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Estratto da:
ISTITUTO E MUSEO DI STORIA DELLA SCIENZA
FIRENZE

NUNCIUS
ANNALI DI STORIA DELLA SCIENZA

Anno XIX, 2004, fasc. 1

ATOMS IN FRENCH CHEMISTRY TEXTBOOKS DURIN
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FIRENZE
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RIASSUNTO

Gli *Eléments de chimie médicale* di Mateu Orfila i Rotger (1787-1853) costituiscono una eccellente fonte storica per lo studio dell'ascesa e caduta della teoria atomica nella Francia della prima metà dell'ottocento. Il libro fu ristampato otto volte fra il 1817 e il 1851; inoltre parecchie versioni ridotte furono pubblicate in inglese, spagnolo, tedesco, italiano e olandese. Vogliamo analizzare in primo luogo come la teoria atomica fu ricevuta dai libri di testo francesi appartenenti alle prime due decadi dell'ottocento. Gli atomi furono visti dagli autori francesi come strumenti pratici e non come novità teoriche. Vedremo come ciò occorre nelle prime edizioni dei libri di testo di Orfila e Thenard. Alla fine del 1820 nuovi metodi per il calcolo di pesi atomici furono introdotti nei libri di testo, insieme alle formule di Berzelius. Vedremo come la teoria atomica raggiunge il suo punto culminante nei libri di Orfila e Thenard tra le edizioni del 1827 e 1835. Per ultimo discuteremo perché Orfila cancellò i pesi atomici della settima edizione del suo libro pubblicato nel 1843. Analizzeremo i suoi argomenti epistemologici, la sua visione della differenza fra atomi ed equivalenti, i suoi interessi per la chimica vegetale e animale e le costrizioni istituzionali (programmi ufficiali) per quello che si riferisce alla teoria atomica. Non si può ridurre ad un solo motivo la reazione di Orfila rispetto alla teoria atomica nella decade del 1840. Lui scelse una posizione particolare fra le varie prese in quegli anni dagli autori francesi di libri di testo

* This research has been supported by the BHA2000-0434 program and a grant of the *Conselleria de Cultura i Educació (Valencia)*. We are grateful to Bernadette Bensaude-Vincent,

The *Elémens de chimie médicale* by Mateu Orfila i Rotger (1787-1853) was edited eight times between 1817 and 1851. Several abridged versions were also published as well as translations into English, Spanish, German, Italian and Dutch.¹ In every new edition, Orfila made changes both in structure and content in order to maintain the textbook «au courant de la science» – as a reviewer remarked.² The book was intended to be used by his students at the medical faculty but probably reached a far wider audience. It is worth mentioning that no other contemporary French textbook was reedited on so many occasions and over such a long period of time during the first half of nineteenth century. While the author is not usually mentioned by historians of nineteenth-century chemistry, Mateu Orfila's textbook serves as an excellent historical source for a reappraisal of the rise and fall of French atomic theory over the first half of the nineteenth century.

Mateu Orfila mentioned atomic theory in the second edition of his popular chemistry textbook published in 1819. Not only did he write a completely new paragraph on *Dalton's atomic theory* but he also rewrote paragraphs about the composition of substances by using atomic weights. At the end of the 1820s, atomic theory gained ground in Orfila's textbook until coming to the fore in the 6th edition, published between 1835 and 1836. In this edition, Orfila extended his introductory chapter on atomic

Ana Carneiro and Mary Jo Nye for their valuable comments and support during the development of this research.

