difference with tantalum from Swedish origin; retrospectively this can be explained by the fact that pyrochlore contains only niobium, Swedish tantalite only tantalum, and Bodenmais tantalite a mix of both.[182]

Rose was aware of these and other differences between tantalum from different sources and provided a careful comparative analysis between different tantalite minerals. In his paper, Rose provided a number of comparative tests by which niobic acid could be distinguished from tantalic acid.[183] Most notably, the presence of niobium was indicated by its characteristic blue and orange colorations: after fusion with soda in the blowpipe and addition of acids to the solution of the resulting globule, the orange precipitate could be obtained by adding tincture of galls, and the blue coloration by plunging a piece of metallic zinc into the solution. This blue coloration had initially been identified by Wöhler (1839) as a property of tantalic acid, but Rose now used it as a way to distinguish between the two metals because tantalum did not colour blue. Another way to detect niobium was by fusing its oxide with phosphate salts using the blowpipe: the result was a blue-purple globule. Separately, these reactions could be indicative of different metals, but combined they showed the presence of niobium. Rose also claimed he was able to produce metallic niobium, using a method developed by Berzelius (1825b) for the reduction of tantalum.[184]

Following Rose's publication, Hermann (1846) detected niobium in his Siberian samples of the minerals aeschynite, pyrochlore and columbite. Besides confirming the existence of niobium, he provided additional information on how to identify it: he listed seven characteristic reactions by which niobium could be identified, as well as five properties by which to distinguish it from titanium, to which it was very similar. Then, having re-identified some of the supposed tantalum minerals as niobium minerals, Hermann provided a new analysis of the properties of 'true' tantalum in order to distinguish more clearly between the two metals and their compounds. He proposed a composition for

[182] For the Bodenmais minerals, the names 'tantalite' and 'columbite' were both used. The minerals are almost indistinguishable.

[183] 'Tantalic acid' ("Tantalsäure") and 'niobic acid' ("Niobsäure") were higher oxides of the two metals (containing more oxygen than oxides). Rose suspected both these acids to be dioxides, but they were later identified as $Ta_2O_5$ and $Nb_2O_5$.

[184] Blomstrand later showed that Rose's method actually produced niobium monoxide, see below.

tantalum's most important compounds and a list of ten properties by which it could be distinguished from other bodies. Hermann thus confirmed Rose's results, and it seems that niobium was generally accepted as a new simple substance without giving rise to any debate.

| | **Tantalic acid** | **Niobic acid** | **Titanic acid** |
|---|---|---|---|
| Blowpipe | Colourless globule after fusion with phosphate salts and borax | Blue-purple globule after fusion with phosphate salts | Dark yellow globule after fusion with potassium sulphate |
| Solubility | Soluble after fusion with alkalis | Soluble after fusion with alkalis | Soluble (in warm water) after fusion with potassium phosphate, insoluble after fusion with alkalis |
| Tincture of galls in solution of alkaline salt, after addition of acid | Light yellow precipitate | Dark orange precipitate | (alkaline salt insoluble) |
| Metallic zinc in solution of alkaline salt, after addition of acid | No change in colour, gradual precipitation of white powder (hydrated tantalic acid) | Solution turns blue and then slowly brown | (alkaline salt insoluble) When zinc is added to a solution of titanic acid in hydrochloric acid: solution turns amethyst-colour then gradually dark purple, almost black |

*Table 4 - A selection of properties by which to distinguish between niobic, tantalic and titanic acid. Summarized from Rose (1844) and Hermann (1846).*

Thus, the identification of niobium as distinct from tantalum also required a new view of tantalum itself. Hermann and Rose not only had to show by which properties niobium could be identified, but also what the new characteristic properties of tantalum were (see Table 4 for a selection of their characteristic properties). As a result, their view of tantalum and how it could be characterized was not the same as that of Wöhler a few years earlier – and as chemists continued to study these metals, their characterization would continue to evolve. A very similar development happened in the study of the rare earths during the same period. During the late 1830s and early 1840s, Berzelius' successor at the Karolinska Institute Carl Gustaf Mosander (1797-1858) discovered lanthanum, didymium, erbium and terbium in samples of cerium. This required not only a method to distinguish all of these metals from each other but also a re-characterization of cerium itself, because what had previously been seen as cerium oxide now became a mixture of several metallic oxides (Tansjö 1996).

With each discovery, additional chemical tests were also added to the chemists' toolbox as new ways to detect the presence of a specific element. Overall, however, analytical methods remained largely the same. Rose's textbook of analytical chemistry explained how to detect the presence of specific metals by the characteristic reactions of their compounds (see Figure 7), and the main analytical methods he described were the blowpipe, gravimetry and chemical reagents (Rose 1829).[185] Like in the beginning of the century, the main aim of chemical analysis was identification rather than the isolation of simple bodies. Even gravimetric (quantitative) methods relied on the indirect determination of composition from the isolation of compounds because these were easier to precipitate. Rose's textbook, for example, contained conversion tables in which one could read the amount of (simple) substance sought based on the amount of precipitate that had been weighed.[186]

Likewise, even though niobium is generally named as Rose's most important discovery, he did not develop any drastically new methods in order to identify it.[187] Rather,

[185] German textbooks did not include volumetry until the middle of the 1850s (Homburg 1999, 20–21).

[186] Fresenius' textbook contained similar tables. On gravimetric methods, see Szabadváry (1966, 174–81).

[187] One could argue he was not the first since this episode could be seen as a rediscovery of columbium. Even at the time, some (unsuccessfully) argued in favour of renaming the metal 'columbium' (Connell 1854).

he relied on various chemical tests which had been added as additional steps to the classical wet and dry methods during the previous decades. Rose followed the analytical procedure that Berzelius (1818) had developed in his analysis of Finnish tantalite. Rose's textbook likewise described the detection of tantalum following methods developed by Berzelius (Rose 1829, 456). Berzelius' method in turn consisted of the same procedures that had been used in the first decades of the century, except that they were applied to a study of metallic chlorides in addition to the oxides. This was a significant addition to the analytical tests that were generally carried out, and the characterization of new substances included metallic chlorides from the 1820s. Sometimes the study of chlorides could take on quite a central role, as in the case of Rose's pelopium: he claimed the discovery of this additional tantalum metal on the basis of the production of a distinct metallic acid from a while chloride which, contrary to tantalum and niobium chloride, turned yellow when heated (Rose 1846; 1844).[188]

However, it is hard to know whether Hatchett's columbium was really identical to Rose's niobium. The metals did share some characteristic reactions, such as the formation of a blue-purple globule with phosphates and an orange precipitate with tincture of galls. Both chemists were almost certainly working with impure samples.

[188] Rose named pelopium after Pelops, the son of Tantalus and brother of Niobe. Again, this indicates that he quite literally saw these elements as a family.

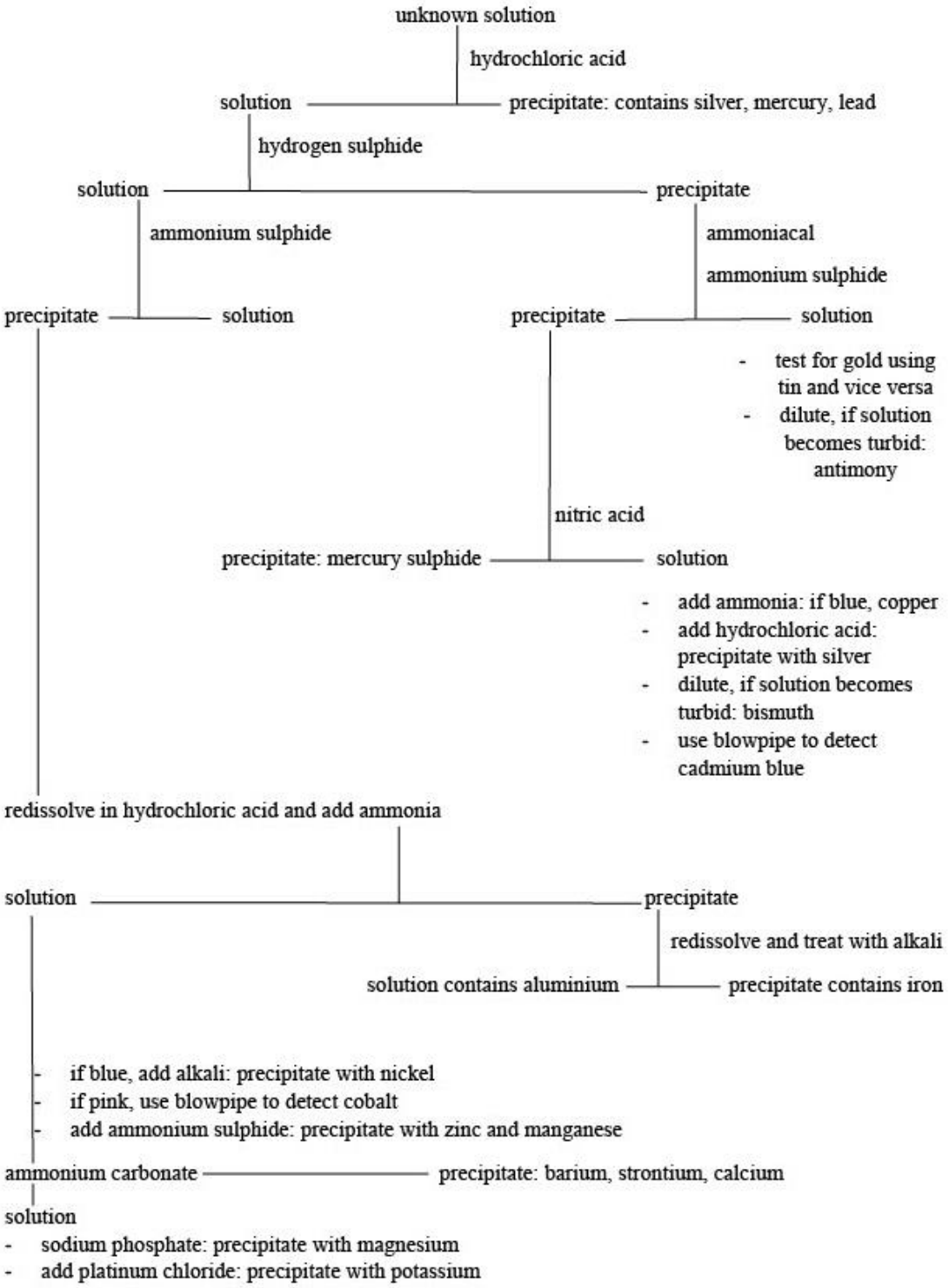



*FIGURE 7 - Summary of Rose's analytical scheme for detecting chemical elements in an unknown solution (based on a summary by Szabadváry 1966, 166). Each addition of a reagent produces a precipitate, which is filtered out and separated from the filtrate.*

## Ilmenium, dianium and the continued importance of characteristic reactions

Niobium was accepted without any debate, but the controversies surrounding other so-called tantalum metals show that the arguments in such debates remained fairly stable as well. Besides confirming the presence of niobium in Siberian samples, Hermann also claimed to have isolated a metallic oxide which reacted differently from tantalic and niobic acid, which he concluded was the oxide of a new metal called 'ilmenium'.[189] In Rose's debate with Hermann on the existence of ilmenium, the main issue was the correct identification of its properties, rather than Hermann's claim that he had produced metallic ilmenium. According to Hermann (1846; 1847b), ilmenium could be characterized by the production of brown precipitates upon the addition of tincture of galls and a strong acid to a solution of its alkaline salts, as well as its low atomic weight compared to that of niobium and tantalum. Rose (1847) was unable to replicate his results and argued that Hermann's observations were probably due to his failure to eliminate tungsten impurities that modified the colour of the niobium compounds. He therefore concluded that ilmenic acid was a mixture of niobic acid and tungstic acid and it did not contain a new metal.

The debate between these two men continued as they went back and forth replicating each other's analyses. Hermann defended his discovery on the basis of the differences between niobic and ilmenic acids: their reaction to the blowpipe (the absence of blue colour for ilmenic acid), the blue coloration of niobic acid in acidic solution in presence of zinc, a difference in solubility in their hydrates in acids, a difference in solubility of their double sulphate salts and different colorations of their precipitates with tincture of galls (Hermann 1847a). He argued that these differences could not be explained by the presence of tungsten impurities, because the substance exhibited none of the characteristic properties of tungsten. Rose (1848) again replied by replicating an analysis of ilmenite minerals and arguing that he could not detect any ilmenium. Hermann (1855) attempted to continue the debate but Rose considered the discussion on ilmenium closed.

The correct identification of characteristic reactions was also of key importance in the debate surrounding dianium, the discovery of which was announced in 1860 by

[189] Ilmenium was named after the Ilmen mountains where its minerals were found.

Franz von Kobell (1802-1882), professor of mineralogy at the University of Munich (Kobell 1860). Kobell isolated a substance which produced a blue coloration in a solution with hydrochloric acid and tin. He was unable to obtain the same coloration using niobium compounds and therefore concluded that he was dealing with a previously unknown metallic acid. Rose (1861) repeated Kobell's analyses and objected to his discovery claim because all niobium minerals he investigated produced a blue coloration, regardless of their geographical origin. The French mineralogist Alexis Damour (1808-1902) and chemist Henri Sainte-Claire Deville (1818-1881) confirmed that the characteristic blue coloration of dianium could be found in all niobium minerals.[190] There were two options: either all these minerals contained dianium, or this was just another property of niobium. Deville and Damour concluded that this property alone was insufficient to claim the discovery of a new metal, and that dianic acid could not be considered a distinct chemical species:

> "Mr. Kobell will therefore (…) have to find a different characteristic of dianic acid, without which its existence will in no way be necessary and he will have to give up his new metal as a result" (Sainte-Claire Deville and Damour 1861, 1046).[191]

Their conclusion illustrates the continued importance of clearly identifying characteristic reactions in support of discovery claims. They did not require Kobell to actually isolate his metal, but rather inferred its non-existence from the lack of characteristic reactions.

## Personal reputation and the reception of analytical results

When it comes to the debates on the tantalum metals, it is impossible to distinguish between social factors on the one hand and purely chemical arguments on the other, because mineral analysis required a tremendous amount of mostly tacit skills. Impurities were incredibly difficult to detect because their presence was indicated only by a subtle lack of uniformity in the coloured precipitates produced by various reagents. For example, such subtle differences in colour alerted Mosander that cerium oxide was likely a mixture – something that even Berzelius had not remarked in 35 years (Tansjö 1996).

[190] Deville was professor of chemistry at the Ecole Normale Supérieure, see Paquot (2005). For information on Damour, who was an administrator and independent scholar, see Lacroix (1905).

[191] "M. de Kobell sera donc obligé, selon nous, de trouver un autre caractère de l'acide dianique, sans quoi son existence n'aura aucune nécessité et par suite il faudra renoncer à son nouveau métal."

Analytical results were therefore generally seen as more reliable if they were published by someone with the reputation of a skilled analytical chemist.

In addition, the discoveries of pelopium, ilmenium and dianium were announced during a period of institutional and pedagogical reform in German chemistry (see Rocke 1993a, chap. 1). Increased funding for both research and teaching, as well as a growing student demand furthered the professionalization of academic careers and the development of teaching laboratories where practical education took place at a large scale.[192] Rose and Hermann were among the last generation of chemists to have acquired their skills through individual apprenticeships, and they were working at a time when analytical chemistry was increasingly institutionalized. In order to fully understand the debates on the tantalum metals, we therefore have to take into account the reputations and institutional positions of the chemists that took part in them.

By the time Rose published his discovery claim of niobium, he was already a central figure in the emerging field of analytical chemistry. He came from a well-known family of apothecaries (of whom Klaproth was a family friend) and had studied for a year in Stockholm with Berzelius, one of the most famous chemists of the period. He became a Privatdozent at the University of Berlin in 1822 and ordentliche Professor in 1835. In 1840, the famous Justus Liebig (1803-1873) spared Rose in his harsh attack on Prussian chemistry as the only chemist in Berlin with the talent and inclination to actually teach students something (R. S. Turner 1982, 131). Although Rose did not have a state-funded teaching laboratory at the University, he privately taught junior chemists who also assisted him in his research.[193] Moreover, Rose was the author of a very successful handbook in analytical chemistry which ran through six editions and was translated into English, French and Dutch. Rose's career provides a stark contrast with that of Hermann, who had no

[192] This instutional and pedagogical reform has been linked to the influence of the practical methods and the material culture of analytical chemistry on chemistry as a whole (see Homburg 1999; Jackson 2015). For an overview of courses in analytical chemistry taught in nineteenth-century Germany, see Homburg (1993).

[193] Rose mentioned his assistant "Mr. Weber" on multiple occasions, and also referred to the fact that his analyses were carried out collectively. One of the other junior chemists may have been K. F. Rammelsberg, who was a Privatdozent at the University of Berlin during the 1840s. Rose did not provide any additional names of chemists who contributed to this discovery.

academic position. After his pharmaceutical apprenticeship, he moved to Moscow where he produced and sold artificial mineral waters.[194] Even though he did publish a large number of papers on mineral analysis, Hermann did not enjoy the same reputation as Rose.[195]

This difference in status influenced the reception of their respective discovery claims. When Wöhler learned that Rose had identified the 'second tantalum' that he had been so close to discovering, he wrote that he did not regret the course of events because "good Heinrich" deserved to have his discovery.[196] Moreover, Rose's second metal pelopium was described in various textbooks and its existence remained unquestioned until Rose retracted his own discovery claim.[197] In 1853, he announced that he had obtained pelopium chloride by treating a sample of niobic acid with chlorine (Rose 1853). Since transmutation was generally thought to be impossible, he concluded that he had been working with two different niobium compounds. For seven years, he had not been aware that niobium was capable of producing two chlorides and two acids. He renamed pelopic acid 'niobic acid', whereas his old niobic acid became 'hyponiobic acid' (*Unterniobsäure*).

By contrast, Hermann's discovery of ilmenium was immediately questioned. Rose (1848, 454) criticized his analysis as not "careful" enough and Berzelius (1847, 8:59) found it "difficult to conceive" how Hermann could have thought that he was handling a previously unknown metal. Hermann eventually retracted his discovery and admitted that ilmenic acid had been a mixture of different niobium compounds (Hermann 1856). In 1865, however, he once again announced the discovery of ilmenium, only to receive another poor reaction (Hermann 1865). Hermann's works were reviewed anonymously in *the Journal für Praktische Chemie* (1866):

---

[194] Biographical information on Hermann is very rare. A brief description of his life and works is contained in Minina (2008).

[195] For Hermann's publications, see the Royal Society Catalogue of Scientific Papers (Royal Society 1869, v. 3:310–14).

[196] "Ich (…) gönne dem guten Heinrich die Entdeckung von Herzen". Wöhler to Berzelius, 2 January 1845 (Berzelius and Wöhler 1901, 519).

[197] For example, analytical handbooks explained how to identify pelopium compounds (Wöhler 1854; Northcote and Church 1858). Likewise, pelopium was listed as a metal by Pelouze and Frémy (1848, 289). Ilmenium, on the other hand, was not named in any of these books.

> "About Hermann's newest work [of 1865], in which ilmenium resurfaces in a Proteus-like way after having been given up on multiple times, the author will only say that it causes confusion and fails to bring any clarity to the knowledge of the tantalum metals."[198]

The difference in authority between Rose and Hermann was also very apparent in the debate on the topic of dianium, to which they both contributed. Kobell's (1861a) main argument in response to Rose, Deville and Damour was to insist that he could not obtain the blue coloration when using (hypo)niobic acid from Bodenmais columbite, the mineral in which Rose had originally identified niobium. If the original niobium did not have this characteristic property, then it was not a property of niobium, he argued. Hermann (1861) quickly proposed an explanation: (hypo)niobic acid produced from this mineral using Rose's original instructions contained about one third of tantalic acid, and these impurities needed to be removed in order for the blue coloration to appear.[199] Rose (1863) refused this explanation and continued to deny that the Bodenmais mineral contained any tantalum until the end of his life.[200] Kobell's (1861b) initial refutation of Hermann's explanation explicitly relied on Rose's authority, and when Hermann was later proven correct, Kobell (1865, 300) defended himself by restating that he had "accepted the information on the authority of this famous chemist [Rose]".[201] Thus we see how Rose's reputation in part shaped the debates on the tantalum metals; nevertheless, even these explicit references to authority were linked to the question of correctly identifying compounds and their properties.

---

[198] "Ueber Hermann's neueste Arbeiten, in denen das schon mehrmals aufgegebene Ilmenium mit proteus artiger Gestalt wieder auftaucht, spricht sich der Vf. dahin aus, dass sie nur Verwirrung und keine Aufklärung in die Kenntnisse von den Tantalmetallen gebracht haben." Most of this review consisted of a summary of Blomstrand's work on tantalite minerals (see below), but this quote is not a direct translation of Blomstrand's original paper.

[199] Hermann had already argued that Bodenmais columbite contained tantalic acid in 1856 (see Hermann 1856).

[200] A possible explanation for the fact that Rose did obtain the blue coloration for his samples of hyponiobic acid might be that he produced his hyponiobic acid indirectly, from hyponiobic chloride, rather than isolating it directly from the mineral. This would have eliminated most impurities (This is the explanation proposed by Marignac 1865a, 176).

[201] "Ich hatte auf die Autorität des berühmten Chemikers hin dessen Angaben angenommen."

## Differences with publications from the early nineteenth century

In the previous sections, I have mostly highlighted the continuity between the publications of the middle of the nineteenth century and the earlier works that I discussed in the previous chapter. Despite this continuity, there were two noteworthy differences that set these later publications apart from the initial discovery claims of tantalum and columbium. I will discuss those here and show how they can in turn point towards another underlying similarity.

The first difference is that Rose and Hermann provided atomic weights for their newly discovered metals, as opposed to Hatchett, Ekeberg and Wollaston. By the 1840s, most chemists had come to accept some form of chemical atomism. Accordingly, Rose and his contemporaries systematically provided chemical formulae and atomic weights in addition to qualitative characterizations. The most striking example is Hermann's reference to atomic weight as 'the main difference' ("Hauptverschiedenheit") between ilmenium and niobium (Hermann 1847a, 135).[202] His remark can be contrasted with Wollaston's reaction to a difference in specific weight between tantalite and columbite minerals in 1809: although Wollaston (1809, 251) noted the "very remarkable difference", he did not see it as a sufficient reason to distinguish between the two minerals and their constituents at the time.

Yet, despite the acceptance of the chemical atomic theory, Rose and Hermann's publications overall showed little concern with the ultimate constitution of matter. This constituted a second difference with earlier publications in analytical chemistry, and it illustrates the importance of Alan Rocke's (1984) distinction between chemical atomism and ideas regarding the corpuscular nature of matter. The nearly 300 papers that Rose published during his lifetime were almost exclusively dedicated to the analyses of specific mineral substances and the practical issues of determining the composition of specific

[202] The atomic weights of the three substances as determined by Hermann at this time were Ta=1331,15, Nb=1251,53 and Il=786,59. He did not specify which referent weight he used, but it likely was O=100. Hermann added that their order in terms of atomic weight corresponded to an order in terms of properties, with ilmenium closely resembling niobium which in turn resembled tantalum.

mineral substances. They do not contain any passages similar to Hatchett's reflection on the growing number of simple substances.