¹ See bibliography in J.R. BERTOMEU SÁNCHEZ, A. GARCÍA BELMAR, *Mateu Orfila y las clasificaciones químicas: un estudio sobre los libros de texto en Francia a principios del siglo XIX*, «Cronos», vol. 2, 1999, 3-35 and *Id.*, *Mateu Orfila's Elémens de chimie médicale and the Debate about the Medical Applications of Chemistry in Early-nineteenth Century France*, «Ambix», vol. 47, 2000, pp. 1-25. For updated information about Mateu Orfila, including bibliographic orientation and links to digital versions of his main books, see <http://www.uv.es/~bertomeu/orfila>. In the subsequent notes, we will quote the following editions: M. ORFILA, *Elémens de chimie médicale*, Paris, Crochard, 1817; *Id.*, *Elémens de chimie appliquée à la médecine et aux arts* 2nd ed., Paris, Crochard, 1819; 3rd ed. (Paris, Gabon, 1824); 4th ed. (Paris, Baillière, Gabon et Cie. 1828); 5th ed. (Paris, Crochard, 1831); 6th ed. (Paris, Crochard, 1835-1836); 7th ed. (Paris, Fortin, Masson et Cie, 1843); 8th ed. (Paris, Labé Editeur). Orfila's textbook will be compared with Thenard's *Traité*, which went through six editions: J. THENARD, *Traité de chimie élémentaire, théorique et pratique*, Paris, Crochard, 1813-16. *Id.*, 1817-18, 2nd ed.; 1821, 3rd ed.; Paris, 1824, 4th ed.; Paris, 1827, 5th ed.; Paris, 1834-35, 6th ed. For a broad study about nineteenth-century French chemistry textbooks, see B. BENSUADE-VINCENT, A. GARCÍA-BELMAR, J.R. BERTOMEU-SÁNCHEZ, *L'émersion d'une science des manuels. Les livres de chimie en France (1789-1852)* Paris, Editions des Archives Contemporaines, 2003.

² «Depuis de l'époque où parut la première édition des *Elémens de Chimie* de M. Orfila, c'est-à-dire depuis trente-quatre ans, le savant professeur de la faculté de médecine de Paris, s'est constamment attaché à tenir son ouvrage au courant de la science, et à mettre ses nombreux lecteurs à portée d'en suivre la marche et les progrès». Cfr. «*Journal de Pharmacie*», 1851, 19 (1), pp. 460-461. Review by A.F.B.

theory and, for the first time, broadly employed Berzelius's formulae. However, in the seventh edition (1843), the word «atom» suddenly vanished and Orfila prevented his students from mixing up Berzelius's formulae with atomic theory, «a hypothesis» which he said he would never «deal with anymore». This trend was further consolidated in the eighth and final edition (1851).

At first sight, this reconstruction seems to be in consonance with traditional historiography about nineteenth-century atomic theory. Atomic theory was introduced in France through translations of books such as Thomson's *System of Chemistry* or Berzelius's *Essay on chemical proportions*. Between the 1810s and the 1820s, atomic theory was broadly used by French chemists and even improved by Dumas's first research on vapour densities, which opened up new ways of calculating atomic weights. At the same time, Dumas's research on densities introduced unforeseen problems as it threatened Avogadro's hypothesis in cases such as sulphur, phosphor or mercury. The crisis was portrayed by Dumas's dramatic lectures at the Collège de France in 1836, in which he said that he would erase the word «atom» from science. In following years, Dumas and other French chemists changed to equivalents and claimed that these corresponded to «raw empirical data» without a compelling commitment regarding the structure of matter. This shift came along with the emergence of positivism in France during the 1840s. This being the standard reason employed to explain the 'French rejection of atoms'. The centralisation of the French scientific system and Dumas's control over the syllabuses of secondary education are also frequently mentioned to explain why French chemists did not use atomic theory by the mid nineteenth century.³

However, this general conformity is thrown into disarray when Orfila's textbooks are analysed in full and when taking some recent historical research into account. Firstly, and surprisingly enough, after the 1840s, Orfila, together with other French textbook writers, continued to employ the word «atom» and «molecules» with a physical meaning in his book, especially in his preliminary chapters dealing with affinity forces. The persistence of the microscopic physical approach seems to be at odds with the strong influence of positivistic philosophy. As Bernadette Bensaude-

³ For an excellent introduction to the topic, see A. ROCKE's books which include a broad discussion of relevant historical literature. See, for instance, A.J. ROCKE, *Chemical Atomism in Nineteenth Century: From Dalton to Cannizzaro*, Columbus, Ohio State Univ. Press, 1984; *Id.*, *The Quiet Revolution. Hermann Kolbe and the Science of Organic Chemistry*, Berkeley, Univ. California Press, 1993; and *Id.*, *Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry*, Cambridge, MIT Press, 2001.