The lack of metaphysical reflection on Rose's part might seem an indication that "the problem of the chemical element ceased to be critical about the time of the appearance of Dalton's atomic theory" as Siegfried and Dobbs (1968, 293) have claimed. However, reflections regarding the true nature of the elements had not disappeared from chemistry altogether – on the contrary, the detection of radicals in organic compounds led to a renewed interest in the possible complexity of elements among organic chemists in the early 1840s (see Farrar 1965; Knight 1978). Likewise, around the same time, the substitution debate opposed Dumas, Laurent and Berzelius on similar questions that had occupied Davy a few decades earlier (Brooke 1969, 150–64): was it the nature of the elements or their arrangement within a molecule that determined the properties of organic substances? Rose simply did not engage with these questions and instead practiced analytical chemistry as a kind of exploratory experimentation that was not aimed at testing theoretical hypotheses.

Rose (1857) did publish a single article in which he expressed views that had broader implications than just specific analyses. In this paper he defended Berzelian atomic weights against the reform proposed by Leopold Gmelin (1788-1853) in multiple editions of his *Handbuch der theoretischen Chemie.* Equivalent weights had remained popular in England since their development by Wollaston in the 1810s, whereas Berzelius atomic weight had been dominant in Germany (see Chang 2012b; Rocke 1984). Gmelin adopted and slightly adapted the English weights and after Liebig's conversion to this system in 1838, it gradually became dominant in France, Germany and England over the course of the 1840s. Rose refused to follow Gmelin's recommendations and stuck with Berzelian weights until the end of his life (see Rammelsberg 1866). His 1857 article provides a rare glimpse at his general views on chemical composition, which remained implicit in all his other publications.

Rose's main issue with Gmelin's proposal was that it broke "all rules of analogy" (Rose 1857, 279). Atomic weights and chemical formulae were closely linked because formulae were required for the calculation of weights and vice-versa. Gmelin's doubling of some atomic weights therefore required the adaptation of the corresponding chemical

formulae, and this broke some of the analogies in the composition of substances that behaved very similar. For Rose, this was unacceptable:

> "It is of great influence for the study of chemistry, and it immensely improves the overall view, when one sees how *analogous chemical composition is also the cause of analogous properties of compounds*. This analogy, however, is completely destroyed by the acceptance of Gmelin's atomic weights of many simple bodies" (Rose 1857, 274).[203]

This quote shows a strong Berzelian influence on Rose's view of chemical composition, as also becomes clear from other parts of the paper where Rose defended a Berzelian view of acidity.[204] Most importantly, however, this quote shows that Rose implicitly adhered to the rule that his predecessors had explicitly defended: that analogy in properties was correlated with analogy in composition. Rose's argument against Gmelin therefore reinforces my conclusion from the previous chapter regarding a similar, but implicit, link between chemical analogy and composition in mineral analysis. The inference that a new metallic oxide contained a previously unknown metal could be made on the basis of this assumption, just like the inferences that had pointed towards the existence of aluminium, ammonium and fluorine a few decades earlier. A difference with these earlier inferences is that Rose saw an analogy in chemical formulae: in addition to the type of elements contained in the substances, he also thought their proportions would be the same.

In short, the publications on the tantalum metals show a continuity in the identification of chemical elements using mineral analysis, despite the changing institutional and theoretical context of the middle of the nineteenth century. Rose, Hermann and their contemporaries inherited not only their predecessors' main analytical procedures, but also their practice of primarily characterizing metals on the basis of their compounds. They did not worry about isolating them in the form of metals. Although we can identify differences with the beginning of the century, underlying these inferences is the same use of analogy

[203] "Es ist von einem grossen Einfluss für das Studium der Chemie, und es befördert die Übersicht ungemein, wenn man sieht, wie die analoge chemische Zusammensetzung auch die Ursach der analogen Eigenschaften der Verbindungen ist. Diese Analogie wird aber durch die Annahme der Gmelin'schen Atomgewichte vieler einfacher Körper ganz vernichtet (…)". Emphasis added.

[204] According to this view, the acidity of oxygen compounds was due to both the intrinsic nature of the acidified radicals and the amount of oxygen in them (on Berzelius' view, see Melhado 1981).

as was common a few decades earlier. Rose continued to be considered the main expert on the tantalum metals until the end of his life, but many of his conclusions came to be revised shortly after his death in 1864.

## Marignac and Blomstrand's work on the tantalum metals (1864-1866)

When Rose passed away in 1864, it was generally thought that tantalum formed one acid (tantalic acid) whereas niobium produced two (niobic acid and hyponiobic acid). Both formed a white chloride, but niobium additionally produced a yellow chloride, which had originally been identified by Rose as pelopium chloride before he renamed it hyponiobium chloride.[205] Rose had identified the chemical formulae for the acids as $TaO_2$, $NbO_2$ and $Nb_2O_3$, and the atomic weights for tantalum and niobium as 137,64 and 97,64 respectively.[206] Between 1864 and 1866, much of this knowledge came to be revised, most notably through the contributions of the Swedish chemist Christian Wilhelm Blomstrand (1826-1897) and the Swiss Jean-Charles Galissard de Marignac (1817-1894) (see Partington 1964, 4:188 for a summary of their findings). Working independently, they each confirmed that niobium and tantalum were the only tantalum metals, definitively refuting the existence of all others. They also found that niobium produced only one acid and one chloride; hyponiobic chloride was in fact an oxychloride of niobium and Rose's second niobic acid (the original pelopic acid) was a mixture of tantalic and niobic acids in varying proportions. This section will analyse these works and those of their colleagues on the same topic in order to show the differences and similarities with earlier characterizations of chemical elements.

### The chemical formulae of niobium compounds

Blomstrand mostly relied on the same methods as Berzelius and Rose. After succeeding his mentor Nils Johannes Berlin (1812-1891) as professor of chemistry and mineralogy at

[205] These compounds were later reidentified and are now known as tantalum pentachloride ($TaCl_5$), yellow niobium pentachloride ($NbCl_5$) and niobium oxychloride ($NbOCl_3$).

[206] For H=1 and O=16. Not everyone adhered to such a system, as will become clear below.

the University of Lund in 1862, he became interested in the tantalum metals.[207] Blomstrand had already been working on the analysis of various minerals and extensively studied the halide compounds of molybdenum and tungsten. In 1864 he published the results of a large number of analyses of the compounds of niobium and tantalum (Blomstrand 1864). He proposed his corrections for the composition of various niobium compounds mainly on the basis of a quantitative analysis of sulphides and chlorides. Blomstrand also showed that Rose's reduction method did not produce pure niobium but rather NbO; he was the first to obtain metallic niobium through the reduction of niobium chloride with hydrogen (Blomstrand 1865b).

Working independently, Marignac arrived at very similar results.[208] As opposed to Blomstrand, he developed a new method for the study of chemical composition by relying on crystallography. Marignac was born in Genève but studied in Paris and Giessen with two of the foremost chemists of his time, Jean-Baptiste Dumas (1800-1884) and Justus Liebig (1803-1873).[209] After six months at the porcelain manufactory in Sèvres, Marignac became professor of chemistry (in 1841) and mineralogy (in 1845) at the Academy of Geneva. Although his professors were mainly known for their work in organic chemistry, Marignac turned to atomic weight determinations when he arrived in Geneva. In order to determine these weights he initially followed a method suggested by Dumas: by first establishing the atomic weight of chlorine, the atomic weights of the metals could then be determined by neutralizing a solution of each of their chlorides with silver nitrate.[210] However, in 1859, Marignac (1859) developed a new way to identify chemical composition and atomic weights using the law of isomorphism. According to this law, which had been published in 1821 by Eilhard Mitscherlisch (1794-1863),

[207] For biographical information on Blomstrand, see Lindman (1942) and Kauffmann (1975). Berlin in turn was an old student of Berzelius.

[208] Marignac gave Blomstrand priority over these findings because he published them at an earlier date; however, Marignac had been unaware of the original Swedish paper until the German translation appeared in the *Annalen der Physik* (Marignac 1865c).

[209] For biographical information on Marignac, see Ador (1894). For Dumas' influence on him, see Klosterman (1985).

[210] Similar methods had been used since the 1820s, see Brock (1985, chap. 7).

the shape of a crystal depended on the number of atoms rather than on the chemical identity of the crystallized substance (see Rocke 1984, 154–56). In other words, salts with analogous compositions crystallized in similar forms.

As I have discussed in previous chapters, chemical composition had been inferred on the basis of chemical analogy since at least the late eighteenth century. However, Marignac's use of crystal shape made this type of prediction much more precise: the exact number and type of atoms could be inferred from analogy. Analogous substances thus not only contained the same elements, they also contained them in the same proportions. In the words of Marignac's colleague and son in law Emile Ador (1845-1920):

> "Marignac considered these methods to be subordinated to a more reliable law, namely: that the analogy of various groups of compounds must be explained by the analogy of their constitution, and consequently, of their formulae" (Ador 1894, 40).[211]

For Marignac, the study of crystal forms thereby became the most certain way to study chemical formulae by analogy.

When using his new method, Marignac generally relied on the study of double fluoride salt crystals. He found that hyponiobium fluoride crystals had the same shape as those of tin fluoride ($SnF_4$) and titanium fluoride ($TiF_4$). Since quantitative analysis had shown that hyponiobium fluoride contained only three atoms of fluorine, it had to contain an additional metalloid atom that could take fluorine's place in the crystal structure. Marignac (1865b) proposed that this would be oxygen, and the formula for the 'hyponiobium' radical should be changed to NbO. Thus, hyponiobium fluoride was in fact an oxyfluoride with the formula $NbOF_3$; by analogy, hyponiobic chloride became an oxychloride $NbOCl_3$ and hyponiobic acid $(NbO)_2O_3$ or $Nb_2O_5$. Marignac's predictions regarding the chlorides were confirmed experimentally by Louis Troost (1825-1911) and Deville (1865), both through vapour density measurements and by reacting hyponiobic chloride with magnesium in order to detect oxygen.[212] Marignac (1865a) also confirmed the composition of

[211] "Aussi Marignac estimait-il que ces methods sont subordonnées à une loi plus sûre, savoir: que l'analogie des divers groupes de composés doit s'expliquer par l'analogie de leur constitution et par suite de leurs formules."

[212] Troost was a pupil and assistant of Deville at the Ecole Normale before becoming a high school teacher. In 1874 he was appointed professor at the Sorbonne in Paris (Partington 1964, 4:498).

fluoxyhyponiobate of potassium ($NbOF_3$, 2KF) experimentally: he was able to replace oxygen with fluorine in the salt, and return to its original composition. Later, Marignac (1866b) also studied tantalum compounds and determined the formulae of a brown tantalum oxide ($TaO_2$), tantalic acid ($Ta_2O_5$) and tantalum fluoride ($TaF_5$) and described their (chemical and cystallographical) properties and methods of preparation.

## Marignac's experimental methods

Marignac's new method added to, but did not replace, earlier analytical procedures. The elimination of impurities remained a central issue in the identification of the tantalum metals, especially because their presence could significantly modify the outcome of chemical tests. For instance, Marignac (1866c; 1867) argued that all the supposed characteristic properties of Hermann's ilmenium could be explained by the presence of titanium impurities, including the difference in atomic weight. Once the titanium and niobium compounds were isolated from columbite and aeschynite minerals, Marignac could not detect any other metals. He therefore concluded that ilmenium was a fluoride salt of titanium and niobium and that its existence as an element was based "only on hypotheses related to errors of calculation" (*ibid*., 467). He dismissed Hermann's results as uncertain, and doubted whether he had taken all the necessary precautions during his analyses.[213] Despite these criticisms, Hermann continued to publish on ilmenium, and even announced a second tantalum metal called 'neptunium' in 1877 (1866; 1871; 1877; see also Fontani, Costa, and Orna 2015, 48–49). Hermann passed away two years later and had little opportunity to defend his final discovery.

Since impurities could modify a substance's properties beyond recognition, adequate separation methods were of key importance for the correct identification of elementary composition. In order to avoid the errors caused by Rose and Hermann's "highly imprecise" ("gänzlich ungenau") methods, Marignac (1866c) developed a new way to separate tantalum and niobium compounds that relied on the difference in solubility

[213] Thus Marignac cited the titanium impurities as an example, stating: "dieses Beispiel giebt dem Zweifel Raum, ob der Vf. [Verfasser] bei seinen übrigen Analysen alle die Vorsichtmaassregeln angewendet habe, welche erforderlich sind, um ihre Genauigkeit zu verbürgen" (Marignac 1867, 468).

between potassium-niobium oxyfluoride and potassium-tantalum fluoride.[214] Only the former was soluble in cold water, which meant that it could be easily washed out of a mixture of the two fluorides.

This separation method enabled Marignac to confirm Hermann's suspicion that columbite from Bodenmais contained about one third of tantalic acid (Marignac 1865a). The new metallic acid that Kobell had identified as dianic acid was therefore just pure niobic (formerly hyponiobic) acid. Tantalum and niobium were so similar that they could take each other's place in a mineral without changing its crystal structure, and chemists could have therefore easily produced a mixture without noticing. Despite the impurity of Rose's original sample, Marignac (1865a, 176) argued that niobium should not be renamed in honour of Kobell because it was Rose who had "first discovered the presence of a distinct acid". In other words, even when it came to the retrospective attribution of credit for the discovery of niobium, he saw the detection of a metallic oxide as the most important factor.

It might seem surprising that spectroscopy did not play a role in this debate, as it had newly been developed as a tool for chemical analysis by Robert Bunsen (1811-1899) and Gustav Kirchhoff (1824-1887). This incredibly sensitive new method enabled the identification of new elements on the basis of their unique spectral patterns, and seemed to provide a solution to any difficulty regarding the unambiguous identification of chemical elements.[215] As Dumas enthusiastically wrote after Bunsen's visit to Paris in 1862:

> "[Spectroscopy] indicates in any compound or mixture what elements are present, what elements are missing, and, something even more marvellous, it shows with incomparable precision the very presence of any element hitherto unknown. (...) It will no longer be necessary to touch a body in order to determine its chemical nature; it will suffice to look at it" (cited in Figuier 1862, 6:109–10).[216]

[214] The modern formulas for these salts are $K_2TaF_7$ and $K_3NbOF_5.2H_2O$ (Tressaud 2019, 44).

[215] On the development of spectroscopy as a new method of qualitative analysis, see James (1983). On its role in the discoveries of new elements see Weeks (1956) and James (1984).

[216] "[La spectroscopie] indique dans tout composé ou dans tout mélange quels éléments s'y trouvent, quels éléments y manquent, et, chose plus merveilleuse encore, elle y manifeste avec une incomparable precision la presence même de tout élément inconnu jusqu'ici. (…) Il ne sera plus necessaire de toucher un corps pour en determiner la nature chimique; il suffira de le voir."

Why then did Marignac not rely on spectroscopy in order to definitively show the nature of tantalum and niobium and refute the other elements? There are a number of possible explanations.

One possibility is that chemists were simply not very keen to adopt the new technique. Charlotte Bigg (2003, 773), for instance, states that besides being limited in their use of spectroscopy by the high level of skill needed, "chemists were moreover reluctant to take up a technique they associated with physics". However, the number of (attempted) identifications of new elements and the production of spectroscopes by chemical instrument makers point towards the contrary: chemists came to see the study of spectra as part of their subject within a few years.[217] Bigg is right to point out the difficulty of using spectroscopy, and Dumas' exclamation that it would suffice to simply look at a body in order to know its composition is clearly an exaggeration.[218] Nevertheless, it is clear that chemists did attempt to use the technique and its adoption was not limited to only ex-students of Bunsen who may have learned its use directly from him. This explanation therefore seems unlikely.

The absence of spectroscopy also cannot be explained by a personal unfamiliarity with the technique. Marignac was at least aware of its existence, because his Genevan colleague Jacques Louis Soret (1827-1890) and student Marc Delafontaine (1837-1911) used the technique in their research on the rare earths (see Fontani, Costa, and Orna 2015, 119–27). Evans and Szabadváry (1996, 55) mention Marignac was "among the first to seize upon the new opportunities afforded by spectroscopy", but curiously, he did not actually publish any works on spectroscopy himself. It is unclear why Evans and Szabadváry made this claim about Marignac, as they do not describe any of his spectroscopic works and only refer to work on the study of various chemical reactions. There are no publications on spectroscopy in Marignac's *Oeuvres Complètes* and the biographical sketch by Ador does

[217] The adoption of Bunsen and Kirchhoff methods for spectrochemical analysis in Britain and France, respectively, is described in James (1988) and Aubin (2002). Both articles also discuss instrument makers. See also James (1985) on the historiography of spectroscopic analysis.

[218] This is most clearly illustrated by the difficulties in the separation of the rare earths despite the use of spectroscopy. The new technique did not lead to any new findings until the 1880s (see Evans and Szabadváry 1996; DeKosky 1973).

not refer to the technique either. Nevertheless, it is possible that Marignac worked together with his colleagues on some of their spectroscopic work.

When it comes to the tantalum metals, the most likely explanation for the lack of spectroscopic analyses is therefore that Marignac and his colleagues simply did not think it would be of use. Delafontaine (1866) did publish one paper on niobium compounds, but in it he did not reference any spectroscopic methods even though he was already using them elsewhere. Spectroscopy had indeed led to a number of spectacular discoveries and would continue to do so, but it was not applicable in every case. Although dry analysis was gradually replaced by spectroscopy from the 1860s onwards, wet analysis remained the most important strategy for qualitative analysis throughout the nineteenth century (Hudson 2005; Meyer 1891, 358–72). As Davis Baird (1993) has argued, chemical substances continued to be identified primarily by their chemical properties (that is, their reactions to analytical tests) rather than their physical properties until the middle of the twentieth century. Likewise, Marignac's method for separating niobium and tantalum compounds continued in use until at least the turn of the twentieth century, when an industrial interest in metallic tantalum and niobium arose (Weeks 1956, chap. 13)

## Atomic weight, valence and classification

Despite this relative continuity in the use of classical methods, there are clear differences that set apart Marignac and Blomstrand's publications from those of Rose and Hermann. Since the 1840s, important developments had taken place in organic chemistry that had consequences for the entire field of chemistry and the conception of composition. They were able to take advantage of the new conception of chemical composition that resulted from these developments, and they therefore appear very clearly in their publications. In addition to atomic weight, Blomstrand and Marignac identified a 'valence' or 'atomicity' for each element, which corresponded to its capacity of binding other atoms in a compound.

The discovery of the property of valence was one of the key steps towards the standardization of chemical notation, formulae and atomic weights around the middle of the nineteenth century (see Rocke 1984). It constituted a turning point in what Alan Rocke (1993a; 1993b) has called "the quiet revolution". This transitional period in chemistry started with an 1842 paper by the French chemist Charles Gerhardt (1816-1856),

in which he conceived of different types of molecules in which some (groups of) elements could be replaced by others without disturbing the general structure of the molecule.[219] In 1851, Alexander Williamson (1824-1904) provided the provided the empirical basis for Gerhardt's water type and showed that it could be applied to alcohols, ethers and acids: each of these molecules could be viewed as a water molecule in which the hydrogen atoms had been replaced by other (groups of) atoms. This meant that oxygen functioned as a 'bibasic' radical in these molecules, in the sense that it could connect to two other radicals, whereas hydrogen was 'monobasic'. This idea continued to be developed by a number of chemists during the 1850s, until August Kékulé (1829-1896) published two papers that generalized the idea of valence in 1857 and 1858. His structure theory made valence (then called atomicity) a property of the elements themselves, rather than radicals or groups of elements that occupied a certain place in a molecule.[220]

Kékulé also championed a reform in atomic weights by organizing an international conference in Karlsruhe in 1860, which could be seen as the culmination of the quiet revolution (see Rocke 1984, 292–99; Bensaude-Vincent 1990b). Gerhardt and his colleague Auguste Laurent (1807-1853) had initially proposed this reform as the return to a modified version of Berzelian atomic weights. Though it had very little success in their home country, Laurent's and Gerhardt's ideas travelled via England to Germany where they convinced many younger and mid-career theoretically minded chemists (Rocke 1993b). With a group of his colleagues, Kékulé organized the Karlsruhe conference with the aims of defining key terms (such as atom, molecule, equivalent, atomic weight), reviewing equivalent weights and formulae, and standardizing notation and nomenclature. During this conference, Stanislao Cannizzarro (1826-1910) proposed a standardization of atomic weights which was not immediately successful but became widely accepted by the late 1860s (except in France). Marignac was among the first French-speaking chemists to adopt the new notation and atomic weights (see Ador 1894).

Moreover, Blomstrand and Marignac did not just accept these reforms: both of them also actively contributed to debates regarding the chemical elements and their properties.

[219] On the history of type theory see Rocke (1984, chap. 8).

[220] On the life and work of Kékulé (and relevant work of his colleagues) see Partington (1964, 4:533–65).

Whereas Kékulé argued that valence was an intrinsic property by which each element could be characterized, Blomstrand was opposed to the idea of fixed valence (see Kauffman 1975). Blomstrand's aim was to revive Berzelian electrochemical dualism and combine it with type theory in an attempt to explain the properties of compounds on the basis of their structure, elementary composition and the varying valence of their constituent elements. In other words, he did not want to explain the properties of compounds solely on the basis of their structure, nor solely on the basis of their elementary composition. From 1870 onwards, his work focused on proving the idea of varying valence in order to establish this complex explanation of chemical properties on the basis of composition.

Meanwhile, Marignac was mainly motivated by the question of the inner complexity of chemical elements. His interest in atomic weight had originated with Dumas's investigation of William Prout's hypothesis, according to which the atomic weights of all elements were multiples of hydrogen.[221] He continued to defend this hypothesis for decades, arguing that it was at least approximately true. Thus, while both Blomstrand and Marignac were known for their impressive experimental work, throughout their careers they were each motivated by questions that had broader theoretical implications. This sets their approach apart from that of Rose and illustrates the ways in which developments in organic chemistry sparked a renewed interest in the nature of the elements during the 1860s.

Although discussions regarding the inner complexity of the elements happened independently from the actual identification of the elements in question, their respective views on the recent chemical reforms were relevant for the interpretation of experimental results. Thus, while their results mostly coincided, Marignac and Blomstrand did have some slight disagreements regarding the valences and atomic weights of tantalum and niobium and on the composition of their compounds. This was due in part to the fact that they adhered to different systems of atomic weights: whereas Marignac attributed a weight of sixteen to oxygen, Blomstrand believed its atomic weight would be eight. As a result,

[221] On the work of Dumas and his students on Prout's hypothesis, see Klosterman (1985). On the history of Prout's hypothesis more generally, see Brock (1985).