Vincent has recently pointed out, historians of science have used the word «positivism» with several meanings. It could be an awkward label for nineteenth-century chemists who had never read Comte's philosophical writings. Furthermore, the founder of positivism never condemned the atomic hypothesis and some of his followers played a key role in the promotion of atomism.⁴ Moreover, when taking Orfila's case into account, institutional reasons such as Dumas's control over the French educational system cannot replace the above causes. Perhaps secondary school teachers were compelled to follow an anti-atomistic syllabus but Orfila held a powerful institutional position which largely allowed him to decide the content and structure of his lectures.

In this paper, we shall analyse Orfila's views taking into account his multiple constraints, as well as the changing meanings of atomic theory over the first half of the nineteenth century. When considering these changes, we will employ the term «atomic theory» in its broadest sense and will pay attention to the different meanings and ambiguities that have been attached to it in the past. It should be borne in mind that the expression «atomic theory» might suggest more coherence, continuity or consistency than knowledge pertaining to atoms ever really had during those years. We will employ it because this was how it was referred to by historical actors and not due to its current epistemological implications. We shall also offer evidence that French chemistry textbook authors did not establish a clear distinction between what historians such as Alan Rocke call «physical atomism» and «chemical atomism». Rocke compares physical atomism to an image of microworld in terms of indivisible particles, whereas chemical atomism is related to macroscopical portions, sometimes called «chemical proportions», in which chemical elements react to each other. Rocke, who recognises that these categories were unknown to historical actors, has argued that these concepts might pave the way to the study of nineteenth-century atomism. He has claimed that «chemical atoms» were accepted by the entire chemical community, whereas «physical atoms» were not.⁵

⁴ B. BENSUADE-VINCENT, *Atomism and Positivism: A Legend about French Chemistry*, «Annals of Science», vol. 56 (1), 1999, pp. 81-95.

⁵ We will employ the terms «physical» and «chemical» atomism with the meaning which has been accorded by A. Rocke [see literature quoted in note (3)]. The main problem of using these terms is that they were not employed by the historical actors, as A. Rocke recognised. However, other possible expressions such as «stoichiometric atoms», «chemical portions», «theory of proportions» also have their problems. See U. KLEIN, *The Creative Power of Paper Tools in Early Nineteenth-Century Chemistry*, in ID. (ed.), *Tools and Modes of Representation in the Laboratory Sciences*, Boston, Kluwer, 2001, 1335, on pp. 14-15. See also Rocke's paper in this collective book.

By using these categories, the analysis of French textbooks suggests a more complex landscape. Almost all analysed French textbooks refer to physical «molecules» or «atoms» in their first chapters, just some pages before chapters on «chemical atomism», which usually come under headings such as «laws of combination of bodies», «proportional numbers», «atomic theory», etc. Moreover, in those chapters describing chemical properties of bodies, «physical» and «chemical» atoms were employed and, in some cases, chemistry textbook writers moved from one meaning to another within the same paragraph. While this may seem to be a flagrant inconsistency to the modern reader it, indeed, serves as one of the key clues to understanding the problem.

We shall first analyse how atomic theory was received in French chemistry textbooks during the 1810s and 1820s. Atoms were regarded by French authors as a practical tool and not as a theoretical novelty. We shall follow atomic theory through the first editions of Orfila's and Thenard's textbooks. At the end of the 1820s, new methods for calculating atomic weights were introduced in textbooks as well as Berzelian formulae. As a result, atomic theory reached its apex in Thenard's and Orfila's textbooks between 1827 and 1835. We shall also study new unforeseen uses of atomic theory that appeared during the 1830s and the differences between atomic and equivalent weights in Orfila's and Thenard's textbooks. Finally, we shall discuss why Orfila gave up atomic weight in his 7th edition (1843) by concentrating on several related issues. Consideration is also given to Orfila's epistemological constraints, the differences between atoms and equivalents in French textbooks, the difficult passage from plant and animal chemistry to organic chemistry and institutional restrictions related to atomic theory. No single reason can be used to explain Orfila's rejection of atomic weights during the 1840s. He, indeed, chose a particular position on atomic theory among the many positions adopted by French chemistry textbook writers over these years.

1. THE INTRODUCTION OF ATOMIC THEORY IN FRENCH TEXTBOOKS OVER THE 1810s AND 1820s: THEORETICAL INNOVATION OR A TOOL FOR QUANTITATIVE ANALYSIS?

Dalton's atomic theory was introduced in France on the basis of several translations of English textbooks, which were originally written by Thomson, Henry and Davy.⁶ However, particulate images of matter were widely

⁶ See, M. CROSLAND, *The First Reception of Dalton's Atomic Theory in France*, in D.S.L.

employed by French chemists long before Dalton. Eighteenth-century theories of chemical affinity pictured chemical reactions in molecular terms and French chemistry textbooks usually included a preliminary chapter on the subject. The concepts of «integrand» and «constituent» molecules were discussed together with cohesion and affinity forces.⁷ It is then easy to understand why French authors did not see Dalton's theory as a substantial innovation regarding the structure of matter. In a long foreword to the translation of Thomson's textbook, Berthollet critically commented on Dalton's atomic theory and referred to it as «an ingenious hypothesis». He recognized that Dalton's hypothesis was valuable in as much as it provided an explanation of «the constant proportions to be observed in some compounds» but he asked for a more «accurate analysis» and «greater experimental precision» instead of «hypothetical speculations about the number, arrangement and figure of the molecules», which were not accessible by experiment.⁸

Neither Orfila nor Thenard regarded Daltonian atoms as an important innovation concerning the structure of matter but they praised its practical use in chemical analysis. Thenard first mentioned atomic theory in an «addition» to the fourth volume of his *Traité*, which was published in 1816. Even though he employed atomic theory as early as 1813 in a paper on phosphor,⁹ he did not use it either in the introductory chapters or in the description of chemical substances in the textbook. In fact, he simply reproduced certain passages from a paper by Wollaston which was translated in the «Journal des mines».¹⁰ In this well-known paper,

CARDWELL (ed.), *John Dalton and the Progress of Science*, Manchester, Univ. Press, 1968, pp. 274-290 and K. KOUNELIS, *Atomism in France. Chemical Textbooks and Dictionaries, 1810-1835*, in A. LUNDGREN, B. BENSUADE-VINCENT (eds.) *Communicating Chemistry. Textbooks and Their Audiences, 1789-1939*, Canton, Science History Publications, 2000, pp. 207-231.

⁷ See, for instance, A. BAUME, *Chymie expérimentale et raisonnée*, Paris, Didot, 1773, vol. I, pp. 12-13; A. FOURCROY, *Système des Connaissances Chimiques*, Paris, Baudouin, 1800, vol. I, pp. 63-86, and THENARD, *Traité*, cit. (1), (1813-16), I, pp. 1-3. A similar approach was also in Orfila's textbook. Cfr. ORFILA, *Eléments*, cit. (1), (1817), I, pp. 1-2.

⁸ «Spéculations hypothétiques sur le nombre, l'arrangement et la figure des molécules qui échappent à toute expérience». Cfr. T. THOMSON, *Système de Chimie*, Paris, Veuve Bernard, 1809, vol. I, pp. 21-27. See M. CROSLAND (1968), *First Reception*, cit. (6) and P. GRAPÉ, *The Marginalization of Berthollet's Chemical Affinities in the French Textbook Tradition at the Beginning of Nineteenth Century*, «Annals of Science», vol. 58, 2001, pp. 111-135, which includes a discussion of Thenard's and Orfila's textbooks on pp. 129-134.

⁹ See ROCKE, *Chemical Atomism*, cit. (3), pp. 114-115.

¹⁰ THENARD, *Traité*, cit. (1), (1813-16), IV, pp. 247-254: «Sur une Echelle synoptique des équivalens chimiques, par M. Wollaston». Two French translations of Wollaston's paper (1814) were published in «Annales de Chimie», XC (1814), pp. 138-174 and «Journal des Mines», XXXVII (1815), pp. 101-131. Thenard mentioned the last one. On Wollaston, see D.C. GOODMAN, *Wollaston and the Atomic Theory of Dalton*, «Historical Studies in the