Blomstrand's weights for niobium and tantalum were initially around half those of Marignac. In addition, they attributed different valences to the metals and different chemical formulae to their compounds (see Blomstrand 1865b). Whereas Marignac thought niobium would have an atomicity of either four or five, Blomstrand argued it would be strictly 'tetratomic' at first ("tétratomique", meaning tetravalent) (Blomstrand 1865b, 338–40). After a brief disagreement, Blomstrand (1865a) was willing to take on Marignac's formulae, which were simpler and agreed better with the analytical results, but he doubled the amount of oxygen in the oxyfluorides. Marignac (1866a) eventually accepted this doubling, and they agreed that tantalum and niobium formed a chemical family characterized by a valence of five.

Furthermore, Marignac and Blomstrand had differing views on the most fruitful ways to classify the chemical elements. In various passages of their publications, Blomstrand and Marignac reflected on the potential placement of niobium and tantalum in classifications of the elements and the properties on which such a placement should be based. It appears to have been completely self-evident to them that tantalum and niobium would be placed together, because their placement was discussed only as a group. Blomstrand saw (varying) valence as a potential foundation for a natural classification of the elements. He identified the tantalum metals as a distinct chemical family characterized by their valence of five, which he argued should be placed next to the tetravalent family of tin, silicon and titanium.

Marignac (1866a), on the other hand, used the example of the tantalum metals to argue against the choice of valence as a principle of classification: he argued that tin, silicon, titanium, niobium and tantalum should all be seen as members of a single natural group on the basis of their analogous chemical properties. In his view, the variety of valences within this group illustrated the inadequacy of classifications on the basis of valence:

> "[By using valence as a basis for classification,] we are thus led to bring together bodies that are different in all other respects and to separate those of which the analogies are

> most obvious. The union of silver with the alkaline metals, for example, does not seem any more justified to me than the separation of silicon from niobium would be" (Marignac 1866a, 183).[222]

Instead of valence, Marignac focused on atomic weight. In 1859, he defended his systematic investigation of atomic weights as the best way towards establishing a natural classification of the chemical elements (Marignac 1859). His interest in the quantitative relations between atomic weights across chemical families also clearly appears in his work on the tantalum metals (Marignac 1866b), where he remarked a striking similarity of their difference in atomic weight and the differences across other families. We might schematically represent the increases as follows, similarly to the representation used by Dumas (1859):

Nb = 94  Mo=96

Ta = 182  W=184

Thus, the question of elementary nature had once again made its way into the debate on the tantalum metals during the middle of the 1860s. Crystal structure, atomic weight and valence provided a way of characterizing elements using both the types of compounds they formed and the exact stoichiometric composition of these compounds.

# Conclusion

In this chapter I have discussed the discovery claims of niobium, pelopium, dianium and ilmenium and their reception during the middle of the nineteenth century. The positive reception of niobium and pelopium could be explained by multiple factors, including Rose's reputation and the existing suspicion that there might be multiple tantalum metals. The discovery claims of dianium and ilmenium were less successful, and opponents of these metals claimed that they could not be clearly distinguished from others on the basis

[222] "On est amené par là en effet à rapprocher des corps qui offrent sous tous les autres rapports les plus grandes différences et à séparer au contraire ceux dont les analogies sont les plus manifestes. La réunion de l'argent aux métaux alcalins, par exemple, ne me paraît pas plus justifiée que ne le serait la séparation du silicium et du niobium." Marignac's comments echo the main criticism of 'artificial' classifications of elements that were common in France at the time (see Bensaude-Vincent and García-Belmar 2015).

of their characteristic reactions. When Marignac developed a new separation method between tantalum and niobium, they were definitively refuted.

These debates point towards a continuity in the methods used to identify new chemical elements in mineral sources, despite the various ways in which chemical practice changed during the middle of the nineteenth century. Throughout the first half of the century, methods to distinguish between different types of metallic compounds gradually improved by the additional of new chemical tests and analytical procedures, but the overall methodology remained the same. In the 1860s, a more complex characterization of composition became possible thanks to the use of crystallography and reforms in chemical atomism that were linked to the idea of valence. Nevertheless, even during this time, metals continued to be characterized on the basis of their compounds. The main questions in debates on the existence of specific metals continued to be the correct identification of their characteristic reactions, and with that the elimination of impurities.

While Rose, Marignac and their colleagues barely reflected on their use of analogy, contrary to Davy and Berzelius earlier in the century, they did use analogical inferences in a similar way. Moreover, the use of chemical formulae shaped these inferences: instead of just predicting that similar compounds contained similar elements, Rose thought that they would moreover have analogous chemical formulae. 'Analogous composition' during the 1840s thus implied a similar proportion of atoms of each type of element as well. Marignac's analogical inference of composition was even more complex, since he was able to rely on crystal shape in order to predict the exact number and type of atoms. Chemical analogy thus became no longer just a question of tendencies to combine but also included a number of additional properties such as crystal shape and valence.

This development shows a gradual move towards the type of information on the basis of which Dmitri Mendeleev (1834-1907) would come to make his predictions of previously unknown elements in 1871 (Pulkkinen 2019b). Mendeleev also cited Marignac's work on niobium as an inspiration for his periodic table (Partington 1964, 4:894). This was not just a question of the precise determination of atomic weights, for which Marignac was known; Mendeleev relied on knowledge of the composition of series of oxides in order to perfect his system (Pulkkinen 2019a, chap. 5).

Similarly, although the question of establishing 'natural' (as opposed to artificial) classifications of the chemical elements had occupied chemists for a long time already, Marignac and Blomstrand's exchange on the topic of classification is particularly noteworthy in the context of the 1860s, during which six different chemists independently published periodic tables (Scerri 2007). In 1870, Blomstrand published his own classification of the chemical elements, both in a separate article (Blomstrand 1870) and in a revised edition of Berlin's textbook (Lundgren 2015).[223]

In short, although the classical analytical methods remained dominant, there was a change in the properties by which chemical elements could be characterized. The reforms of the quiet revolution had a definite influence on many aspects of chemical practice even though they originated in the study of organic substances. Here I have only provided a glimpse into the history of analytical chemistry during this period, a topic which has not often been the object of historical studies. Many questions could be investigated in more detail, including, but not limited to, the link between mineral analysis and classifications of chemical elements.

[223] Blomstrand's classification was not really a periodic table because it was established on the basis of valence and electronegativity and weight was only added later. Neither Mendeleev's nor Blomstrand's system found immediate application within the Swedish pedagogical system (Lundgren 2015).

# Conclusion to Part II

In chapters four, five and six I have investigated the identification of new metals via the chemical analysis of minerals between 1801 and 1866, focusing on the controversies surrounding the group of tantalum metals. Throughout the eighteenth and nineteenth centuries, mineral analysis was the most consistent source of discoveries of new elements. Chapter four retraced the eighteenth-century origins of analytical chemistry by the combination of influences from mineralogy, pharmacy and other arts and industries. The need to characterize mineral substances on the basis of their composition motivated the development of a variety of methods to study them, such as the blowpipe and the use of reagents in mineral water analysis. The immediate goal of each full analysis was to determine the composition of the substance under study and I have argued that this was more important than the decomposition of the substance in order to isolate its constituents. Most of these analytical methods remained in use throughout the nineteenth century.

Chapter five focused on the first decade of the nineteenth century. In it, I analysed the arguments that motivated Hatchett and Ekeberg's claims to the discoveries of columbium and tantalum, as well as Wollaston's conclusion that they were identical. On the basis of these and other examples, I argued that the most important issue in establishing the elementary nature of a new metal was to identify a replicable series of characteristic reactions by which its compounds could be distinguished from others. Implicit in many of these publications was the same type of analogical inference that I highlighted in the first three chapters of the thesis: chemists regularly inferred the existence of a new metal from the identification of a new metallic oxide.

During the middle of the nineteenth century, Rose, Hermann and Kobell each announced their discoveries of additional tantalum metals. As I discussed in chapter six, the debates on the nature of these metals lasted until the 1860s when Marignac and Blomstrand confirmed that only niobium and tantalum existed. Despite the many theoretical and institutional changes that chemistry underwent during the nineteenth century, the story of the tantalum metals shows a continuity in the identification of metals using mineral analysis. During the first half of the nineteenth century, methods to distinguish between various metallic compounds gradually improved by the development

of additional analytical procedures. In the 1860s, a more complex characterization of composition became possible thanks to the use of crystallography, the development of chemical atomism and ideas like valence and molecular structure, but metals continued to be characterized by the reaction of their compounds to various chemical tests.

These three chapters have provided numerous examples which show that the identification of new metals using mineral analysis did not happen on the basis of their isolation in the form of simple substances. Although chemists working after Lavoisier saw metals (at least provisionally) as simple substances, the question of simplicity was relatively unimportant in their assessment of the nature of metals. Chemists did generally attempt to decompose oxides or halides in order to isolate a new metal, but they did not always succeed, and instead they regularly inferred the existence of a previously unknown metal from the identification of its compounds. The most important aspect of establishing the identity of a new metal was the identification of a series of characteristic reactions by which it could be detected and distinguished from other metals.

The prediction of metals on the basis of their compounds implicitly relied on analogical inferences. The fact that chemists reflected very little on their use of analogy in these cases indicates that they did not feel the need to explicitly justify their reasoning. When they did reflect on broader ideas regarding chemical composition, both Marignac and Rose appealed to the same general rule on which their predecessors relied: the idea that analogous properties indicated similarities in composition. This inference became increasingly sophisticated over the course of the nineteenth century as additional properties were attributed to chemical elements, such as valence and atomic weight. By the middle of the century it was possible to predict exact chemical formulae.

I have suggested that analytical chemists did not feel the need to explicitly reflect as much on chemical analogy because they were working within a relatively well-established tradition of identification of metals. They could feel relatively confident in their abilities to successfully characterize metals on the basis of their compounds. The identification methods that they used had a much longer history than the idea of metals as simple substances, which also explains the relative unimportance of simplicity in their identifications. Although Lavoisier had changed the generally accepted view of the

composition of metals (they came to be seen as chemical elements), he did not change the analytical procedures by which they were identified.

This conclusion reinforces existing arguments that have limited the scope of the chemical revolution. Indeed, according to Frederic Holmes (1989, 107), the reforms brought about by Lavoisier and his colleagues did not extend to all areas of chemistry.[224] In addition, Ursula Klein has repeatedly shown that alternative historical periodizations can be established on the basis of chemical practice. She has linked chemists' shifting ontologies to their changing practices of production and individuation of substances rather than to theoretical reforms.[225] Outside of the history of chemistry, Reviel Netz (1999) has argued that the study of shared practices can show continuities that lie beyond moments of rupture in shared beliefs.

By showing that Lavoisier's criterion of simplicity was simply laid on top of an older, continuous tradition of identification of metals, the second part of this thesis likewise illustrates the need to look beyond theoretical definitions towards identification practices. As Friedrich Paneth (1931, 115–16) noted in his famous paper on the concept of chemical element, Lavoisier "demanded that [chemical elements] could *in principle* be prepared as non-decomposable substances."[226] However, as I have argued here, preparation of simple substances was not required *in practice*.

[224] Likewise, Oldroyd (1975, 66) states that "we do not find much evidence for the [supposedly] profoundly beneficial effect of the new chemistry on mineralogical investigations".

[225] For example Klein (2005; 2008a).

[226] For an English translation, see Paneth (1962; or 2003).

# CONCLUSION

In an 1865 paper on the specific heats of solid bodies, chemist and historian Hermann Kopp (1865, 199) reflected on the nature of elements:

> "What bodies are to be regarded as chemical elements? Does the mere fact of indecomposability determine this? or may a body be indecomposable in point of fact and yet from reasons of analogy be regarded not as an element but as a compound? The history of chemistry furnishes numerous examples of cases in which sometimes one and sometimes another mode of view led to results which at present are regarded as accurate."

Kopp's brief remark summarizes some of the main arguments of this thesis regarding the importance of chemical analogy in the identification of chemical elements.

In this thesis I have investigated what it meant to identify a substance as elementary in chemical practice between 1770 and 1870. During this period, chemical elements were defined on the basis of the negative-empirical criterion as suggested by Lavoisier at the end of the eighteenth century. I started the thesis with a prologue explaining this Lavoisian view, its origins and practical implications. The prologue described how a view of substances as characterized by their level of composition as well as their tendencies to combine emerged over the course of the eighteenth century. Lavoisier took this characterization one step further and did away with the four elements, which he replaced with a list of so-called 'simple substances'. He argued against speculation regarding the internal composition of bodies that could not be decomposed, and in favour of a strictly experimental identification of any indecomposable substances as the constituents of compounds. In practice however, he distinguished between indecomposable substances, chemical elements and 'true' elements or principles. I have argued that this distinction provided him with a solution to the practical insufficiencies of his definition: the negative-empirical criterion alone could not suffice to identify chemical elements. The development of chemical atomism in the early nineteenth century did not do away with the metaphysical and procedural difficulties of the Lavoisian definition, nor did it lead to a different definition of chemical elements.

Indeed, as the first part of this thesis has shown, early nineteenth-century chemists continued to characterize chemical elements in a similar way as Lavoisier had done in

practice. In chapter one, I argued that the elementary nature of aluminium was generally accepted around 1810 because early nineteenth-century chemists relied on analogies as evidence in the study of chemical composition. Chemists such as Berzelius, Thomson and Thenard were willing to accept that alumina was a compound of aluminium and oxygen despite also viewing it as an indecomposable body. Using the very similar substances magnesia, barites, lime and strontia they were able to indirectly access the composition of alumina by analogical inference. This inference provided them with a coherent explanation for the indecomposability of alumina on the basis of aluminium's high affinity for oxygen and it was eventually confirmed by the isolation of aluminium around fifteen years later.

The identification of the composition of the similar substance ammonia was much more complicated, as I discussed in chapter two. Whereas ammonia behaved in many ways like a metallic oxide, its repeated decomposition produced only nitrogen and hydrogen. Davy and Berzelius' attempts to make sense of this contradiction show that they based their knowledge of chemical composition on the consilience of experimental results, analogical inference and knowledge of the composition of other substances. Such consilience was established by an iterative process during which they adapted their experimental setups, hypotheses regarding composition and classifications of substances in the hope of achieving a convergence. The premise that analogous substances were composed of similar elements motivated them to question the elementary nature of nitrogen (and, briefly, that of hydrogen).

During their exchanges on ammonia, Davy and Berzelius gradually grew apart as Davy became increasingly distrusting of analogical inference and Berzelius came to attribute a law-like status to his patterns of chemical composition. The opposition between the two chemists became especially clear in their debate on chlorine, which I described in chapter three. Davy and his brother insisted on the idea that chlorine was indecomposable and therefore a chemical element, but many chemists refused to accept this. I have shown that it was not until after the discovery of the analogous simple substance iodine that chemists were willing to rearrange their classifications in order to make room for chlorine as a chemical element. This story shows that even something as seemingly factual as the impossibility to decompose a substance had to be established in accordance with existing knowledge, taking into account all the ways in which the substance combined with others.

There could be no evaluation of composition independently from classification on the basis of analogy.

The second part of the thesis focused on a different kind of chemical practice aimed at studying chemical composition: the analysis of mineral substances. As I explained in chapter four, a relatively standardized methodology of analytical chemistry emerged at the end of the eighteenth century and remained in use throughout the nineteenth century. Many of the procedures used in this methodology, such as reagents and the blowpipe, enabled the identification of a substance's composition without decomposing it into simple substances. I have therefore argued that chemical analysis should not be seen as synonymous with decomposition: the direct aim of a mineral analysis was to characterize the substance under study in terms of its composition, not to break it down into simple bodies.

Chapters five and six described the repeated controversies on the family of tantalum metals between 1801 and 1866. Despite the theoretical and institutional changes that chemistry underwent during this time, the debates on the tantalum metals point towards a continuity in the identification of metals. For most of the nineteenth century, chemists continued to use the same types of analytical procedures as their mid-eighteenth-century predecessors. These methods enabled the identification of metals using the chemical behaviour of their compounds without requiring their isolation in the form of simple substances (that is, as metals). Accordingly, the central questions in all of the debates on the tantalum metals were the correct identification of the properties of compounds and the elimination of impurities, rather than the simplicity of the new metals.

The identification of metals on the basis of their compounds implicitly relied on a similar analogical inference as Davy and his colleagues made: the idea that similarities in properties indicated a similarity in composition. As a possible explanation for the fact that analytical chemists reflected very little on their use of analogy, I have proposed that they were confident in the fact that their methods worked relatively well for the identification of metals. Long before metals were seen as simple substances, they had already been identified using the same chemical tests. The negative-empirical criterion was simply laid atop of this continuous tradition, without changing analytical practice itself. Analogical inferences did become more precise as chemical atomism developed: while early nineteenth-century chemists predicted composition in terms of types of elements, their

successors in the middle of the century were able to infer the properties of combining elements as well. By the 1860s, Marignac used similarities in crystal shape to infer the numbers and types of atoms in niobium compounds. Likewise, atomic weight and valence provided chemists with more properties by which to characterize and classify chemical elements.

Generalizing from these chapters, it is possible to sketch out the way in which elementary nature was established between 1770 and 1870. On the one hand, indecomposability alone was not sufficient to prove elementary nature, because a substance might be indecomposable for different reasons. If an indecomposable substance was similar enough to a group of compounds in order for it to be classified with them, this was an argument against its identification as a chemical element. Only indecomposable substances that were similar to a certain type of chemical element could be seen as elementary, as the example of chlorine best illustrates. Likewise, Davy's argumentation in favour of the elementary nature of potassium, sodium, magnesium, and iodine mainly relied on their analogies with other chemical elements. Only indecomposable substances that could be placed within a classification of chemical elements were provisionally seen as simple.

On the other hand, it was not necessary for a chemical element to exist in the form of an indecomposable substance, as its existence could be inferred on the basis of analogy. Since chemically analogous substances were thought to be composed of similar compounds, such similarities could be used to infer the presence of a certain type of constituent in indecomposable compounds. This happened in the case of various metals that were first identified as elementary constituents of metallic oxides, such as cerium, columbium and aluminium. The fate of ammonium shows that analogy alone was not sufficient either: if other experimental results were incoherent with the analogical inference, chemists continued to test out different hypotheses until they arrived at a coherent result.

The result was a provisional identification of chemical elements on the basis of the consilience of various types of evidence. As opposed to 'true' elements, chemical elements were not identified as absolutely simple but only as relatively simple compared to compounds. They were added to lists and classifications if chemists considered that there

were good reasons to do so, and only until there were good reasons to take them off again. The clearest example of this provisional status is nitrogen, of which the elementary nature was repeatedly questioned during the eighteenth and nineteenth centuries. In practice, the Lavoisian 'provisional' identification therefore did not mean that chemical elements were identified strictly on the basis of the operations of decomposition but rather that the attribution of elementary status was subject to revision. The only idea that generally was not revised was the link between analogous chemical properties and analogous composition.

The status and development of this link between chemical properties and composition could provide a basis for many more historical studies. How did chemists' view of the relation between properties and composition evolve? How did elementary composition relate to the arrangement of particles and constitution of the molecules? What was the influence of ideas like isomerism and molecular structure? What role did properties like electronegativity and valence play in the explanations of the properties of a compound? Many more questions could be asked about the ways in which chemists related the transformations of matter to elementary composition. Here, I will only point out some of the implications of my findings for the current literature in history and philosophy of chemistry. Although I have focused on specific elements and their characterizations in the chapters of this thesis, I will now evaluate what this might tell us about the concept of chemical element itself.

## From Lavoisier to Mendeleev: a break in the history of the chemical element?

In various works, Bernadette Bensaude-Vincent (1986; 2019; 2020) has argued that Mendeleev's definition of the concept of chemical element constituted a break from his predecessors. Whereas Lavoisier defined chemical elements as simple substances, Mendeleev explicitly distinguished between the two. He reserved the term 'element' for the constituents of substances which he characterized only by their atomic weight and not by any directly observable properties. In other words, Mendeleev's definition replaced the negative-empirical criterion with atomic weight as a positive characteristic by which elements can be detected and tracked throughout their different combinations. Instead of focusing on provisional simplicity in isolated form, Mendeleev's definition therefore

highlighted the function of the chemical element as a stable constituent. These are all ways in which their definitions and explicit characterizations of the concept of chemical element differed, and I will not challenge these differences.

However, for Bensaude-Vincent, this was more than just a change in definition: she has argued that Mendeleev's way of defining the chemical element also enabled him to use the concept in new ways. In her view, Mendeleev's emphasis on stability provided the concept of element with predictive and explanatory power:

> "(..) given its concrete and empirical mode of existence, Lavoisier's element has a limited explanatory potential" (Bensaude-Vincent 2020, 49).

> "Had he relied on Lavoisier's definition of elements, Mendeleev could have made neither predictions nor corrections of atomic weight values. Simple substances, being merely concrete residues of analytic operations, are literally unpredictable. They only have a factual existence, whereas abstract elements can be known in advance and their properties can be induced from those of neighbour elements" (Bensaude-Vincent 2019, 306).

Much of this difference comes down to the idea that Mendeleev characterized elements-as-constituents on the basis of the compounds that they formed, whereas Lavoisier could only see them as the residues of chemical decomposition. Bensaude-Vincent (2019, 302) has therefore concluded that Mendeleev's emphasis on the properties of compounds constituted a shift from a 'compositional' to a 'combinatorial' paradigm in chemistry. In earlier work, she concluded that Mendeleev established "a new concept of 'element' (…) distinct from the empirical concept of 'simple body'"(Bensaude-Vincent 1986, 12). A key premise supporting this conclusion is that in their actual use of the concept, chemists relied strictly on their definition.

The results of my historical study of the identification of chemical elements between 1770 and 1870 contradict Bensaude-Vincent's view by showing that in practice, chemists did not strictly follow their own definitions of the concept of element. In order to understand the development of the concept from Lavoisier to Mendeleev we therefore have to look beyond definitions towards its function in chemistry. While I do not claim to have provided an exhaustive history of the development of the concept of element from Lavoisier to Mendeleev, the identifications of chemical elements that I have described in

this thesis do provide new insights into the ways in which nineteenth-century chemists relied on this concept.

Firstly, in (post)-Lavoisian chemistry the chemical element was characterized by relational properties.[227] As I have summarized, simple substances were characterized from the eighteenth century onwards by the different compounds that they formed with other substances. Chemical analogy was doubly relational because it relied on a comparison between multiple substances' tendencies to combine: for example, iodine is analogous to chlorine because its reacts in a similar way with hydrogen and potassium. No chemical element could therefore be viewed in isolation, because its chemical properties included the tendencies to form certain compounds. Knowledge of the compounds that chemical elements formed was necessary in order to classify and characterize them, and often even in order to identify them as chemical elements in the first place. Likewise, elements' intrinsic properties such as atomic weight and valence were identified on the basis of the different compounds that an element formed. In other words, chemical elements were characterized as constituents even when they were defined as simple substances.

Secondly, early nineteenth-century chemists relied on this idea of chemical elements as constituents in order to explain the properties of bodies on the basis of their composition. Hendry (2005; 2006; 2019) has argued that Lavoisier, Dalton and Mendeleev shared a commitment to the idea of chemical elements as constituents of compounds that survive chemical change and which can be used to explain chemical behaviour. My results suggest that many other nineteenth-century chemists relied on the chemical element in this way. Berzelius' theory of oxidation provides a clear example, as do Blomstrand's efforts to explain properties on the basis of valence, electronegativity and composition. Even in cases where no specific causal explanation was proposed, chemists systematically relied on the correlation of properties with composition, which in turn required a concept of composition in terms of elements.

In short, during the period that separated Lavoisier's works from those of Mendeleev, chemical elements were not just simple substances. I have argued that the distinction between chemical elements and indecomposable substances was implicit in the way in

[227] On chemical properties as relation, see also Llored and Bitbol (2013).

which elementary nature was identified. Calling a substance an element was much more than pointing out the impossibility to decompose it: elementary nature implied the possibility to track it throughout a variety of chemical reactions. This possibility even enabled the prediction of previously unknown elements: for example, aluminium and fluorine could be tracked through various operations long before they could be isolated as simple substances. I have described a number of predictions that were made long before Mendeleev published his works, suggesting that his redefinition was not required in order to provide the concept of element with predictive power. Mendeleev's use of analogy in the prediction of unknown chemical elements in 1871 lay in direct continuity with Marignac's work on chemical formulae and atomic weights during the 1860s.

I therefore suggest that the change from Lavoisier to Mendeleev may not have been as drastic a break as it may seem. Without saying that Lavoisier anticipated all of Mendeleev's work, I want to point out a continuity between their views. Instead of a paradigm shift we might see the change between Lavoisier and Mendeleev's definition as yet another example of a process of epistemic iteration. Lavoisier relied on the negative-empirical criterion because he simply had to start somewhere in order to operationalize the notion of chemical element. Mendeleev was able to adjust the definition of the chemical element by building on the increasingly detailed knowledge of chemical elements that had developed within the Lavoisian system. By distinguishing between chemical elements and simple substances, he was able to make explicit a distinction that was already implicit in his predecessors' work. My view of the development of the concept of element during this time is therefore more closely aligned with that of Hasok Chang (2016).

## Philosophical implications for the concept of chemical element

For historians and philosophers of chemistry, a central aim in studying the development of the concept of element has often been to trace the origins of the modern-day view (for example Hooijkaas 1933; Partington 1948; Boas Hall 1968), and this is still the case today. The way in which the history of the concept is interpreted therefore also has philosophical implications, especially when it comes to the current debate regarding its possible duality. Today, the view according to which there are "two concepts of element-hood" is most strongly defended by Eric Scerri (2020, 25), but it originated in the work of Friedrich Adolf (Fritz) Paneth (1887-1958). In a lecture in 1931, Paneth proposed to

distinguish between two 'aspects' of the concept of chemical element: the simple substance ("einfacher Stoff") on the one hand and the element as a constituent on the other.[228] Paneth called the latter "Grundstoff", which has been translated by Heinz Post as "basic substance".[229]

Paneth's aim in proposing this distinction was to disambiguate between two ways in which the term 'element' is commonly used. For instance, if one were to ask a chemist to describe the element sulphur, they would likely characterize it as "a substance of pale yellow colour, without taste or smell, insoluble in water, etc." (Paneth 2003, 129). All of these properties are lost as sulphur combines with oxygen to form "the gaseous, colourless, pungently smelling sulphur dioxide" (*ibid*.) – yet, no one would deny that sulphur dioxide contains sulphur, even though it does not exhibit the same properties. Paneth's solution to this contradiction was to distinguish between two ways in which the term 'sulphur' is used: sulphur dioxide only contains sulphur as a constituent (in the form of a 'basic substance') and it does not contain the actual simple substance yellow sulphur. Since Paneth only attributed the property of atomic number to his basic substances, their stability throughout chemical change did not lead to any contradiction in terms of changing properties.

Paneth's view might seem similar to that of Mendeleev, who distinguished between chemical elements and simple substance for the same reason. It would appear logical to reserve the term element for the *Grundstoff*, as Joseph Earley (2009; 2020) has proposed. However, both Paneth and Scerri have argued against this idea. Paneth's argument against

[228] The original publication can be found in *Schriften der Königsberger Gelehrten Gesellschaft* (Paneth 1931). The English translation first appeared in *The British Journal for the Philosophy of Science* (Paneth 1962) but here I cite from a republication in *Foundations of Chemistry* (Paneth 2003). For biographical information on Paneth and a summary of his 1931 lecture, see Ruthenberg (1997). For a summary of Paneth's contributions to history and philosophy of chemistry see the introduction of *Chemistry and Beyond* (Paneth 1964b). For his role role in the redefinition of the chemical element on the basis of atomic number in the early twentieth century, see Kragh (2000). See Ruthenberg (2009) on his philosophy of science.

[229] Heinrich Rudolph Post was the son of Paneth and founder of the department of History and Philosophy of Science at Chelsea College in London. He was also the translator of Paneth's famous paper and the supervisor of Eric Scerri's PhD thesis. For information on his life and work, see the introduction of French and Kamminga (1993). The German word 'Stoff' is difficult to translate to English. Depending on the context it could be translated as 'matter', 'stuff', or 'substance'.

Mendeleev's distinction was to say that Lavoisier tied the existence of elements to specific simple substances and introduced the two terms as synonyms (see Paneth 2003, 133; 1964b, 57). Scerri has similarly pointed towards a historical link between simple substances and chemical elements: according to this view, the change in definition from Lavoisier to Mendeleev corresponds to a shift between these two concepts as part of a longer historical "shifting emphasis between an abstract notion (Greek philosophers) to a more concrete notion (Lavoisier) and back to an abstract notion (Mendeleev and Paneth)" (Scerri 2020, 29; see also 2000; 2005; 2007, 112–17; 2009; 2012). In other words, Paneth and Scerri have both explicitly justified the double meaning of the concept on the basis of their interpretation of its history.

This is where my historical conclusions might provide more insight. Lavoisier and his followers did define chemical elements as simple substances, but in practice these two notions did not completely overlap. Moreover, it is impossible to distinguish between two separate 'abstract' and 'empirical' notions of chemical element in the nineteenth-century publications that I have studied. Provisional simplicity was not just a fact that could simply be observed; rather, identifying a substance as simple was already an interpretation of experimental results that required additional hypotheses regarding composition. Likewise, Mendeleev's 'abstract' characterization of chemical elements required just as much empirical data regarding the observable properties of chemical elements and the different compounds that they formed. It is therefore not clear what the distinction between empirical and abstract meanings refers to during this historical period.

The concept of element itself therefore is not purely empirical or abstract; instead, I would suggest that it is the notion of chemical element that makes it possible to speak of composition in abstraction from specific chemical substances. Looking back at the example of sulphur dioxide, the substance yellow sulphur indeed does not explain anything about its chemical composition. However, sulphur itself cannot be identified as an element without a knowledge of the different types of compounds that it forms. The different properties that characterize yellow sulphur as an elementary substance are not just its colour and lack of smell, but also its tendency to produce sulphur dioxide by combustion. The label 'element' is what enables us to point at both yellow sulphur and sulphur dioxide and say that they contain the same thing. In other words, identifying something as an

element already implies that it is possible to track it through different chemical reactions; this is what enables the correlation of changes in properties with changes in elementary composition.

Therefore, what may seem like a duality in the notion of 'element-hood' is simply this puzzling relation between macroscopic transformations of substances and the ways in which chemists represent them, a question that has interested many other historians and philosophers of chemistry (see for example Brakel 2000; Klein 2003; Rocke 2010; Bensaude-Vincent and Eastes 2020). Chemical composition provides us with an interesting example of the ways in which theory and experiment are completely intertwined within chemistry. Chemists, it is often said, do not only think with their heads but also with their hands. By inviting us to rethink these distinctions, history and philosophy of chemistry can lead towards a different view of scientific knowledge and practice more generally (see Rampling 2017; Chang 2017). This thesis has hopefully provided an additional illustration that the study of chemical practice can be a fruitful approach for any future work regarding these questions.

# Bibliography


Abney Salomon, Charlotte A. 2019. “The Pocket Laboratory: The Blowpipe in Eighteenth-Century Swedish Chemistry.” *Ambix* 66 (1): 1–22. https://doi.org/10.1080/00026980.2019.1573497.

Académie des Sciences, (France). 1853. *Table générale des comptes rendus de l’académie des sciences*. Vol. 1 (1835-1850). Paris: Mallet-Bachelier.

Accum, Friedrich Christian. 1818. *A Practical Treatise on the Use and Application of Chemical Tests with Concise Directions for Analysing Metallic Ores, Metals, Soils, Manures, and Mineral Waters*. 2nd ed. London: Thomas Boys.

Ador, E. 1894. “Notice sur la vie et les travaux de Jean-Charles Galissard de Marignac.” *Bibliothèque Universelle de Genève : Archives des Sciences Naturelles* 32: 5–61, 183–215.

Aikin, Charles Rochemont, and Arthur Aikin. 1807. *A Dictionary of Chemistry and Mineralogy with an Account of the Processes Employed in Many of the Most Important Chemical Manufactures*. 2 vols. London: John & Arthur Arch.

Ampère, André-Marie. 1816a. “Essai d’une classification naturelle des corps simples.” *Annales de Chimie et de Physique* 1: 295–308 and 373–94.

———. 1816b. “Suite de l’essai d’une classification naturelle des corps simples.” *Annales de Chimie et de Physique* 2: 5–31.

Arabatzis, Theodore. 2017. “What’s in It for the Historian of Science? Reflections on the Value of Philosophy of Science for History of Science.” *International Studies in the Philosophy of Science* 31 (1): 69–82. https://doi.org/10.1080/02698595.2017.1370924.

Arabatzis, Theodore, and Kostas Gavroglu. 2016. “From Discrepancy to Discovery: How Argon Became an Element.” In *The Philosophy of Historical Case Studies*, edited by Tilman Sauer and Raphael Scholl, 203–22. Dordrecht: Springer.

Ashbee, Ruth. 2007. “The Discovery of Chlorine: A Window on the Chemical Revolution.” In *An Element of Controversy: The Life of Chlorine in Science, Medecine, Technology and War,* by Hasok Chang and Catherine M. Jackson, 15–40. London: British Society for the History of Science.

Aubin, David. 2002. “Orchestrating Observatory, Laboratory and Field: Jules Janssen, the Spectroscope, and Travel.” *Nuncius* 17 (2): 615–33. https://doi.org/10.1163/182539102X00144.

Baird, Davis. 1993. “Analytic Chemistry and the ‘big’ Scientific Instrumentation Revolution.” *Annals of Science* 50: 267–90.

Banchetti-Robino, Marina. 2020. “The Changing Relation between Atomicity and Elementarity: From Lavoisier to Dalton.” In *What Is A Chemical Element? A Collection of Essays by Chemists, Philosophers, Historians, and Educators*, edited by Eric R. Scerri and Elena Ghibaudi, 87–108. Oxford: Oxford University Press.

Banks, R. E. 1986. “Isolation of Fluorine by Moissan: Setting the Scene.” *Journal of Fluorine Chemistry* 33: 3–26.

Bartha, Paul. 2010. *By Parallel Reasoning: The Construction and Evaluation of Analogical Arguments*. New York: Oxford University Press.

———. 2019. “Analogy and Analogical Reasoning.” In *Stanford Encyclopedia of Philosophy*, edited by Edward N. Zalta, Spring 2019 Edition. https://plato.stanford.edu/archives/spr2019/entries/reasoning-analogy/.

Beckman, Jenny. 2016. “The Publication Strategies of Jöns Jacob Berzelius (1779–1848): Negotiating National and Linguistic Boundaries in Chemistry.” *Annals of Science* 73 (2): 195–207. https://doi.org/10.1080/00033790.2016.1138503.

Belmar, Antonio García, and José Ramón Bertomeu-Sánchez. 2010. “Louis Jacques Thenard’s Chemistry Courses at the Collège de France, 1804–1835.” *Ambix* 57 (1): 48–63. https://doi.org/10.1179/174582310X12629173849962.

Bensaude-Vincent, Bernadette. 1981. “Les Pièges de l’Elémentaire : Contribution à l’Histoire de l’Elément Chimique.” PhD, Paris: Université Paris 1.

———. 1986. “Mendeleev’s Periodic System of Chemical Elements.” *The British Journal for the History of Science* 19 (1): 3–17.

———. 1990a. “A View of the Chemical Revolution through Contemporary Textbooks: Lavoisier, Fourcroy and Chaptal.” *British Journal for the History of Science* 23: 435–60.

———. 1990b. “Karlsruhe, Septembre 1860: L’atome En Congrès.” *Relations Internationales* 62: 149–69.

———. 1993. *Lavoisier : mémoires d'une révolution*. Figures de la science (Paris). Impr. SEPC. https://bibliotheques.paris.fr/Default/doc/SYRACUSE/284694/lavoisier-memoires-d-une-revolution.

———. 2008. *Matière à penser: essais d'histoire et de philosophie de la chimie*. Saint-Cloud: Presses universitaires de Paris Ouest.

———. 2010. "Lavoisier lecteur de Condillac." *Dix-huitième siècle*, Dix-huitième siècle, 42 (1): 472–89.

Bensaude-Vincent, Bernadette. 2019. "Reconceptualizing Chemical Elements through the Construction of the Periodic System." *Centaurus* 61 (4): 299–310. https://doi.org/10.1111/1600-0498.12228.

Bensaude-Vincent, Bernadette. 2020. "From Simple Substance to Chemical Element." In *What Is A Chemical Element? A Collection of Essays by Chemists, Philosophers, Historians, and Educators*, edited by Eric R. Scerri and Elena Ghibaudi, 32–52. Oxford: Oxford University Press.

Bensaude-Vincent, Bernadette, and Richard-Emmanuel Eastes. 2020. *Philosophie de la chimie*.

Bensaude-Vincent, Bernadette, Antonio García Belmar, and José Ramón Bertomeu Sánchez. 2003. *L'émergence d'une science des manuels: les livres de chimie en France (1789-1852)*. Histoire des sciences, des techniques et de la médecine. Paris: Archives contemporaines.

Bensaude-Vincent, Bernadette, and Antonio García-Belmar. 2015. "Mendeleev's Periodic Classification and Law in French Chemistry Textbooks." In *Early Responses to the Periodic System*, edited by Masanori Kaji, Helge Kragh, and Gábor Palló, 103–18. Oxford: Oxford University Press. https://doi.org/10.1093/oso/9780190200077.003.0013.

Bensaude-Vincent, Bernadette, and Andres Lundgren. 2000. *Communicating Chemistry: Textbooks and Their Audiences, 1789-1939*. Canton: Science History Publications.

Bensaude-Vincent, Bernadette, and Isabelle Stengers. 1992. *Histoire de La Chimie*. Histoire Des Sciences. Paris: La Découverte.

Beretta, Marco. 2008. “Lavoisier, Antoine-Laurent.” In *New Dictionary of Scientific Biography*, edited by Noretta Koertge, 213–20. Detroit: Charles Scribner’s Sons/Thomson Gale.

Bernhard, Carl Gustaf. 1992. “Berzelius as a European Traveler.” In *Enlightenment Science in the Romantic Era: The Chemistry of Berzelius and Its Cultural Setting*, edited by Evan Marc Melhado and Tore Frängsmyr, 222–41. Uppsala Studies in History of Science, v. 10. Cambridge ; New York: Cambridge University Press.

Berthollet, Claude-Louis. 1785. “Analyse de l’alkali volatile.” *Comptes rendus de l’Académie des Sciences*.

———. 1803. *Essai de Statistique Chimique*. Paris: Firmin-Didot.

———. 1811. “Rapport fait sur un ouvrage de MM. Gay-Lussac et Thénard, ayant pour titre: Recherches Physico-Chimiques, faites sur la pile etc. etc.” *Journal des Mines* 30: 6–56.

———. 1817. “Note sur la composition de l’acide oxymuriatique.” *Mémoires de Physique et de Chimie de la Société d’Arcueil* 3: 603–12.

Berthollet, Claude-Louis, Jean-Antoine Chaptal, and Louis-Nicolas Vauquelin. 1811. “Rapport sur un mémoire de M. Curaudau.” *Annales de Chimie* 80: 54–80, 121–39.

Bertomeu-Sánchez, José Ramon, Antonio Garcia-Belmar, and Bernadette Bensaude-Vincent. 2002. “Looking for an Order of Things: Textbooks and Chemical Classifications in Nineteenth Century France.” *Ambix* 49 (3): 227–50. https://doi.org/10.1179/amb.2002.49.3.227.

Berzelius, Jöns Jacob. 1807. “Extrait d’une lettre de M. Berzelius à M. Vauquelin.” *Annales de Chimie* 61: 256–59.

———. 1808a. “Alkaliernas decomposition.” *Economiska Annaler* 6: 114–21.

———. 1808b. *Lärbok i Kemien*. 1st ed. Stockholm: Nordström.

———. 1810a. “Einige prüfende Versuche über die Theorie der Voltaïschen Säule, und Nachricht von seinen Untersuchungen über die Metallisirung der Alkalien, und über die Zahlverhältnisse, wonach Sauerstoff und Schwefel sich mit den Metallen verbinden.” *Annalen der Physik* 35: 269–77.

———. 1810b. “Försök rörande de bestämde proportioner, hvari den oorganiska naturens beståndsdelar finnas förenade.” *Afhandlingar i Fysik, Kemi och Mineralogi* 3: 162–275.

———. 1810c. “Schreiben des Hrn. Prof. Berzelius in Stockholm an den Prof. Gilbert, über einige Gegenstände, welche zwischen Davy und den HH. Gay - Lussac und Thenard streitig sind, und über ein zweites neues Gesetz, welches er im Verfolge seiner Untersuchungen aufgefunden hat.” *Annalen der Physik* 37: 208–20.

———. 1811a. “Essai sur la nomenclature chimique.” *Journal de Phyisque, de Chimie et d’Histoire Naturelle* 73: 253–86.

———. 1811b. “Lettre de M. Berzelius à M. Berthollet.” *Annales de Chimie* 77: 63–82.

———. 1811c. “Versuch, die bestimmten und einfachen Verhältnisse aufzufinden, nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind.” *Annalen der Physik* 37: 249–334.

———. 1811d. “Versuch, die bestimmten und einfachen Verhältnisse aufzufinden, nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind, erste Fortsetzung.” *Annalen der Physik* 38: 161–226.

———. 1811e. “Versuch, die bestimmten und einfachen Verhältnisse aufzufinden, nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind, zweite Hälfte.” *Annalen der Physik* 37: 415–72.

———. 1812a. *Lärbok i Kemien*. 1st ed. Vol. 2. Stockholm: Nordström.

———. 1812b. “Versuch, die bestimmten und einfachen Verhältnisse aufzufinden, nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind, dritte Fortsetzung.” *Annalen der Physik* 40: 235–320.

———. 1812c. “Versuch, die bestimmten und einfachen Verhältnisse aufzufinden, nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind, zweite Fortsetzung.” *Annalen der Physik* 40: 162–208.

———. 1813a. “Experiments on the Nature of Azote, of Hydrogen and of Ammonia, and upon the Degrees of Oxidation of Which Azote Is Susceptible.” *Annals of Philosophy* 2: 357–68.

———. 1813b. “On the Nature of Muriatic Acid.” *Annals of Philosophy* 2 (10): 254–59.

———. 1815. “Objections to Sir H. Davy’s Theory of Chlorine.” *Annals of Philosophy* 6: 211–13.

———. 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 and 8: 272–80, 429–41, 200–209, 256–64, 470 (correction).

———. 1817. *Lärbok i kemien*. 2nd ed. 6 vols. Stockholm: Nordström.

———. 1818. “Undersökning af den Tantalit-art från Kimito i Finland, som ger canelbruns pulver.” *Afhandlingar i Fysik, Kemi och Mineralogi* 6: 237–46.

———. 1819. *Essai sur la Théorie des Proportions Chimiques*. Paris: Mequignon-Marvis.

———. 1821. *Lehrbuch der Chemie*. Translated by Karl August Blöde, Carl Palmstedt, and Friedrich Wöhler. 6 vols. Reutlingen: J.J. Macken’schen Buchhandlung.

———. 1824. “Untersuchungen über Flussspathsäure und deren merkwürdigsten Verbindungen.” *Annalen der Physik* 77: 169–230.

———. 1825a. *Lehrbuch der Chemie*. Translated by Friedrich Wöhler. 4 vols. Dresden: Arnoldischen Buchhandlung.

———. 1825b. “Untersüchungen über die Flussspathsäure und deren merkwurdigen Verbindungen.” *Annalen der Physik und Chemie*, 2, 4: 1–22.

———. 1827a. *Jahresbericht über die Fortschritte der physischen Wissenschaften*. Translated by Friedrich Wöhler. Vol. 6. Tübingen: Heinrich Laupp.

———. 1827b. *Lehrbuch der Chemie*. Translated by Friedrich Wöhler. 2nd ed. 3 vols. Dresden: Arnoldischen Buchhandlung.

———. 1829. *JahresBericht über die Fortschritte der physischen Wissenschaften*. Translated by Friedrich Wöhler. Vol. 8. Tübingen: Heinrich Laupp.

———. 1830. “Extrait d’une lettre de Berzelius à Dulong.” *Annales de Chimie et de Physique* 45: 332–35.

———. 1845. *Traité de chimie minérale, végétale et animale*. Translated by Ferdinand Hoefer and Esslinger. 2nd ed. 6 vols. Paris: Firmin-Didot.

———. 1847. *Rapport annuel sur les progrès de la chimie*. Vol. 8. Paris: Victor Masson.

———. 1912a. *Jac. Berzelius bref.* Edited by Henrik Gustaf Söderbaum. 17 vols. Uppsala: Kungl. Svenska Vetenskapsakademien.

———. 1912b. *Jac. Berzelius bref. II, Brefväxling mellan Berzelius och Sir Humphry Davy, 1808-1825*. Edited by Henrik Gustaf Söderbaum. Uppsala: Kungl. Svenska Vetenskapsakademien.

———. 1913. *Jac. Berzelius bref. III, Brefväxling mellan Berzelius och Alexandre Marcet, 1812-1822*. Edited by Henrik Gustaf Söderbaum. Uppsala: Kunglige Svenska Vetenskapsakademien.

Berzelius, Jöns Jacob, and Magnus Martin Pontin. 1808. "Försök med Alkaliernas och Jordarternas sönderdelning." *Economiska Annaler* 6: 110–30.

Berzelius, Jöns Jacob, and Friedrich Wöhler. 1901. *Briefwechsel zwischen J. Berzelius und F. Wöhler*. Edited by O. Wallach. 2 vols. Leipzig: Wilhelm Engelmann.

Bigg, Charlotte. 2003. "Spectroscopic Metrologies." *Nuncius* 18: 765–77.

Birembaut, Arthur. 1953. *Les préoccupations des minéralogistes français au 18e siècle*. Extrait des Actes du Congrès de Luxembourg. 72e session de l'Association française pour l'avancement des sciences. Luxembourg: Bourg-Bourger.

———. 1986. "L'enseignement de la minéralogie et des techniques minières." In *Enseignement et diffusion des sciences en France au dix-huitième siècle*, edited by René Taton and Charles Bedel, 2. éd., rev. éd. Histoire de la pensée 11. Paris: Hermann.

Bjerrum, Niels. 1926. "Die Entdeckung des Aluminiums." *Zeitschrift für Angewandte Chemie* 39 (9): 316–17. https://doi.org/10.1002/ange.19260390907.

Blomstrand, Christian Wilhelm. 1864. "Om metallsyrorna af Tantalgruppen, samt några mineralier, hvari dessa syror ingå." *Öfversigt af Kongl. Vetenskaps-akademiens forhandlingar* 21: 541–58.

———. 1865a. "Sur le niobium." *Comptes rendus de l'Académie des Sciences* 61: 852–55.

———. 1865b. "Sur les métaux du groupe du tantale." *Comptes rendus de l'Académie des Sciences* 61: 337–40.

———. 1870. "Bemerkungen über die Elemente." *Berichte der deutschen chemischen Gesellschaft* 3: 533–39.

Boas Hall, Marie. 1968. "The History of the Concept of Element." In *John Dalton and the Progress of Science,* 21–39. Manchester: Manchester University Press.

Boyce, Conal. 2019. “Mendeleev’s Elemental Ontology and Its Philosophical Renditions in German and English.” *HYLE - International Journal for the Philosophy of Chemistry* 25 (1): 49–70.

Brakel, Jaap van. 2000. *Philosophy of Chemistry: Between the Manifest and the Scientific Image*. Louvain Philosophical Studies 15. Leuven: Leuven University Press.

———. 2008. “Pure Chemical Substances.” In *Stuff: The Nature of Chemical Substances*, edited by Klaus Ruthenberg and Jaap Van Brakel, 145–61. Würzburg: Königshausen & Neumann.

Bret, Patrice. 2016. “The Letter, the Dictionary and the Laboratory: Translating Chemistry and Mineralogy in Eighteenth-Century France.” *Annals of Science* 73 (2): 122–42. https://doi.org/10.1080/00033790.2015.1034780.

Bret, Patrice, and Keiko Kawashima. 2019. “Madame Lavoisier’s Diffusion and Defence of Oxygen Against Phlogiston: Her Translations of Richard Kirwan’s Essays.” In *Women in Their Element*, by Annette Lykknes and Brigitte Van Tiggelen, 85–98. WORLD SCIENTIFIC. https://doi.org/10.1142/9789811206290_0004.

Brock, William H. 1985. *From Protyle to Proton: William Prout and the Nature of Matter, 1785-1985*. Bristol ; Boston: A. Hilger.

———. 1992. *The Fontana History of Chemistry*. London: Fontana Press.

———. 2003. “Breeding Chemists in Giessen.” *Ambix* 50 (1): 25–70. https://doi.org/10.1179/amb.2003.50.1.25.

Brooke, John Hedley. 1969. “The Role of Analogical Argument in the Development of Organic Chemistry.” PhD, Cambridge: University of Cambridge.

———. 1980. “Davy’s Chemical Outlook: The Acid Test.” In *Science and the Sons of Genius: Studies on Humphry Davy*, edited by Sophie Forgan, 121–75. London: Science Reviews Ltd.

Brooks, Nathan. 2020. “Dmitrii Mendeleev’s Concept of the Chemical Element Prior to the Periodic Law.” In *What Is A Chemical Element? A Collection of Essays by Chemists, Philosophers, Historians, and Educators*, edited by Eric R. Scerri and Elena Ghibaudi, 53–68. Oxford: Oxford University Press.

Bycroft, Michael. forthcoming. “Chemistry.” In *Gems and the New Science: Matter and Value in the Scientific Revolution*. University of Chicago Press.

Caswell, Lyman R. 2003. “Andrés Del Rio, Alexander von Humboldt, and the Twice-Discovered Element.” *Bull. Hist. Chem.* 28 (1): 7.

Chabot, Hugues. 2000. “Le tribunal de la science. Les rapports négatifs à l’Académie des sciences comme illustrations d’un scientifiquement (in)correct (1795-1835).” *Annales historiques de la Révolution française*, no. 320 (June): 173–82. https://doi.org/10.4000/ahrf.161.

———. 2006. “Les Origines d’un Nouvel Elément Chimique: l’Affaire du Chlore.” In *Du nouveau dans les sciences: recueil issu du séminaire Lyon-Grenoble d’histoire et de philosophie des sciences*, 121–69. St-Martin-d’Hères: Groupe de recherches sur la philosophie et le langage, Université des sciences sociales de Grenoble.

Chang, Hasok. 2004. *Inventing Temperature: Measurement and Scientific Progress*. Oxford Studies in Philosophy of Science. Oxford ; New York: Oxford University Press.

———. 2007. “Scientific Progress: Beyond Foundationalism and Coherentism.” *Royal Institute of Philosophy Supplement* 61 (October): 1–20. https://doi.org/10.1017/S1358246107000124.

———. 2011a. “Compositionism as a Dominant Way of Knowing in Modern Chemistry.” *History of Science* 49: 247–68.

———. 2011b. “The Persistence of Epistemic Objects Through Scientific Change.” *Erkenntnis* 75 (3): 413–29.

———. 2012a. “Beyond Case Studies: History as Philosophy.” In *Integrating History and Philosophy of Science: Problems and Prospects*, edited by Seymour Mauskopf and Tad Schmaltz, 109–24. Dordrecht: Springer.

———. 2012b. *Is Water H2O? Evidence, Pluralism and Realism*. Boston Studies in the Philosophy of Science 293. Dordrecht: Springer.

———. 2015. “The Chemical Revolution Revisited.” *Studies in History and Philosophy of Science Part A* 49 (February): 91–98. https://doi.org/10.1016/j.shpsa.2014.11.002.

———. 2016. “The Rising of Chemical Natural Kinds Through Epistemic Iteration.” In *Natural Kinds and Classification in Scientific Practice*, edited by Catherine Kendig, 33–46. New York: Routledge.

———. 2017. “What History Tells Us about the Distinct Nature of Chemistry.” *Ambix* 64 (4): 360–74. https://doi.org/10.1080/00026980.2017.1412135.

———. 2022. *Realism for Realistic People: A New Pragmatist Philosophy of Science*. Cambridge: Cambridge University Press.

Chemla, Karine. 2014. “Observing Mathematical Practices as a Key to Mining Our Sources and Conducting Conceptual History. Division in Ancient China as a Case Study.” In *Science After the Practice Turn in the Philosophy, History and Social Studies of Science*, edited by Léna Soler, Sjoerd Zwart, and Michael Lynch, 238–68. New York: Routledge.

Chevreul, Michel Eugène. 1816. “Aluminium.” In *Dictionnaire des Sciences Naturelles*, edited by F. G. Levrault, 1:134. Paris: Le Normant.

Christensen, Dan Charly. 2013. *Hans Christian Ørsted: Reading Nature’s Mind*. Oxford: Oxford Univ. Press.

Collet-Descotils, H.-V. 1805. “Analyse de la mine brune de plomb de Zimapan, dans le royaume du Mexique, envoyée par M. Humboldt, et dans laquelle M. Del Rio dit avoir découvert un nouveau métal,.” *Annales de Chimie* 53: 268–71.

Connell, A. 1854. “Observations on the Nomenclature of the Metals Contained in Columbite and Tantalite.” *The Philosophical Magazine*, 4, 7: 461–63.

Cornu, Armel. 2019. “Appraising Waters — The Assimilation of Chemists into the Trade of Mineral Waters in Eighteenth-Century France.” *Circumscribere: International Journal for the History of Science*, no. 24 (October). https://doi.org/10.23925/1980-7651.2019v24;p66-82.

———. 2022. “Enlightening Water: Science, Market & Regulation of Mineral Waters in Eighteenth-Century France.” PhD, Uppsala: Uppsala University.

Crosland, Maurice. 1962. *Historical Studies in the Language of Chemistry*. London: Heinemann.

———. 1973. “Lavoisier’s Theory of Acidity.” *Isis* 64 (3): 306–25.

———. 1978. *Gay-Lussac, Scientist and Bourgeois*. Cambridge ; New York: Cambridge University Press.

———. 1980. “Davy and Gay-Lussac: Competition and Contrast.” In *Science and the Sons of Genius: Studies on Humphry Davy*, edited by Sophie Forgan. London: Science Reviews Ltd.

———. 1992. *Science under Control: The French Academy of Sciences, 1795-1914*. Cambridge ; New York: Cambridge University Press.

———. 1994. *In the Shadow of Lavoisier: The Annales de Chimie and the Establishment of a New Science*. BSHS Monographs 9. Oxford: The Alden Press.

———. 2003. “Research Schools of Chemistry from Lavoisier to Wurtz.” *The British Journal for the History of Science* 36 (3): 333–61. https://doi.org/10.1017/S0007087403005077.

———. 2009. “Lavoisier’s Achievement; More Than a Chemical Revolution.” *Ambix* 56 (2): 93–114. https://doi.org/10.1179/174582309X441417.

Crowther, Karen, Niels Linnemann, and Christian Wuthrich. 2019. “What We Cannot Learn from Analogue Experiments.” *ArXiv:1811.03859 [Gr-Qc, Physics:Physics]*, March. http://arxiv.org/abs/1811.03859.

Currie, Adrian. 2016. “Ethnographic Analogy, the Comparative Method, and Archaeological Special Pleading.” *Studies in History and Philosophy of Science Part A* 55 (February): 84–94. https://doi.org/10.1016/j.shpsa.2015.08.010.

———. 2018. *Rock, Bone, and Ruin: An Optimist’s Guide to the Historical Sciences*. Life and Mind: Philosophical Issues in Biology and Psychology. Cambridge: The MIT Press.

Dalton, John. 1810. *A New System of Chemical Philosophy*. Vol. 1 part 2. Manchester: Russell.

Dardashti, R., K. P. Y. Thebault, and E. Winsberg. 2015. “Confirmation via Analogue Simulation: What Dumb Holes Could Tell Us about Gravity.” *The British Journal for the Philosophy of Science*, May, axv010. https://doi.org/10.1093/bjps/axv010.

Davis, Tenney L. 1931. “Boyle’s Conception of Element Compared with That of Lavoisier.” *Isis* 16 (1): 82–91.

Davy, Humphry. 1800. *Researches Chemical and Philosophical; Chiefly Concerning Nitrous Oxide, or Dephlogisticated Nitrous Air, and Its Respiration*. London: J. Johnson.

———. 1808a. “Electro-Chemical Researches, on the Decomposition of the Earths; with Observations on the Metals Obtained from the Alkaline Earths, and on the Amalgam Procured from Ammonia.” *Philosophical Transactions of the Royal Society of London* 98: 333–70.

———. 1808b. “The Bakerian Lecture, on Some New Phenomena of Chemical Changes Produced by Electricity, Particularly the Decomposition of the Fixed Alkalies, and the Exhibition of the New Substances Which Constitute Their Bases; and on the General Nature of Alkaline Bodies.” *Philosophical Transactions of the Royal Society of London* 98 (1): 1–45.

———. 1809a. “New Analytical Researches on the Nature of Certain Bodies, Being an Appendix to the Bakerian Lecture for 1808.” *Philosophical Transactions of the Royal Society* 99: 450–70.

———. 1809b. “Suite des recherches électrochimiques sur la décomposition des terres, avec des observations sur les métaux obtenus des terres alcalines, et sur un amalgame produit avec l’ammoniaque.” Translated by C. A. Prieur. *Annales de Chimie* 70: 225–55.

———. 1810a. “Observations sur les recherches de MM. Gay-Lussac et Thenard, relativement a l’amalgame de l’ammoniaque.” *Journal de Phyisque, de Chimie et d’Histoire Naturelle* 70: 389–92.

———. 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: 231–57.

———. 1810c. “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.

———. 1811a. “On a Combination of Oxymuriatic Gas and Oxygene Gas.” *Philosophical Transactions of the Royal Society* 101: 155–62.

———. 1811b. “The Bakerian Lecture. On Some of the Combinations of Oxymuriatic Gas and Oxygene, and on the Chemical Relations of These Principles, to Inflammable Bodies.” *Philosophical Transactions of the Royal Society of London* 101: 1–35.

———. 1812. *Elements of Chemical Philosophy*. 1 vols. London: J. Johnson.

———. 1813a. “On a New Detonating Compound – in a Letter to the Right Hon. Sir Joseph Banks.” *Philosophical Transactions of the Royal Society* 103: 1–7.

———. 1813b. “Some Experiments and Observations on the Substances Produced in Different Chemical Processes on Fluor Spar.” *Philosophical Transactions of the Royal Society* 103: 263–79.

———. 1813c. “Some Further Observations on a New Detonating Substance. In a Letter from Sir Humphry Davy to the Right Hon. Sir Joseph Banks.” *Philosophical Transactions of the Royal Society* 103: 242–51.

———. 1814a. “Some Experiments and Observations on a New Substance Which Becomes a Violet Coloured Gas by Heat.” *Philosophical Transactions of the Royal Society* 104: 74–93.

———. 1814b. “An Account of Some New Experiments on the Fluoric Compounds; with Some Observations on Other Objects Chemical Inquiry.” *Philosophical Transactions of the Royal Society of London* 104 (December): 62–73. https://doi.org/10.1098/rstl.1814.0006.

———. 1816a. “On the Analogies between the Undecompounded Substances, and on the Constitution of Acids.” *Quarterly Journal of Science* 1: 283–88.

———. 1816b. “Two Letters to Mr. Ampère.” *Annales de Chimie et de Physique* 1: 21–23.

———. 1839. *The Collected Works of Sir Humphry Davy*. Edited by John Davy. 9 vols. London: Smith, Elder &co.

———. 1840. *The Collected Works of Sir Humphry Davy*. Edited by John Davy. Vol. 8. 9 vols. London: Smith, Elder &co.

Davy, John. 1811a. “On the Nature of Oximuriatic Gas, in Reply to Mr Murray.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 29: 39–44.

———. 1811b. “Some Remarks on the Observations and Experiments of Mr Murray on the Nature of Oximuriatic Acid, and Its Relations to Muriatic Acid.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 28: 193–206.

———. 1812a. “An Account of a New Gas, With a Reply to Mr Murray’s Last Observations on Oximuriatic Gas.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 30: 28–33.

———. 1812b. “On the Nature of Oximuriatic and Muriatic Acid Gas, in Reply to Mr Murray.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 31: 310–16.

———. 1813. “An Account of an Experiment Made in the College Laboratory, Edinburgh, Drawn up by John Davy, Esq.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 34: 68–72.

Dawson, Gowan, Bernard V. Lightman, Sally Shuttleworth, and Jonathan R. Topham, eds. 2020. *Science Periodicals in Nineteenth-Century Britain: Constructing Scientific Communities*. Chicago: University of Chicago Press. https://books.google.fr/books?id=tC7PDwAAQBAJ&pg=PA1&hl=fr&source=gbs_toc_r&cad=2#v=onepage&q&f=false.

Debus, Allen. 1967. “Fire Analysis and the Elements in the Sixteenth and the Seventeenth Centuries.” *Annals of Science* 23: 127–47.

DeKosky, Robert K. 1973. “Spectroscopy and the Elements in the Late Nineteenth Century: The Work of Sir William Crookes.” *The British Journal for the History of Science* 6 (4): 400–423.

Del Rio, Andrés. 1822. “Ein Paar Anmerkungen zu dem Handbuche der Mineralogie von Hoffmann fortgesetzt von Breithaupt (über das Braunbleierz aus Mexico und die ManganBlende).” *Annalen der Physik* 71: 7–12.

———. 1832. *Elementos de orictognósia: ó del conocimiento de los fósiles*. 2nd ed. Philadelphia: Imprenta de J. F. Hurtel. https://archive.org/details/elementosdeoric00werngoog/page/n6.

Delafontaine, Marc. 1866. “Sur les oxydes de niobium.” *Bibliothèque Universelle de Genève : Archives des Sciences Naturelles* 27: 167–73.

Delafosse, Gabriel. 1822. “Alumine.” In *Dictionnaire classique d’histoire naturelle*, edited by Bory de Saint Vincent, 1:235–36. Paris: Rey et Gravier.

Delamétherie, Jean-Claude. 1812. “Discours Préliminaire.” *Journal de Phyisque, de Chimie, d’Histoire Naturelle et Des Arts* 74: 1–120.

Descola, Philippe. 2005. *Par Delà Nature et Culture*. Paris: Gallimard.

Deterville, Jean-François-Pierre, ed. 1818. “Métaux.” In *Nouveau dictionnaire d’histoire naturelle*, 20:377–415.

Dolan, Brian P. 1998. “Blowpipes and Batteries: Humphry Davy, Edward Daniel Clarke, and Experimental Chemistry in Early Nineteenth-Century Britain.” *Ambix* 45 (3): 137–62. https://doi.org/10.1179/amb.1998.45.3.137.

———. 2003. “Embodied Skills and Traveling Savants.” In *Travels of Learning: A Geography of Science in Europe*, 115–41. Dordrecht: Springer.

Dumas, Jean-Baptiste. 1828. *Traité de Chimie Appliquée aux Arts*. 8 vols. Paris: Bechet Jeune.

———. 1855. “Présentation d’échantillons d’aluminium au nom de M. Deville.” *Comptes rendus de l’Académie des Sciences* 40: 1296–97.

———. 1859. *Mémoire sur les équivalents des corps simples*. Paris: Mallet-Bachelier.

Duncan, A. M. 1970. “The Functions of Affinity Tables and Lavoisier’s List of Elements.” *Ambix* 17: 28–42.

———. 1996. *Laws and Order in Eighteenth-Century Chemistry*. Oxford : New York: Clarendon Press ; Oxford University Press.

Earley, Joseph E. 2005. “Why There Is No Salt in the Sea.” *Foundations of Chemistry* 7: 85–102.

———. 2009. “How Chemistry Shifts Horizons: Element, Substance, and the Essential.” *Foundations of Chemistry* 11 (2): 65–77. https://doi.org/10.1007/s10698-008-9054-5.

———. 2020. “Origins of the Ambiguity of the Current Definition of Chemical Element.” In *What Is A Chemical Element? A Collection of Essays by Chemists, Philosophers, Historians, and Educators*, edited by Eric R. Scerri and Elena Ghibaudi, 109–23. Oxford: Oxford University Press.

Ekeberg, Anders. 1802. “Uplysning om Ytterjordens egenskaper, i synnerhet i jämförelse met Berryljorden: om de Fossilier, hvari förstnämnde jord innehålles, samt om en ny uptäckt kropp af metallisk natur.” *Kungliga Vetenskaps Academiens Handlingar* 23: 68–83.

Engeström, Gustav von. 1788. “Description of a Mineralogical Pocket-Laboratory; and Especially the Use of the Blowpipe in Mineralogy.” In *An Essay Towards a System of Mineralogy*, by Axel Fredrik Cronstedt, 2nd ed., 2:925–76. London: Charles Dilly.

Evans, C. H., ed. 1996. *Episodes from the History of the Rare Earth Elements*. Chemists and Chemistry, v. 15. Dordrecht & Boston: Kluwer Academic Publishers.

Evans, C. H., and Ferenc Szabadváry. 1996. “The 50 Years Following Mosander.” In *Episodes from the History of the Rare Earth Elements*, edited by C. H. Evans, 55–66. Chemists and Chemistry, v. 15. Dordrecht & Boston: Kluwer Academic Publishers.

Farrar, W. V. 1965. “Nineteenth-Century Speculations on the Complexity of the Chemical Elements.” *The British Journal for the History of Science* 2 (8): 297–323.

Feest, Uljana, and Friedrich Steinle, eds. 2012. *Scientific Concepts and Investigative Practice*. Berlin Studies in Knowledge Research, volume 3. Berlin: De Gruyter.

Ferrand, Louis. 1961. *Histoire de la science et des techniques de l’aluminium: et ses développements industriels...* France: l’auteur.

Figuier, Louis. 1862. *L’année scientifique et industrielle*. Vol. 6. Paris: Hachette.

Fisher, Amy A. 2018. “Inductive Reasoning in the Context of Discovery: Analogy as an Experimental Stratagem in the History and Philosophy of Science.” *Studies in History and Philosophy of Science Part A* 69 (June): 23–33. https://doi.org/10.1016/j.shpsa.2018.01.008.

Fontani, Marco, Mariagrazia Costa, and Mary Virginia Orna. 2015. *The Lost Elements: The Periodic Table’s Shadow Side*. Oxford: Oxford Univ. Press.

Fors, Hjalmar. 2014. “Elements in the Melting Pot: Merging Chemistry, Assaying, and Natural History, Ca. 1730–60.” *Osiris* 29 (1): 230–44. https://doi.org/10.1086/678105.

———. 2015. *The Limits of Matter: Chemistry, Mining and Enlightenment*. Chicago: University of Chicago Press.

Fourcroy, Antoine-François. 1782. *Leçons élémentaires d'histoire naturelle et de chimie*. 2 vols. Paris: Simon.

———. 1800. *Système des Connaissances Chimiques et de Leurs Applications Aux Phénomènes de la Nature et de l'Art*. 10 vols. Paris: Baudouin.

French, Steven, and Harmke Kamminga, eds. 1993. *Correspondence, Invariance and Heuristics: Essays in Honour of Heinz Post*. Dordrecht; London: Springer.

Fulford, Tim, and Sharon Ruston, eds. 2020. *The Collected Letters of Humphry Davy*. New York, NY: Oxford University Press.

Fullmer, Juke Z. 1975. "Davy's Priority in the Iodine Dispute: Further Documentary Evidence." *Ambix* 22 (1): 39–51. https://doi.org/10.1179/amb.1975.22.1.39.

Fyfe, Aileen, Noah Moxham, Julie McDougall-Waters, and Camilla Mørk Røstvik. 2022. *A History of Scientific Journals: Publishing at the Royal Society, 1665-2015*. London: UCL Press.

Gadolin, Johan. 1794. "Undersökning af en svart tung Stenart ifrån Ytterby Stenbrott i Roslagen." *Kongl. Vetenskaps Academiens Nya Handlingar* 15: 137–55.

Gay-Lussac, Louis-Joseph. 1809. "Mémoire sur la combinaison des substances gazeuses, les unes avec les autres." *Mémoires de Physique et de Chimie de la Société d'Arcueil* 2: 207–34.

———. 1813. "Sur un nouvel acide formé avec la substance découverte par M. Courtois." *Annales de Chimie* 83: 311–18.

———. 1814. "Mémoire sur l'iode." *Annales de Chimie* 91: 5–160.

———. 1816. "Observations sur les combinaisons formées par l'iode et par le chlore." *Annales de Chimie et de Physique* 1: 157–73.

Gay-Lussac, Louis-Joseph, and Louis-Jacques Thenard. 1809. "Extrait des mémoires lus à l'institut national, depuis le 7 mars 1808 jusqu'au 27 février 1809." *Mémoires de Physique et de Chimie de la Société d'Arcueil* 2: 295–358.

———. 1810a. "Observations sur les trois précédens mémoires de M. Davy." *Annales de Chimie* 75: 290–316.

———. 1810b. “Recherches sur la production d’un amalgame par l’ammoniaque et les sels ammoniacaux au moyen de la pile voltaïque.” *Annales de Chimie* 73: 197–214.

———. 1811. *Recherches Physico-Chimiques*. Vol. 2. Paris: Determille.

Gilbert, Ludwig Wilhelm. 1811. “Zusatz. Ist der den Tantalit oder Columbit charakterisirende Körper ein Metalloxyd oder eine Erde?” *Annalen der Physik* 37: 105–8.

Gingras, Yves, and Alexandre Guay. 2011. “The Uses of Analogies in Seventeenth and Eighteenth Century Science.” *Perspectives on Science* 19 (2): 154–91. https://doi.org/10.1162/POSC_a_00035.

Gmelin, Leopold. 1843. *Handbuch der Chemie*. 10 vols. Heidelberg: Karl Winter.

Golinski, Jan. 1992. *Science as Public Culture: Chemistry and Enlightenment in Britain, 1760–1820*. New York: Cambridge University Press.

———. 1994. “Precision Instruments and the Demonstrative Order of Proof in Lavoisier’s Chemistry.” *Osiris* 9: 30–47.

———. 2019. “‘The Fitness of Their Union’: Travel and Health in the Letters of Humphry and Jane Davy.” *Ambix* 66 (2–3): 181–94. https://doi.org/10.1080/00026980.2019.1616945.

Grand, H. E. Le. 1975. “The ‘Conversion’ of C.-L. Berthollet to Lavoisiers’ Chemistry.” *Ambix* 22 (1): 58–70. https://doi.org/10.1179/amb.1975.22.1.58.

Gray, Tamsin, Rosemary Coates, and Mårten Åkesson. 2007. “The Elementary Nature of Chlorine.” In *An Element of Controversy: The Life of Chlorine in Science, Medecine, Technology and War*, edited by Hasok Chang and Catherine M. Jackson, 41–72. London: British Society for the History of Science.

Griffith, W. P., and P. J. T. Morris. 2003. “Charles Hatchett FRS (1765-1847), Chemist and Discoverer of Niobium.” *Notes and Records of the Royal Society of London* 57 (3): 299–316. https://doi.org/10.1098/rsnr.2003.0216.

Guerlac, Henry. 1973. “Lavoisier, Antoine-Laurent.” In *Dictionary of Scientific Biography*, 8:66–91. New York: Scribner.

Guyton de Morveau, Louis-Bernard. 1777a. *Elémens de chymie théorique et pratique, rédigé dans un nouvel ordre, d’après les découvertes modernes, pour servir aux cours publics de l’Académie de Dijon*. Dijon: Frantin.

———. 1777b. “HEPAR.” In *Supplément à l’Encyclopédie, ou Dictionnaire raisonné des sciences, des arts et des métiers*, edited by Denis Diderot and Jean le Rond d’Alembert, 3:347–48. Amsterdam: Rey.

Hatchett, Charles. 1802. “An Analysis of a Mineral Substance from North America, Containing a Metal Hitherto Unknown.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 2: 129–38 and 176–80.

Heilbron, John. 2000. “Analogy in Volta’s Exact Natural Philosophy.” *Nuova Voltiana* 1: 1–24.

Henderson. 2014. “The Physics and Poetry of Analogy.” *Victorian Studies* 56 (3): 389. https://doi.org/10.2979/victorianstudies.56.3.389.

Hendry, Robin Findlay. 2005. “Lavoisier and Mendeleev on the Elements.” *Foundations of Chemistry* 7: 31–48.

———. 2006. “Substantial Confusion.” *Studies in History and Philosophy of Science Part A* 37 (2): 322–36. https://doi.org/10.1016/j.shpsa.2006.03.002.

———. 2019. “Elements and (First) Principles in Chemistry.” *Synthese*, July. https://doi.org/10.1007/s11229-019-02312-8.

Henry, William. 1809. “Experiments on Ammonia, and an Account of a New Method of Analyzing It, by Combustion with Oxygen and Other Gases; in a Letter to Humphry Davy.” *Philosophical Transactions of the Royal Society of London* 99: 430–49. https://doi.org/10.1098/rstl.1809.0028.

Hermann, Hans Rudolph. 1846. “Untersuchungen russischer Mineralien.” *Journal für praktische Chemie* 38 (1): 91–123. https://doi.org/10.1002/prac.18460380112.

———. 1847a. “Bemerkungen zu H. Rose’s Urtheil über das IImenium.” *Journal für praktische Chemie* 42 (1): 129–35. https://doi.org/10.1002/prac.18470420116.

———. 1847b. “Untersuchungen über das Ilmenium.” *Journal für praktische Chemie* 40 (1): 457–80. https://doi.org/10.1002/prac.184704001110.

———. 1855. “Untersuchungen Über Ilmenium, Niobium und Tantal.” *Journal für praktische Chemie* 65 (1): 54–90. https://doi.org/10.1002/prac.18550650104.

———. 1856. “Untersuchungen über Niobium.” *Journal für praktische Chemie* 68: 65–97.

———. 1861. “Bemerkungen über das Dianium.” *Journal für praktische Chemie* 83 (1): 106–9. https://doi.org/10.1002/prac.18610830107.

———. 1865. “Untersuchungen über Tantal und Niobium, sowie über Ilmenium, ein neues Metall.” *Journal für praktische Chemie* 95 (1): 65–118. https://doi.org/10.1002/prac.18650950108.

———. 1866. “Bemerkungen zu Marignac’s Untersuchungen über Niobium und Ilmenium.” *Journal für praktische Chemie* 99 (1): 21–33. https://doi.org/10.1002/prac.18660990105.

———. 1871. “Fortgesetzte Untersuchungen über die Verbindungen von Ilmenium und Niobium, sowie über die Zusammensetzung der Niobmineralien.” *Journal für praktische Chemie* 112: 178–210.

———. 1877. “Fortgesetzte Untersuchungen über die Verbindungen der Metalle der Tantalgruppe, so wie über Neptunium, ein neues Metall.” *Journal für praktische Chemie* 123: 105–50.

Hesse, Mary B. 1966. *Models and Analogies in Science*. Notre Dame: University of Notre Dame Press.

Hijmans, Sarah N. 2022a. “Analogy and Composition in Early Nineteenth-Century Chemistry The Case of Aluminium.” *European Journal for Philosophy of Science* 12 (1): 5. https://doi.org/10.1007/s13194-021-00442-w.

———. 2022b. “The Tantalum Metals (1801–1866): Nineteenth-Century Analytical Chemistry and the Identification of Chemical Elements.” *Ambix* 69 (4): 399–419. https://doi.org/10.1080/00026980.2022.2133806.

Hirsh, Richard F. 1981. “A Conflict of Principles: The Discovery of Argon and the Debate over Its Existence.” *Ambix* 28 (3): 121–30. https://doi.org/10.1179/amb.1981.28.3.121.

Hisinger, Wilhelm, and Jöns Jacob Berzelius. 1804. “Cerium, ein neues Metall aus einer schwedischen Steinart, Bastnas Tungstein genannt.” *Neues allgemeines Journal der Chemie* 2: 397–418.

Holmes, Frederic Lawrence. 1971. “Analysis by Fire and Solvent Extractions: The Metamorphosis of a Tradition.” *Isis* 62 (2): 128–48.

———. 1985. *Lavoisier and the Chemistry of Life: An Exploration of Scientific Creativity*. Madison: University of Wisconsin Press.

———. 1988. “Lavoisier’s Conceptual Passage.” *Osiris* 4: 82–92.

———. 1989. *Eighteenth-Century Chemistry as an Investigative Enterprise: Five Lectures Delivered at the International Summer School in History of Science, Bologna, August 1988*. Berkeley (Calif.): University of California at Berkeley.

Holmes, Harry N. 1930. “The Story of Aluminium.” *Journal of Chemical Education* 7: 233–44.

Homburg, Ernst. 1993. *Van beroep “Chemiker”: de opkomst van de industriële chemicus en het polytechnische onderwijs in Duitsland, 1790-1850*. Delft: Delftse Universitaire Pers.

———. 1999. “The Rise of Analytical Chemistry and Its Consequences for the Development of the German Chemical Profession (1780–1860).” *Ambix* 46 (1): 1–32. https://doi.org/10.1179/amb.1999.46.1.1.

Hooijkaas, Reijer. 1933. “Het begrip element in zijn historisch-wijsgeerige ontwikkeling.” PhD, Utrecht: Rijksuniversiteit Utrecht.

Hricko, Jonathon. 2021. “What Can the Discovery of Boron Tell Us about the Scientific Realism Debate?” In *Contemporary Scientific Realism: The Challenge from the History of Science*, edited by Timothy D. Lyons and Peter Vickers, 1st ed., 33–55. New York: Oxford University Press.

Hudson, John A. 2005. “Analytical Chemistry.” In *Chemical History: Reviews of the Recent Literature*, edited by Colin A. Russell and Gerrylynn K. Roberts, 154–84. Cambridge: Royal Society of Chemistry.

Jackson, Catherine M. 2015. “The ‘Wonderful Properties of Glass’: Liebig’s Kaliapparat and the Practice of Chemistry in Glass.” *Isis* 106 (1): 43–69.

Jagnaux, R. 1891. *Histoire de la chimie*. Paris: Baudry et Cie.

James, Frank A. J. L. 1983. “The Establishment of Spectro-Chemical Analysis as a Practical Method of Qualitative Analysis, 1854–1861.” *Ambix* 30 (1): 30–53. https://doi.org/10.1179/amb.1983.30.1.30.

———. 1984. “Of ‘Medals and Muddles’, the Context of the Discovery of Thallium: William Crookes’s Early Spectro-Chemical Work.” *Notes and Records of the Royal Society of London* 39 (1): 65–90.

———. 1985. “The Creation of a Victorian Myth: The Historiography of Spectroscopy.” *History of Science* 23: 2–24.

———. 1988. “The Practical Problems of ‘New’ Experimental Science: Spectro-Chemistry and the Search for Hitherto Unknown Chemical Elements in Britain 1860-1869.” *The British Journal for the History of Science* 21 (2): 181–94.

———. 2019. “Humphry Davy’s Early Chemical Knowledge, Theory and Experiments: An Edition of His 1798 Manuscript, ‘An Essay on Heat and the Combinations of Light’ from The Royal Institution of Cornwall, Courtney Library, MS DVY/2.” *Ambix* 66 (4): 303–45. https://doi.org/10.1080/00026980.2019.1684080.

———. 2021. “Making Money from the Royal Navy in the Late Eighteenth Century: Charles Kerr on Antigua ‘Breathing the True Spirit of a West India Agent.’” *The Mariner’s Mirror* 107 (4): 402–19. https://doi.org/10.1080/00253359.2021.1978257.

Jorpes, Johan Erik. 1970. *Jac. Berzelius, His Life and Work*. Berkeley: University of California Press.

Karsten, D. L. W. 1804. *Tablas mineralogicas dispuestas segun los descubrimientos mas recientes e ilustradas con notas*. Translated by Andrés Del Rio. Mexico City: Zuñiga y Ontiveros.

Kauffman, George B. 1975. “Christian Wilhelm Blomstrand (1826-1897) Swedish Chemist and Mineralogist.” *Annals of Science* 32: 13–37.

Kawashima, Keiko. 2013. *Emilie du Châtelet et Marie-Anne Lavoisier. Science et genre au XVIIIe siècle*. Champion essais 21. Paris: Honore Champion Editions.

Kim, Mi Gyung. 2003. *Affinity, That Elusive Dream: A Genealogy of the Chemical Revolution*. Transformations. Cambridge, Mass: MIT Press.

Klaproth, Martin Heinrich. 1810. “Chemische Untersuchung des Tantalits.” *Beiträge zur chemischen Kenntnis der Mineralkörper* 5: 1–5.

Klein, Ursula. 1994. “Origin of the Concept Chemical Compound.” *Science in Context* 7 (2): 163–204. https://doi.org/10.1017/S0269889700001666.

———. 2001a. “Berzelian Formulas as Paper Tools in Early Nineteenth-Century Chemistry.” *Foundations of Chemistry*, 26.

———. 2001b. “Paper Tools in Experimental Cultures.” *Studies in History and Philosophy of Science Part A* 32 (2): 265–302. https://doi.org/10.1016/S0039-3681(01)00010-3.

———. 2003. *Experiments, Models, Paper Tools: Cultures of Organic Chemistry in the Nineteenth Century*. Writing Science. Stanford, Calif: Stanford University Press.

———. 2005. “Shifting Ontologies, Changing Classifications: Plant Materials from 1700 to 1830.” *Studies in History and Philosophy of Science* 36: 261–329.

———. 2008a. “A Historical Ontology of Material Substances, c. 1700-1830.” In *Stuff: The Nature of Chemical Substances*, edited by Klaus Ruthenberg and Jaap Van Brakel, 21–42. Würzburg: Königshausen & Neumann.

———. 2008b. “The Laboratory Challenge: Some Revisions of the Standard View of Early Modern Experimentation.” *Isis* 99 (4): 769–82.

———. 2014. “Klaproth’s Discovery of Uranium.” In *Objects of Chemical Inquiry*, edited by Ursula Klein and Carsten Rheinhardt, 21–46. Nantucket: Science History Publications.

———. 2015. “A Revolution That Never Happened.” *Studies in History and Philosophy of Science Part A* 49 (February): 80–90. https://doi.org/10.1016/j.shpsa.2014.11.003.

———. 2020. *Technoscience in History: Prussia, 1750-1850*. Transformations: Studies in the History of Science and Technology. Cambridge, Massachusetts: The MIT Press.

Klein, Ursula, and Wolfgang Lefèvre. 2007. *Materials in Eighteenth-Century Science: A Historical Ontology*. Cambridge, Mass: MIT Press.

Klosterman, Leo J. 1985. “A Research School of Chemistry in the Nineteenth Century: Jean Baptiste Dumas and His Research Students.” *Annals of Science* 42 (1): 1–80. https://doi.org/10.1080/00033798500200111.

Knight, David. 1967. *Atoms and Elements: A Study of Theories of Matter in England in the Nineteenth Century*. London: Hutchinson & co.

———. 1978. *The Transcendental Part of Chemistry*. Falkestone: Dawson.

———. 1992a. *Humphry Davy: Science and Power*. Blackwell Science Biographies. Oxford: Blackwell.

———. 1992b. *Ideas in Chemistry*. London: The Athlone Press.

———. 2005. "Humphry Davy, the Poet." *Interdisciplinary Science Reviews* 30 (4): 356–72. https://doi.org/10.1179/030801805X64942.

Knuuttila, Tarja, and Andrea Loettgers. 2014. "Varieties of Noise: Analogical Reasoning in Synthetic Biology." *Studies in History and Philosophy of Science Part A* 48 (December): 76–88. https://doi.org/10.1016/j.shpsa.2014.05.006.

Kobell, Franz von. 1860. "Ueber eine eigenthümliche Säure, Diansäure, in der Gruppe der Tantal- und Niobverbindungen." *Annalen der Chemie und Pharmacie* 114 (3): 337–50. https://doi.org/10.1002/jlac.18601140305.

———. 1861a. "Ueber die Diansäure." *Annalen der Chemie und Pharmacie* 119 (3): 283–88. https://doi.org/10.1002/jlac.18611190305.

———. 1861b. "Zu Hermann's Bemerkungen über die Diansäure." *Journal für Praktische Chemie* 83 (1): 193–95. https://doi.org/10.1002/prac.18610830120.

———. 1865. "Ueber Unterniob- und Diansäure." *Annalen der Chemie und Pharmacie* 136 (3): 299–301. https://doi.org/10.1002/jlac.18651360308.

Kopp, Hermann. 1845. *Geschichte der Chemie*. Vol. 3. Braunschweig: Vieweg und Sohn.

———. 1865. "Investigations of the Specific Heat of Solid Bodies." *Philosophical Transactions of the Royal Society* 155: 71–202.

Kornick, David A. 1962. *A History of Scientific and Technological Periodicals: The Origins and Development of the Scientific and Technological Press, 1665-1790*. New York: The Scarecrow Press.

Kragh, Helge. 1995. "From Curiosity to Industry: The Early History of Cryolite Soda Manufacture." *Annals of Science* 52: 285–301.

———. 2000. "Conceptual Changes in Chemistry: The Notion of a Chemical Element, ca. 1900–1925." *Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics* 31 (4): 435–50. https://doi.org/10.1016/S1355-2198(00)00025-3.

———. 2019. “Controversial Elements: Priority Disputes and the Discovery of Chemical Elements.” *Substantia* 3 (2 suppl. 5): 79–90. https://doi.org/10.13128/SUBSTANTIA-740.

Kuhn, Thomas. 1962. “Historical Structure of Scientific Discovery.” *Science* 136 (3518): 760–64.

Lacey, Andrew. 2019. “New Light on John Davy.” *Ambix* 66 (2–3): 195–213. https://doi.org/10.1080/00026980.2019.1620985.

Lacroix, Alfred. 1905. “Note sur A. Damour.” *Bulletin de Minéralogie* 28 (3): 77–84.

Laudan, Rachel. 1987. *From Mineralogy to Geology: The Foundations of a Science, 1650-1830*. Science and Its Conceptual Foundations. Chicago: University of Chicago Press.

Lavoisier, Antoine-Laurent de. 1789. *Traité Elémentaire de Chimie, Présenté dans un Ordre Nouveau, et d’Après les Découvertes Modernes*. Paris: Cuchet.

———. 1790. *Elements of Chemistry: in a New Systematic Order Containing all the Modern Discoveries*. Translated by Robert Kerr. New York, Etats-Unis d’Amérique: Dover Publications.

Law, John, and Annemarie Mol, eds. 2002. “Complexities: An Introduction.” In *Complexities: Social Studies of Knowledge Practices*, 1–22. Durham: Duke University Press.

Le Roux, Muriel. 2015. “From Science to Industry: The Sites of Aluminium in France from the Nineteenth to the Twentieth Century.” *Ambix* 62 (2): 114–37. https://doi.org/10.1179/1745823415Y.0000000001.

Lehman, Christine. 2011. “Les multiples facettes des cours de chimie en France au milieu du XVIIIe siècle.” *Histoire de l’éducation*, no. 130 (April): 31–56. https://doi.org/10.4000/histoire-education.2336.

———. 2012. “Pierre-Joseph Macquer an Eighteenth-Century Artisanal-Scientific Expert.” *Annals of Science* 69 (3): 307–33. https://doi.org/10.1080/00033790.2012.694695.

Lejeal, Adolphe. 1894. *L’aluminium, le manganèse, le baryum, le strontium, le calcium et le magnésium*. Paris: Baillière et fils.

Lemay, Pierre. 1960. “Berthollet découvre la composition de l’ammoniac.” *Revue d’histoire de la pharmacie* 48 (165): 346–48. https://doi.org/10.3406/pharm.1960.6712.

Levere, Trevor Harvey. 1977a. “Coleridge, Chemistry, and the Philosophy of Nature.” *Studies in Romanticism* 16: 349–79.

———. 1977b. “The Rich Economy of Nature: Chemistry in the Nineteenth Century.” In *Nature and the Victorian Imagination*, edited by U. C. Knoepflmacher and G. B. Tennyson, 189–200. Berkeley: University of California Press.

———. 1980. “Gay-Lussac and the Problem of Chemical Qualities.” In *Actes Du Colloque International Gay-Lussac*, 1–11. Palaiseau: SABIX - Ecole Polytechnique.

———. 1992. “Balance and Gasometer in Lavoisier’s Chemical Revolution.” In *Lavoisier et La Révolution Chimique: Actes Du Colloque Tenu à l’occasion Du Bicentenaire de La Publication Du Traité Elémentaire de Chimie, 1789*, edited by M. Goupil, 313–32. Palaiseau: SABIX - Ecole Polytechnique.

Lindman, Sigurd. 1942. “Blomstrand, Christian Wilhelm.” In *Svenska män och kvinnor*, edited by Nils Bohman, 1:370–71. Stockholm: Albert Bonnier.

Llored, Jean-Pierre, and Michel Bitbol. 2013. “From Chemical Practices to a Relational Philosophy of Chemistry.” In *The Philosophy of Chemistry: Practices, Methodologies, and Concepts*, edited by Jean-Pierre Llored, 385–415. Newcastle upon Tyne, UK: Cambridge Scholars Publishing.

Lloyd Edmondson, Hattie. 2019. “Chivalrous Chemistry.” *Ambix* 66 (2–3): 103–20. https://doi.org/10.1080/00026980.2019.1616931.

Lundgren, Anders. 1979. *Berzelius och den kemiska atomteorin*. Studier i idé- och lärdomshistoria 2. Uppsala : Stockholm: Univ. ; Almqvist & Wiksell international (distr.).

———. 1988. “The New Chemistry in Sweden: The Debate That Wasn’t.” *Osiris* 4: 146–68.

———. 1992. “Berzelius, Dalton and the Chemical Atom.” In *Enlightenment Science in the Romantic Era: The Chemistry of Berzelius and Its Cultural Setting*, edited by Evan Marc Melhado and Tore Frängsmyr, 85–106. Cambridge: Cambridge University Press.

———. 2015. “When a Daring Chemistry Meets a Boring Chemistry: The Reception of Mendeleev’s Periodic System in Sweden.” In *Early Responses to the Periodic System*, edited by Masanori Kaji, Helge Kragh, and Gábor Palló, 153–70. Oxford: Oxford University Press. https://doi.org/10.1093/oso/9780190200077.003.0017.

MacArthur, C. W. P. 1985. “Davy’s Differences with Gay-Lussac and Thenard: New Light on Events in Paris and on TheTransmission and Translation of Davy’s Papers in 1810.” *Notes and Records of the Royal Society of London* 39 (2): 207–28.

Macquer, Pierre-Joseph. 1749. *Elémens de Chimie Théorique*. Paris: Hérissant.

———. 1766. *Dictionnaire de Chymie*. 1st ed. 2 vols. Paris: Lacombe.

———. 1778. *Dictionnaire de Chimie*. 2nd ed. 2 vols. Paris: Théophile Barrois.

Marignac, Jean-Charles Gallisard de. 1859. “De l’application de l’étude des formes cristallines à la recherche des poids atomiques des corps simples et des formules atomiques des corps composés.” *Bibliothèque Universelle de Genève : Archives des Sciences Naturelles* VI: 105–21.

———. 1865a. “Recherches sur les combinaisons du niobium, premier mémoire, première partie.” *Bibliothèque Universelle de Genève : Archives des Sciences Naturelles* 23: 167–82.

———. 1865b. “Sur les combinaisons hyponiobiques.” *Comptes rendus de l’Académie des Sciences* 60: 234–37.

———. 1865c. “Sur les métaux des minéraux tantalifères, à propos d’un mémoire de Blomstrand.” *Bibliothèque Universelle de Genève : Archives des Sciences Naturelles* 23: 326–28.

———. 1866a. “Essais sur la réduction du niobium et du tantale.” *Comptes rendus de l’Académie des Sciences* 66: 180–83.

———. 1866b. “Recherches sur les combinaisons du Tantale.” *Annales de Chimie et de Physique*, 4, 9: 249–76.

———. 1866c. “Trennung der Niobsäure und Tantalsäure.” *Fresenius’ Journal of Analytical Chemistry* 5 (1): 389–91.

———. 1867. “Über Hermann’s Untersuchungen, das Niobium, Tantal und Ilmenium betreffend.” *Journal für Praktische Chemie* 101 (1): 459–68. https://doi.org/10.1002/prac.18671010166.

McCoy, Herbert. 1911. “Synthetic Metals from Non-Metallic Elements.” *Science* 34 (866): 138–42.

Melhado, Evan Marc. 1981. *Jacob Berzelius, the Emergence of His Chemical System*. Stockholm, Sweden : Madison, Wis: Almqvist & Wiksell International ; University of Wisconsin Press.

Meyer, Ernst von. 1891. *A History of Chemistry from Earliest Times to the Present Day*. London: Macmillan and company.

Minina, Elena. 2008. “History of Rudolph Hermann’s Mineralogical Collection.” *Berichte Der Geologischen Bundesanstalt* 72: 62–63.

Moissonnier, Prosper. 1903. *L’aluminium : ses propriétés, ses applications*. Paris: Gauthier-Villars.

Murray, John. 1811a. “Farther Observations and Experiments on Oximuriatic Acid.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 29: 187–202.

———. 1811b. “Observations and Experiments on the Nature of Oximuriatic Acid, and Its Relation to Muriatic Acid.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 28: 132–52.

———. 1811c. “On the Nature of Oximuriatic Acid, in Reply to Mr John Davy.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 28: 294–310.

———. 1812a. “Experiments on Muriatic Acid Gas.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 31: 123–33.

———. 1812b. “Experiments on the Existence of Water in Muriate of Ammonia Formed by the Combination of Muriatic Acid and Ammoniacal Gasses.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 32: 185–97.

———. 1812c. “On the Nature of Oximuriatic Acid Gas, and the Conversion of Carbonic Oxide Into Carbonic Acid by It, in Reply to Mr J. Davy.” *(Nicholson’s) Journal of Natural Philosophy, Chemistry, and the Arts* 30: 226–35.

———. 1819a. *A System of Chemistry: In Four Volumes*. 4th ed. 4 vols. Edinburgh: Francis Pillans.

———. 1819b. “Experiments on Muriatic Acid Gas.” *Annals of Philosophy* 13: 26–39 and 285–98.

Netz, Reviel. 1999. *The Shaping of Deduction in Greek Mathematics: A Study in Cognitive History*. Cambridge: Cambridge University Press.

Newcomb, Sally. 2009. “Chemistry in the Service of Geology: Procedures, Reagents, Reactions.” In *The World in a Crucible: Laboratory Practice and Geological Theory at the Beginning of Geology*, 87–105. Boulder: Geological Society of America. https://doi.org/10.1130/978-0-8137-2449-2-449.0.87.

Newman, William R., and Lawrence M. Principe. 1998. “Alchemy Vs. Chemistry: The Etymological Origins of a Historiographic Mistake.” *Early Science and Medicine* 3 (1): 32–65. https://doi.org/10.1163/157338298X00022.

Newman, William R. 2011. “How Not to Integrate the History and Philosophy of Science: A Reply to Chalmers.” *Studies in History and Philosophy of Science* 41: 203–13.

Nicholson, William. 1795. *A Dictionary of Chemistry : Exhibiting the Present State of the Theory and Practice of That Science, Its Application to Natural Philosophy, the Processes of Manufactures, Metallurgy, and Numerous Other Arts Dependant on the Properties and Habitudes of Bodies, in the Mineral, Vegetable, and Animal Kingdoms : With a Considerable Number of Tables, Expressing the Elective Attractions, Specific Gravities, Comparative Heats, Component Parts, Combinations, and Other Affections of the Objects of Chemical Research*. 2 vols. London: G. G. & J. Robinson.

Northcote, A. Beauchamp, and Arthur Herbert Church. 1858. *A Manual of Qualitative Chemical Analysis*. London: J. Van Voorst.

Norton, John D. 2022. *The Material Theory of Induction*. http://www.deslibris.ca/ID/461936.

Nye, Mary Jo. 1993. *From Chemical Philosophy to Theoretical Chemistry: Dynamics of Matter and Dynamics of Disciplines, 1800 - 1950*. Berkeley: Univ. of California Press.

Nyrup, Rune. 2020. “Of Water Drops and Atomic Nuclei: Analogies and Pursuit Worthiness in Science.” *The British Journal for the Philosophy of Science* 71 (3): 881–903. https://doi.org/10.1093/bjps/axy036.

Oldroyd, David R. 1973. “Some Eighteenth Century Methods for the Chemical Analysis of Minerals.” *Journal of Chemical Education* 50 (5): 337. https://doi.org/10.1021/ed050p337.

———. 1974. “A Note on the Status of A. F. Cronstedt’s Simple Earths and His Analytical Methods.” *Isis* 65 (4): 506–12.

———. 1975. “Mineralogy and the ‘Chemical Revolution’.” *Centaurus* 19 (1): 54–71.

Osborn, Emily Lynn. 2016. “From Bauxite to Cooking Pots: Aluminum, Chemistry, and West African Artisanal Production.” *History of Science* 54 (4): 425–42. https://doi.org/10.1177/0073275316681806.

Paneth, Friedrich. 1931. “Über die erkenntnistheoretische Stellung des chemischen Elementbegriffs.” *Schriften der Königsberger Gelehrten Gesellschaft* 8 (4): 101–25.

———. 1962. “The Epistemological Status of the Concept of Chemical Element.” *The British Journal for the Philosophy of Science* 13: 1–14 and 144–60.

———. 1964a. “Chemical Elements and Primordial Matter: Mendeleeff’s View and the Present Position.” In *Chemistry and Beyond*, edited by Herbert Dingle and G. R. Martin, 53–72. New York: Interscience.

———. 1964b. *Chemistry and Beyond*. Edited by Herbert Dingle and G. R. Martin. New York: Interscience.

———. 2003. “The Epistemological Status of the Chemical Concept of Element.” *Foundations of Chemistry* 5 (2): 113–45.

Paquot, Catherine. 2005. *Henri Sainte Claire Deville: Chimie, recherche et industrie*. Paris: Vuibert.

Partington, J. R. 1948. “The Concepts of Substance and Chemical Element.” *Chymia* 1 (January): 109–21. https://doi.org/10.2307/27757118.

Partington, J. R. 1962a. *A History of Chemistry*. Vol. 3. 4 vols. London: Macmillan.

———. 1962b. “The Discovery of Oxygen.” *Journal of Chemical Education* 39: 123–25.

———. 1964. *A History of Chemistry*. Vol. 4. 4 vols. London: Macmillan.

Pelouze, Jules, and Edmond Frémy. 1848. *Cours de Chimie Générale*. 4 vols. Paris: Masson.

Pérez-Bustamante, J. A. 1997. “Analytical Chemistry in the Discovery of the Elements.” *Fresenius’ Journal of Analytical Chemistry* 357: 162–72.

Perkins, John. 2013. “Sites of Chemistry in the Eighteenth Century.” *Ambix* 60 (2): 95–98. https://doi.org/10.1179/0002698013Z.00000000024.

Perrin, C. E. 1973. “Lavoisier’s Table of the Elements: A Reappraisal.” *Ambix* 20 (2): 95–105. https://doi.org/10.1179/amb.1973.20.2.95.

Porter, Dahlia. 2007. “Scientific Analogy and Literary Taxonomy in Darwin’s *Loves of the Plants*.” *European Romantic Review* 18 (2): 213–21. https://doi.org/10.1080/10509580701297950.

Porter, Theodore M. 1981. “The Promotion of Mining and the Advancement of Science: The Chemical Revolution of Mineralogy.” *Annals of Science* 38 (5): 543–70. https://doi.org/10.1080/00033798100200371.

Prieur, C. A. 1810. “Note sur quelques faits concernant le potassium.” *Annales de Chimie* 74: 215–20.

Principe, Lawrence Michael. 2020. *The Transmutations of Chymistry: Wilhelm Homberg and the Académie Royale Des Sciences*. Synthesis. Chicago: The University of Chicago press.

Pulkkinen, Karoliina. 2019a. “Values in Action: Simplicity, Completeness, and Carefulness in the Development of the Systematisations of Chemical Elements.” Cambridge: University of Cambridge.

———. 2019b. “The Value of Completeness: How Mendeleev Used His Periodic System to Make Predictions.” *Philosophy of Science* 86 (5): 1318–29. https://doi.org/10.1086/705521.

Rammelsberg, Karl Friedrich August. 1866. “Biographie: Heinrich Rose.” *Archiv der Pharmazie* 175 (1–2): 1–19. https://doi.org/10.1002/ardp.18661750102.

Rampling, Jennifer M. 2017. “The Future of the History of Chemistry.” *Ambix* 64 (4): 295–300. https://doi.org/10.1080/00026980.2017.1434970.

Rancke-Madsen, Edmond. 1976. “The Discovery of an Element.” *Centaurus* 19 (4): 299–313.

Renaux, Thierry. 2019. “Le dix-neuvième, siècle de l’aluminium français ?” *Cahiers d’histoire de l’aluminium* 62 (2): 42–55.

"Review of Science." 1810. *The Edinburgh Annual Register* 3 (January): 407–37.

Richards, Joseph. 1896. *Aluminium: Its History, Occurrence, Properties, Metallurgy and Applications, Including Its Alloys*. 3rd ed. Philadelphia: Henry Carey Baird.

Roberts, Lissa. 2016. "Exploring Global History through the Lens of History of Chemistry: Materials, Identities and Governance." *History of Science* 54 (4): 335–61. https://doi.org/10.1177/0073275316681805.

Rocke, Alan J. 1978. "Atoms and Equivalents: The Early Development of the Chemical Atomic Theory." *Historical Studies in the Physical Sciences* 9: 225–63.

———. 1984. *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro*. Columbus: Ohio State University Press.

———. 1993a. *The Quiet Revolution: Hermann Kolbe and the Science of Organic Chemistry*. California Studies in the History of Science. Berkeley: University of California Press.

———. 1993b. "The Quiet Revolution of the 1850s: Social and Empirical Sources of Scientific Theory." In *Chemical Sciences in the Modern World*, edited by Seymour Mauskopf, 87–118. Philadelphia: University of Pennsylvania Press.

———. 2010. *Image and Reality: Kekulé, Kopp, and the Scientific Imagination*. Synthesis. Chicago ; London: The University of Chicago Press.

Rose, Heinrich. 1829. *Handbuch der analytische Chemie*. 1st ed. Berlin: E. S. Mittler.

———. 1844. "Über die Zusammensetzung des Tantalits und ein im Tantalit aus Baiern enthaltenes neues Metall." *Annalen der Physik und Chemie* 63: 317–42.

———. 1846. "Über ein neues, im Tantalit (Columbit) von Baiern enthaltenes Metall." *Journal für Praktische Chemie* 38 (1): 501–7. https://doi.org/10.1002/prac.184603801111.

———. 1847. "Über die Zusammensetzung des Uranotantals und des Columbits vom Ilmengebirge in Sibirien." *Annalen der Physik und Chemie* 147 (5): 157–69. https://doi.org/10.1002/andp.18471470519.

———. 1848. "Ueber das Ilmenium." *Annalen der Physik und Chemie* 73: 449–54.

———. 1853. "Bemerkungen über die Niobsäure, die Pelopsäure und die Tantalsäure." *Annalen der Physik und Chemie* 90: 456–71.

———. 1857. “Über die Atomgewichte der einfachen Körper.” *Annalen der Physik* 176: 270–91.

———. 1861. “Über die Unterniobsäure.” *Annalen der Physik und Chemie* 92: 468–85.

———. 1863. “Über die Zusammensetzung der in der Natur vorkommenden niobhaltigen Mineralien.” *Annalen der Physik* 68: 339–57.

Royal Society, (Great Britain). 1868. *Catalogue of Scientific Papers, 1800-1863 [to 1884-1900]*. Vol. v. 2. London: Eyre & Spottiswoode.

———. 1869. *Catalogue of Scientific Papers, 1800-1863 [to 1884-1900]*. Vol. v. 3. London: Eyre & Spottiswoode.

Russell, Colin A. 1959a. “The Electrochemical Theory of Sir Humphry Davy: Part I: The Voltaic Pile and Electrolysis.” *Annals of Science* 15 (1): 1–13. https://doi.org/10.1080/00033795900200018.

———. 1959b. “The Electrochemical Theory of Sir Humphry Davy: Part II: Electrical Interpretations of Chemistry.” *Annals of Science* 15 (1): 15–25. https://doi.org/10.1080/00033795900200028.

———. 1963a. “The Electrochemical Theory of Berzelius: Part I: Origins of the Theory.” *Annals of Science* 19 (2): 117–26. https://doi.org/10.1080/00033796300202883.

———. 1963b. “The Electrochemical Theory of Berzelius: Part II: An Electrochemical View of Matter.” *Annals of Science* 19 (2): 127–45. https://doi.org/10.1080/00033796300202893.

Ruston, Sharon. 2019. “Humphry Davy: Analogy, Priority, and the ‘True Philosopher.’” *Ambix* 66 (2–3): 121–39. https://doi.org/10.1080/00026980.2019.1616947.

Ruthenberg, Klaus. 1997. “Friedrich Adolf Paneth (1887-1958).” *HYLE - International Journal for the Philosophy of Chemistry* 3: 103–6.

———. 2009. “Paneth, Kant, and the Philosophy of Chemistry.” *Foundations of Chemistry* 11: 79–91.

Sainte-Claire Deville, Henri. 1854a. “De l’aluminium et de ses combinaisons chimiques.” *Comptes rendus de l’Académie des Sciences* 38: 279–81.

———. 1854b. “Note sur deux procédés de préparation de l’aluminium et sur une nouvelle forme du silicium.” *Comptes rendus de l’Académie des Sciences* 39: 321–26.

———. 1854c. “Préparation de l’aluminium.” *Comptes rendus de l’Académie des Sciences* 39: 535.

———. 1855. “Recherches sur les métaux et en particulier sur l’aluminium et sur une nouvelle forme du silicium.” *Annales de Chimie et de Physique*, 3, 43: 5–33.

———. 1858. “Lettre de M. Deville.” *Annales de Chimie et de Physique* 53: 504–7.

Sainte-Claire Deville, Henri, and Alexis Damour. 1861. “Sur la véritable nature des colombites et sur le dianium.” *Comptes rendus de l’Académie des Sciences* 53: 1044–47.

Sainte-Claire Deville, Henri, and Louis Troost. 1865. “Recherches critiques sur la constitution des composés du niobium.” *Comptes rendus de l’Académie des Sciences* 60: 1221–26.

Savaresi. 1791. “Mémoire sur la prétendu métallisation des terres.” *Annales de Chimie* 10: 61–103 and 254–75.

Scerri, Eric R. 2000. “Realism, Reduction, and the Intermediate Position.” In *Of Minds and Molecules: New Philosophical Perspectives on Chemistry*, edited by Nalini Bhushan and Stuart Rosenfeld, 51–72. New York: Oxford University Press. https://doi.org/10.1142/p548.

Scerri, Eric R. 2005. “Some Aspects of the Metaphysics of Chemistry and the Nature of the Elements.” *HYLE - International Journal for the Philosophy of Chemistry* 11 (2): 127–45.

———. 2006. “On the Continuity of Reference of the Elements, A Response to Hendry.” *Studies in History and Philosophy of Science Part A* 37: 308–21.

———. 2007. *The Periodic Table: Its Story and Its Significance*. New York: Oxford University Press.

———. 2009. “The Dual Sense of the Term ‘Element,’ Attempts to Derive the Madelung Rule, and the Optimal Form of the Periodic Table, If Any.” *International Journal of Quantum Chemistry* 109: 959–71.

———. 2012. “What Is an Element? What Is the Periodic Table? And What Does Quantum Mechanics Contribute to the Question?” *Foundations of Chemistry* 14 (1): 69–81. https://doi.org/10.1007/s10698-011-9124-y.

———. 2020. “The Many Questions Raised by the Dual Concept of ‘Element.’” In *What Is A Chemical Element? A Collection of Essays by Chemists, Philosophers, Historians, and Educators*, edited by Eric R. Scerri and Elena Ghibaudi, 5–31. Oxford: Oxford University Press.

Schaffer, Simon. 1986. “Scientific Discoveries and the End of Natural Philosophy.” *Social Studies of Science* 16 (3): 387–420.

———. 1994. “Making Up Discovery.” In *Dimensions of Creativity*, edited by Margaret A. Boden, 13–54. Cambridge, Mass: MIT Press.

Scheele, Carl Wilhelm. 1774. “Om Brunsten, Eller Magnesia, Och Dess Egenskaper.” *Kongliga Vetenskaps Academiens Handlingar* 35: 89–116, 177–84.

———. 1901. *The Chemical Essays of Carl Wilhelm Scheele*. London: Scott, Greenwood &co.

Schickore, Jutta. 2017. *About Method: Experimenters, Snake Venom, and the History of Writing Scientifically*. Chicago ; London: The University of Chicago Press.

Schummer, Joachim. 2010. “The Philosophy of Chemistry.” In *Philosophies of the Sciences*, edited by Fritz Allhoff, 162–83. Blackwell-Wiley.

Sefström, N. G. 1831a. “Sur le vanadium, métal nouveau, trouvé dans du fer en barres de Eckersholm, forge qui tire sa mine de Taberg, dans le Smaland.” *Annales de Chimie et de Physique* 46: 105–11.

———. 1831b. “Ueber das Vanadin, ein neues Metall, gefunden im Stangeneisen von Eckersholm, einer Eisenhütte, die ihr Erz von Taberg in Småland bezieht.” *Annalen der Physik und Chemie* 97 (1): 43–49. https://doi.org/10.1002/andp.18310970103.

Sheller, Mimi. 2014. *Aluminum Dreams: The Making of Light Modernity*. Mobility Studies. Cambridge, Massachusetts: The MIT Press.

Siegfried, Robert. 1959. “The Chemical Philosophy of Humphry Davy.” *Chymia* 5: 193–201.

———. 1963. “The Discovery of Potassium and Sodium, and the Problem of the Chemical Elements.” *Isis* 54 (2): 247–58.

———. 1964. “The Phlogistic Conjectures of Humphry Davy.” *Chymia* 9: 117–24.

———. 1966. “Sir Humphry Davy on the Nature of the Diamond.” *Isis* 57 (3): 325–35.

———. 1982. “Lavoisier’s Table of Simple Substances: Its Origin and Interpretation.” *Ambix* 29 (1): 29–48. https://doi.org/10.1179/amb.1982.29.1.29.

———. 2002. *From Elements to Atoms: A History of Chemical Composition*. Transactions of the American Philosophical Society, v. 92, pt. 4. Philadelphia: American Philosophical Society.

Siegfried, Robert, and Betty Jo Dobbs. 1968. “Composition, a Neglected Aspect of the Chemical Revolution.” *Annals of Science* 24 (4): 275–93. https://doi.org/10.1080/00033796800200201.

Simon, Jonathan. 2002. “Analysis and the Hierarchy of Nature in Eighteenth-Century Chemistry.” *British Journal for the History of Science* 35 (1): 1–16.

———. 2017. *Chemistry, Pharmacy and Revolution in France, 1777-1809*. http://www.vlebooks.com/vleweb/product/openreader?id=none&isbn=9781317168072.

Söderbaum, Henrik Gustaf. 1899. *Berzelius’ Werden und Wachsen, 1779-1821*. Monographieen aus der Geschichte der Chemie. 3. Hft. Leipzig: J.A. Barth.

Soler, Léna. 2012. “Etudier les pratiques scientifiques : étudier quoi ? A la place de quoi ?” http://www.sphere.univ-paris-diderot.fr/IMG/pdf/LSoler_Practices_8Feb12.pdf.

Soler, Léna, Sjoerd Zwart, and Michael Lynch, eds. 2014. *Science After the Practice Turn in the Philosophy, History and Social Studies of Science*. New York: Routledge.

Steinle, Friedrich. 2010. “Scientific Facts and Empirical Concepts: The Case of Electricity.” In *Science as Cultural Practice*, edited by Moritz Epple and Claus Zittel, 31–44. Akademie Verlag. https://doi.org/10.1524/9783050087092.31.

———. 2016. *Exploratory Experiments: Ampère, Faraday, and the Origins of Electrodynamics*. Translated by Alex Levine. Pittsburgh: University of Pittsburgh Press.

Sterrett, Susan G. 2002. “Darwin’s Analogy between Artificial and Natural Selection: How Does It Go?” *Studies in the History and Philosophy of Biology & Biomedical Sciences* 33: 151–68.

Stevenson, D. J. 1975. “Does Metallic Ammonium Exist?” *Nature* 258 (5532): 222–23. https://doi.org/10.1038/258222a0.

Sutton, Geoffrey. 1981. “The Politics of Science in Early Napoleonic France: The Case of the Voltaic Pile.” *Historical Studies in the Physical Sciences* 11 (2): 329–66.

Szabadváry, Ferenc. 1966. *History of Analytical Chemistry*. Translated by Gyula Svehla. Oxford: Pergamon Press.

Tansjö, Levi. 1996. “Carl Gustaf Mosander and His Research on Rare Earths.” In *Episodes from the History of the Rare Earth Elements*, edited by C. H. Evans, 37–54. Chemists and Chemistry, v. 15. Dordrecht & Boston: Kluwer Academic Publishers.

Tate, Gregory. 2019. “Humphry Davy and the Problem of Analogy.” *Ambix* 66: 140–57.

Tesnière, Valérie. 2021. *Au Bureau de La Revue: Une Histoire de La Publication Scientifique (XIXe-XXe Siècle)*. En Temps & Lieux 103. Paris: Éditions EHESS.

Thenard, Louis-Jacques. 1813. *Traité de Chimie Elémentaire, Théorique et Pratique*. 1st ed. 4 vols. Paris: Crochard.

———. 1817. *Traité de Chimie Elémentaire, Théorique et Pratique*. 2nd ed. 4 vols. Paris: Crochard.

———. 1821. *Traité de Chimie Elémentaire, Théorique et Pratique*. 3rd ed. 4 vols. Paris: Crochard.

———. 1824. *Traité de Chimie Elémentaire, Théorique et Pratique*. 4th ed. 5 vols. Paris: Crochard.

———. 1834. *Traité de Chimie Elémentaire, Théorique et Pratique*. 6th ed. 5 vols. Paris: Crochard.

Thomson, Thomas. 1802. *A System of Chemistry*. 1st ed. 4 vols. Edinburgh: Bell & Bradfute.

———. 1804. *A System of Chemistry*. 2nd ed. 4 vols. Edinburgh: Bell & Bradfute.

———. 1807. *A System of Chemistry*. 3rd ed. 5 vols. Edinburgh: Bell & Bradfute.

———. 1809. *Système de Chimie*. Translated by Riffault. 9 vols. Paris: Bernard.

———. 1810. *A System of Chemistry*. 4th ed. 5 vols. Edinburgh: Bell & 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.

———. 1817. *A System of Chemistry*. 5th ed. 4 vols. London: Baldwin, Cradock & Joy.

Tomic, Sacha. 2010. *Aux origines de la chimie organique: méthodes et pratiques des pharmaciens et des chimistes (1785-1835)*. Rennes: Presses universitaires de Rennes.

Topham, Jonathan R. 2000. "Scientific Publishing and the Reading of Science in Nineteenth-Century Britain: A Historiographical Survey and Guide to Sources." *Studies in History and Philosophy of Science Part A* 31 (4): 559–612. https://doi.org/10.1016/S0039-3681(00)00030-3.

———. 2016. "The Scientific, the Literary and the Popular: Commerce and the Reimagining of the Scientific Journal in Britain, 1813–1825." *Notes and Records: The Royal Society Journal of the History of Science* 70 (4): 305–24. https://doi.org/10.1098/rsnr.2016.0027.

Tressaud, Alain. 2019. *Fluorine: A Paradoxical Element*. First edition. Progress in Fluorine Science Series, volume. 5. Amsterdam, Netherlands: Elsevier.

Trofast, Jan. 1996. "The Discovery of Cerium - a Fascinating Story." In *Episodes from the History of the Rare Earth Elements*, edited by C. H. Evans, 13–36. Chemists and Chemistry, v. 15. Dordrecht: Kluwer Academic Publishers.

———. 2011. "Berzelius' Discovery of Selenium." *Chemistry International -- Newsmagazine for IUPAC*, 2011. https://old.iupac.org/publications/ci/2011/3305/5_trofast.html.

Turner, Edward. 1834. *Elements of Chemistry: Including the Recent Discoveries and Doctrines of the Science*. 5th ed. London: J. Taylor.

Turner, R. Steven. 1982. "Justus Liebig versus Prussian Chemistry: Reflections on Early Institute-Building in Germany." *Historical Studies in the Physical Sciences* 13 (1): 129–62. https://doi.org/10.2307/27757508.

"Ueber die Columbite und Tantalite." 1866. *Journal für Praktische Chemie* 99 (1): 40–44. https://doi.org/10.1002/prac.18660990107.

Usselman, Melvyn C. 1978. "The Wollaston/Chenevix Controversy over the Elemental Nature of Palladium: A Curious Episode in the History of Chemistry." *Annals of Science* 35 (6): 551–79. https://doi.org/10.1080/00033797800200431.

———. 2015. *Pure Intelligence: The Life of William Hyde Wollaston*. Synthesis. Chicago ; London: The University of Chicago Press.

Vauquelin, Louis-Nicolas. 1812. *Manuel de l'essayeur*. Paris: Klostermann.

Venel, Gabriel François. 1755. "DOCIMASIE, & plus exactement, quoique contre l'usage, DOCIMASTIQUE." In *Encyclopédie, ou Dictionnaire raisonné des sciences, des arts et des métiers*, V:1–4. Paris: Briasson/Durand/David/Le Breton.

Viano, Cristina, ed. 2005. *L' alchimie et ses racines philosophiques: la tradition grecque et la tradition arabe*. Histoire des doctrines de l'antiquité classique 32. Paris: Librairie Philosophique Vrin.

Weeks, Mary Elvira. 1956. *Discovery of the Elements*. 6th ed. Easton: Journal of Chemical Education.

Wöhler, Friedrich. 1827. "Über das Aluminium." *Annalen der Physik* 11: 146–61.

———. 1839. "Analyse des Pyrochlors." *Annalen der Physik und Chemie* 48: 83–95.

———. 1845. "Zur Kenntniss des Aluminiums." *Annalen der Chemie und Pharmacie* 53: 422–26.

———. 1854. *Handbook of Inorganic Analysis*. Edited by Alfred Wilhelm Hofmann. London: Walton & Meberly.

Wollaston, William Hyde. 1805. "On the Discovery of Palladium; with Observations on Other Substances Found with Platina." *Philosophical Transactions of the Royal Society of London* 95 (December): 316–30. https://doi.org/10.1098/rstl.1805.0024.

———. 1809. "On the Identity of Columbium and Tantalum." *Philosophical Transactions of the Royal Society of London* 99 (January): 246–52. https://doi.org/10.1098/rstl.1809.0017.

Wylie, Alison. 1988. "'Simple' Analogy and the Role of Relevance Assumptions: Implications of Archaeological Practice." *International Studies in the Philosophy of Science* 2 (2): 134–50. https://doi.org/10.1080/02698598808573311.

# Résumé long

La définition de l'élément chimique en tant que substance simple, défendue par Antoine de Lavoisier (1743-1794) dans son *Traité Elémentaire de Chimie* de 1789, est rapidement adoptée par les chimistes européens. Malgré l'évolution rapide de la chimie au cours de la première moitié du XIX$^{e}$ siècle, cette définition reste stable au moins jusqu'à la publication du tableau périodique par Dimitri Mendeleïev (1834-1907) en 1869[230]. Mendeleïev distingue explicitement entre substance simple et élément chimique, et réserve le dernier terme pour les constituants stables de la matière qui ont comme seule caractéristique leur masse atomique. Pendant la période qui sépare les travaux de Lavoisier de ceux de Mendeleïev, les éléments chimiques sont donc définis comme des substances chimiques indécomposables par les moyens connus. Toutefois, les chimistes de l'époque admettent de nombreuses exceptions à cette définition lorsqu'ils tentent de déterminer si une substance est élémentaire ou non. La définition lavoisienne n'est, du reste, pas suffisante en elle-même pour identifier des substances élémentaires : la distinction entre substances simples et composées nécessite des connaissances préalables sur la composition des substances étudiées, sans lesquelles il est impossible d'interpréter les résultats expérimentaux.

Par conséquent, l'analyse de l'évolution historique des définitions du concept d'élément ne permet pas à elle seule de comprendre les pratiques chimiques au cours de ce siècle. Pourtant, l'approche dominante se limite presque toujours au savoir propositionnel, et il n'existe pas encore d'étude systématique des critères effectifs de la nature élémentaire. Cette thèse répond à l'ambition de dépasser l'analyse des définitions pour étudier comment, entre 1770 et 1870, les chimistes ont concrètement identifié des substances spécifiques comme étant des éléments chimiques. Elle consiste en une série d'études de cas qui ont été sélectionnés du fait des controverses suscitées par les annonces de découverte, ou parce qu'il s'agit d'exceptions à la définition lavoisienne, forçant dans les deux cas de figures les chimistes à détailler explicitement leur conception de la nature élémentaire des substances

[230] BENSAUDE-VINCENT Bernadette, *Les Pièges de l'Elémentaire : Contribution à l'Histoire de l'Elément Chimique*, PhD, Université Paris 1, 1981, (dactyl.).

en question. La question principale n'est donc pas tant de savoir comment ces chimistes caractérisent les éléments de façon théorique, mais plutôt comment ils identifient la nature des substances qu'ils manipulent et argumentent à ce propos. Afin de saisir cette caractérisation pratique des éléments, il faut analyser les protocoles expérimentaux, la présentation et l'interprétation des résultats, et le raisonnement implicite ou explicite des chimistes de l'époque. Les sources primaires qui permettent cette analyse sont, d'un côté, les publications scientifiques de chimistes français, anglais, allemands et suédois au sujet des différentes controverses, tirées de journaux tels que les *Annales de Chimie*, les *Annalen der Physik*, les *Annals of Philosophy* ou des comptes rendus des Académies des Sciences de ces quatre pays. De l'autre côté, l'étude de manuels, dictionnaires et correspondances complètent ce corpus pour saisir plus finement sur quelles bases se font ces identifications chimiques et comment elles sont présentées et diffusées dans l'Europe du XIX$^{e}$ siècle.

À partir de l'étude de ces sources, cette thèse montre l'importance de l'analogie chimique dans le raisonnement des chimistes de l'époque. Utilisée principalement comme principe de classification, l'analogie chimique permet d'identifier des régularités dans les comportements chimiques de différentes substances. De plus, les chimistes des XVIII$^{e}$ et XIX$^{e}$ siècles admettent communément que ces analogies sont une indication des similarités en termes de composition chimique ; ainsi, deux composés analogues contiendraient des éléments chimiques similaires. Ce lien entre comportement chimique et composition permet de prédire par analogie la composition de substances qui ne peuvent pas être décomposées en laboratoire, et de détecter ainsi la présence de nouveaux éléments chimiques. Ainsi, le raisonnement analogique offre un autre moyen pour étudier la composition, en plus des expériences de décomposition et recomposition au laboratoire.

La thèse débute par un chapitre prologue ayant pour but de clarifier la définition lavoisienne de l'élément, la vision de la composition chimique sur laquelle elle repose et les différents problèmes liés à son application pratique. Au cours du XVIII$^{e}$ siècle émerge une nouvelle façon de caractériser les substances chimiques à la fois par leur composition et par leur comportement chimique, ce dernier étant notamment déterminé par les tendances à se combiner avec d'autres substances. Lavoisier s'appuie sur cette caractérisation pour défendre une vision purement chimique de la composition qui remplace les quatre éléments par une liste de substances simples, seuls constituants des

corps composés dans son nouveau système. Dans l'introduction de son *Traité élémentaire de chimie* (1789), Lavoisier s'oppose à toute spéculation sur la composition de corps qui ne peuvent pas être décomposés, et préconise une identification strictement expérimentale des éléments chimiques à partir de leur isolation sous forme de substances simples. Dans la pratique, cependant, il distingue entre « véritables » éléments ou principes, éléments chimiques, et substances indécomposables. Ces distinctions sont une façon de répondre respectivement aux difficultés métaphysiques (quels sont les vrais éléments de la matière ?) et procédurales (comment déterminer laquelle des deux substances est le plus simple ?) résultant de sa définition purement opérationnelle[231]. Ce sont notamment les difficultés procédurales qui posent problème pour l'identification des éléments chimiques : certaines opérations peuvent être interprétées soit comme des combinaisons, soit comme des décompositions, en fonction du cadre théorique que l'on adopte. Parfois, le suivi gravimétrique des réactifs et produits de réactions permettent d'identifier la nature des opérations, mais dans d'autres cas plusieurs explications restent possibles. De même, le développement de l'atomisme chimique au début du XIX$^{e}$ siècle ne permet de résoudre ni les difficultés métaphysiques, ni les difficultés procédurales de la définition de l'élément chimique en tant que substance simple. Pour résoudre ces difficultés, Lavoisier et ses successeurs doivent donc recourir à d'autres moyens : l'argument principal de cette thèse est qu'ils se servent de raisonnements analogiques pour résoudre les difficultés procédurales liées à l'identification des éléments chimiques.

La définition lavoisienne, avec toutes ses difficultés, subsiste donc au XIX$^{e}$ siècle malgré le développement de l'atomisme chimique. En effet, comme le montre la première partie de cette thèse, les chimistes du XIX$^{e}$ suivent Lavoisier en adoptant la distinction implicite entre substance indécomposable et élément chimique. Ces trois premiers chapitres traitent des travaux des chimistes Humphry Davy (1778-1829), Jöns Jacob Berzelius (1779-1848), Louis-Joseph Gay-Lussac (1778-1850) et Louis Jacques Thenard (1777-1857) au cours des deux premières décennies du XIX$^{e}$ siècle.

[231] La distinction entre difficultés métaphysiques et procédurales est proposée par SIEGFRIED Robert et DOBBS Betty Jo, « Composition, a neglected aspect of the chemical revolution », in *Annals of Science*, n$^{o}$ 4, vol. 24, décembre 1968, p. 275-293.

Le premier chapitre décrit le rôle du raisonnement analogique dans l'identification du nouvel élément aluminium, une quinzaine d'années avant sa première production sous forme de substance simple. À partir de 1811, des chimistes tels que Thenard, Berzelius et Thomas Thomson (1773-1852) acceptent de considérer l'alumine comme l'oxyde d'un nouveau métal, l'aluminium, bien que cette substance demeure indécomposable par les moyens connus à l'époque. La composition interne de l'alumine est donc prédite, et cela grâce à ses analogies avec les substances récemment décomposées par Davy : la magnésie, la baryte, la chaux et la strontiane, qui sont chacune composée d'oxygène et d'un métal. L'hypothèse de l'existence de l'aluminium permet également d'expliquer les résultats expérimentaux : ainsi, l'impossibilité de décomposer l'alumine s'expliquerait par la forte affinité de ce nouveau métal pour l'oxygène. L'exemple de l'aluminium indique que l'analogie chimique peut constituer une forme de preuve indirecte de la composition chimique[232].

Le deuxième chapitre a pour objet les travaux, réalisés notamment par Davy et Berzelius, qui visent à déterminer la composition chimique de l'ammoniac entre 1807 et 1813. En poursuivant cette recherche, ces deux chimistes sont confrontés à une contradiction entre, d'un côté, les propriétés chimiques de l'ammoniac qui semble se comporter comme un oxyde métallique, et de l'autre, les résultats de sa décomposition, qui ne produit ni oxygène, ni métal, mais seulement de l'azote et de l'hydrogène. Les façons dont Davy et Berzelius tentent de résoudre cette contradiction souligne que leur conception de la composition chimique de cette substance se fonde sur la concordance entre résultats expérimentaux, raisonnements analogiques et connaissances préalables de la composition d'autres substances. Ils tentent d'arriver à une telle concordance par un processus itératif au cours duquel ils adaptent un à un leurs montages expérimentaux, leurs hypothèses sur la composition et leurs classifications des substances[233]. Le postulat selon lequel les

[232] La preuve indirecte par analogie est également étudiée par Adrien Currie dans le cadre des sciences historiques. CURRIE Adrian, *Rock, bone, and ruin: an optimist's guide to the historical sciences*, Cambridge, The MIT Press, 2018, 372 p.

[233] Ce processus itératif pourrait être caractérisé comme « itération épistémique ». CHANG Hasok, *Inventing temperature: measurement and scientific progress*, Oxford ; New York, Oxford University Press, 2004, 286 p.

substances analogues sont composées d'éléments similaires est la seule idée qu'ils ne remettent pas en question ; elle les incite à s'interroger sur la nature élémentaire de l'azote (et, brièvement, sur celle de l'hydrogène), ainsi qu'à prédire l'existence de l'élément « ammonium » qu'ils abandonnent quelques années plus tard.

Au cours de leurs échanges sur l'ammoniac, une opposition apparaît entre Davy et Berzelius, Davy se méfiant de plus en plus de l'inférence analogique alors que Berzelius attribue presque le statut de loi aux prédictions de composition chimique. Cette opposition devient particulièrement franche au moment de leur débat sur la nature du chlore, décrit dans le troisième chapitre de cette thèse. Tandis que Davy et son frère insistent sur l'idée selon laquelle le chlore est un élément chimique parce qu'il est indécomposable par les techniques de décomposition connues à l'époque, Berzelius et de nombreux autres chimistes refusent d'accepter leurs arguments. Selon ces derniers, le problème n'est pas tant la définition de l'élément en tant que substance simple, mais plutôt l'affirmation de l'impossibilité de décomposer le chlore – ils proposent une interprétation alternative des expériences selon laquelle le chlore aurait déjà été effectivement décomposé. Si leur explication peut aujourd'hui paraître inutilement complexe, elle est plus cohérente avec les connaissances de l'époque, notamment avec la conception communément admise de la composition des sels et des acides. Ce n'est qu'après la découverte de l'iode, une substance simple analogue au chlore, que ces chimistes acceptent de réorganiser leurs classifications afin de créer une place pour le chlore parmi les éléments chimiques. Ce cas montre que même un constat qui semble être aussi factuel que l'impossibilité de décomposer une substance doit en réalité être établi en tenant compte d'une série de connaissances préalables sur la composition d'autres substances chimiques. L'identification de chaque élément chimique se fait ainsi en accord avec les classifications des autres substances connues et non pas comme s'il s'agissait de cas parfaitement isolés.

La première partie révèle donc que, loin de fournir une méthode univoque pour l'isolement des substances élémentaires, les tentatives de décomposition chimique font partie d'une argumentation plus complexe intégrant résultats expérimentaux, inférences analogiques et connaissances théoriques antérieures. S'appuyant sur la conviction que les ressemblances de propriétés chimiques sont des signes d'une composition chimique

similaire, ces chimistes se servent de l'analogie comme une forme de preuve dans l'étude de la composition.

La deuxième partie de la thèse traite de l'identification de nouveaux éléments par l'analyse chimique des minéraux à partir du débat autour de la nature des « métaux du tantale » dont l'existence est débattue entre 1801 et 1866. Parmi cette famille de métaux, seuls le niobium et le tantale sont aujourd'hui reconnus comme étant des éléments.

Le quatrième chapitre décrit l'apparition, à la fin du XVIII$^{e}$ siècle, d'une méthodologie relativement standardisée d'analyse chimique qui continue à être utilisée tout au long du XIX$^{e}$ siècle. De nombreux procédés utilisés dans cette méthodologie, tels que les réactifs et le chalumeau, permettent d'identifier la composition d'une substance sans nécessiter sa décomposition et ne résultent donc pas en la production de substances simples. Les chimistes analytiques continuent à utiliser ces méthodes pendant la majeure partie du XIX$^{e}$ siècle, comme le montrent les chapitres cinq et six qui analysent une série de controverses au sujet des métaux de tantale. Dans ce cas également, la simplicité expérimentale des substances en question ne joue qu'un rôle secondaire dans l'identification des éléments : la pratique de l'analyse chimique inorganique vise à caractériser les éléments à partir de leurs composés, plutôt que de les étudier sous forme de substance simple. Ainsi, l'existence de nouveaux métaux est régulièrement démontrée à partir de l'identification de leurs oxydes métalliques sur la base d'un raisonnement analogique similaire qui repose sur le lien entre propriétés chimiques et composition. Par conséquent, l'identification correcte des propriétés des composés et l'élimination des impuretés sont les questions centrales de tous les débats sur les métaux du tantale, plutôt que la simplicité des nouveaux métaux. Malgré les transformations théoriques et institutionnelles que la chimie a connu durant cette période, les débats sur cette famille de substances permettent d'identifier une continuité dans la caractérisation des métaux.

Implicitement, l'identification de nouveaux métaux à partir de leurs composés repose sur une inférence analogique similaire à celle de Davy et de ses collègues : l'idée selon laquelle des similarités de propriétés chimiques sont le signe d'une composition similaire. Toutefois, le raisonnement analogique reste implicite dans le cadre de la chimie analytique ; l'existence d'une tradition d'étude de diverses substances métalliques en lien

avec leur intérêt économique permet aux chimistes analytiques de se fier aux méthodes établies sans avoir besoin de proposer des réflexions explicites sur leur usage de l'analogie[234]. Cette étude de cas montre que la définition lavoisienne de l'élément chimique est simplement superposée à cette tradition existante, sans changer les pratiques analytiques elles-mêmes. Au début du XIX^e^ siècle, les inférences analogiques permettent seulement de prédire la composition en termes de types d'éléments (tels que, par exemple, la présence d'un nouveau métal) mais, grâce au développement de l'atomisme et d'autres outils théoriques, les chimistes du milieu du XIX^e^ siècle sont capables de prédire de façon quantitative la composition des substances qu'ils étudient. Ainsi, Jean-Charles Galissard de Marignac (1817-1894) développe pendant les années 1860 une méthode pour prédire la formule chimique des composés chimiques à partir d'analogies dans la forme cristalline. Par ailleurs, la masse atomique et la valence fournissent à la même époque de nouvelles caractéristiques qui permettent la classification des éléments chimiques.

À partir de ces études de cas, cette thèse montre qu'entre 1770 et 1870, les identifications d'éléments ne suivent que rarement la définition communément admise selon laquelle chaque substance indécomposable doit être provisoirement identifiée comme un élément chimique. D'une part, l'indécomposabilité n'est à elle seule pas suffisante pour prouver la nature élémentaire, car une substance peut être indécomposable pour de nombreuses autres raisons, telle que le manque de moyens expérimentaux adéquats. En effet, lorsqu'une substance indécomposable est suffisamment similaire à un groupe de composés pour être classée avec eux, cela constitue un argument contre son identification en tant qu'élément chimique. Seules les substances indécomposables pouvant être placées dans une classification d'éléments de façon cohérente peuvent être considérées comme étant élémentaires, comme l'illustre parfaitement le cas du chlore. D'autre part, au XIX^e^ siècle il n'est pas strictement nécessaire pour les éléments chimiques d'exister sous

[234] L'histoire de cette tradition autour de l'étude des métaux, et son lien avec le concept d'élément, a récemment été étudiée par Hjalmar Fors. FORS Hjalmar, *The Limits of Matter: Chemistry, Mining and Enlightenment*, Chicago, University of Chicago Press, 2015. FORS Hjalmar, « Elements in the Melting Pot: Merging Chemistry, Assaying, and Natural History, Ca. 1730–60 », in *Osiris*, n° 1, vol. 29, janvier 2014, p. 230-244.

la forme d'une substance indécomposable, car leur existence peut être prédite par un raisonnement analogique. À partir de l'idée que les analogies chimiques indiquent une composition similaire, les ressemblances en termes de propriétés chimiques peuvent être utilisées pour déduire la présence d'un certain type de constituant dans les composés indécomposables. Une telle prédiction est faite dans le cas de divers métaux qui ont d'abord été identifiés comme des constituants élémentaires d'oxydes métalliques, tels que le cérium, le columbium et l'aluminium. Toutefois, le destin de l'ammonium montre que l'analogie seule ne suffit pas, si d'autres résultats contredisent ce raisonnement. L'identification d'éléments chimiques se fait uniquement sur la base d'une convergence pragmatique entre différents types de preuve provenant de résultats expérimentaux et raisonnements analogiques.

Cette conclusion indique que certains aspects de la définition de l'élément chimique de Mendeleïev sont déjà implicitement présents dans la chimie du début du XIX$^{e}$ siècle ; de plus, elle contredit la caractérisation courante du concept d'élément chimique comme une notion purement empirique pendant la période qui sépare les travaux de Lavoisier de ceux de Mendeleïev. Ainsi, le concept d'élément chimique se trouve à l'intersection des pratiques expérimentales et théoriques, dont l'imbrication est au cœur de l'histoire de la chimie.

# List of Figures



# List of Tables