Wollaston praised the advantages of «equivalents» for calculating the results of chemical analysis, as well as for evaluating the exact amounts of substances that should be employed in chemical synthesis. Wollaston regarded Dalton's theory as a good explanation of these regularities but said that he was not «desirous of warping his numbers according to an atomic theory» but «endeavoured to make practical convenience his sole guide».¹¹ Following Wollaston's utilitarian approach, Thenard included references to atomic theory in his volume on chemical analysis. In the second edition, he briefly mentioned atomic theory in the opening theoretical chapters but developed it and made further additions in the chapters on chemical analysis. Moreover, Thenard included a table of proportional numbers (*table des nombres proportionnels*) calculated by César Despretz (1792-1863), chemistry demonstrator («répétiteur») at the l'Ecole polytechnique.¹² In the third edition (1821), Thenard added long excerpts from the *Essay on Chemical Proportions* by Jacob Berzelius¹³ to his volume on chemical analysis. In 1824, he extended his preliminary chapter on atomic theory with references to the Equal Volume = Equal Number of Particles (quoted henceforth as «EVEN») hypothesis and Dulong and Petit's law as well as examples of calculations of atomic weights.¹⁴

Orfila did not mention atomic theory in his textbook until its second edition in 1819. He probably learnt atomic theory through Thomson's textbook, whose second French edition was published in 1818. In a review of this book, Orfila pointed out Thomson's abundant use of Dalton's atomic theory which «necessarily contributed to give much

Physical Sciences», vol. 1, 1969, pp. 37-59 and A. ROCKE, *Atoms and Equivalents. The Early Development of the Chemical Atomic Theory*, «Historical Studies in the Physical Sciences», vol. 9, 1978, pp. 225-263.

¹¹ THENARD, *Traité*, cit. (1), (1813-16), IV, pp. 249-250.

¹² *Id.*, *Traité*, cit. (1817-18), IV, pp. 214-221 and (1821), IV, pp. 226-233. Like Wollaston, Thenard used oxygen = 10 as a scale. He made minor amendments to Wollaston atomic weights and also multiplied some of the atomic weights by two. That was the case of mercury and copper. In other words, Despretz and Thenard preferred, as Davy, Thomson or Berzelius did, the formulae CuO^2 y HgO^2 whereas Wollaston regarded these oxides as CuO y HgO . See ROCKE, *Atoms and Equivalents*, cit. (10), pp. 254-255.

¹³ THENARD, *Traité*, cit. (1), (1821), IV, pp. 240-261. Berzelius's book was published in France in 1819.

¹⁴ *Ivi*, I, 21: «[Les chimistes] Ils admettent que tous les gaz, sous le même volume, contiennent le même nombre d'atomes». *Ivi*, 23: «la loi énoncée par MM. Dulong et Petit [...], savoir: que la chaleur spécifique des atomes élémentaires est la même». Dulong and Petit's law was already mentioned in the former edition. Cfr. *Id.*, *Traité*, cit. (1), (1821), I, pp. 102-104. See KOUNELIS *Atomism in France*, cit. (6), pp. 212-215, for a detailed analysis of atomic theory in Thenard's textbook.

more precision to analysis».¹⁵ However, Orfila adopted Thomson's «rounded» atomic weights that were implicitly based on Prout's hypothesis.¹⁶ He also wrote a new chapter at the beginning of his first volume, immediately after dealing with affinity forces, and he then discussed «the laws on the composition of bodies».¹⁷ He mentioned the law of multiple proportions (which he attributed to Berzelius)¹⁸ and Gay-Lussac's law of volumes.¹⁹ Orfila claimed that these laws could be «advantageously applied to chemical analysis» in order to calculate specific weights of compound gases, elemental weight ratios of compounds and the chemical composition of a compound of a gaseous substance and a solid substance.²⁰

Orfila then wrote a completely new chapter on the «atomistic system of Dalton» («système atomistique de Dalton») arguing that it was «broadly accepted» and could be advantageously applied to chemical analysis.²¹ After giving general assumptions, Orfila described the laws of combination adopted by Dalton and provided several examples of atomic weight calculations. Like Wollaston and Thomson, Orfila adopted oxygen (and not hydrogen as Dalton did) as the atomic weight unit because this element was found in a larger number of compounds. Finally, he remarked

¹⁵ M. ORFILA, *Système de Chimie par Tb. Thomson*, «Nouveau Journal de Médecine», vol. 3 (1818), pp. 68-70; vol. 6 (1819), pp. 126-127. Quoted on p. 69: «très-grand usage de la théorie atomique de Dalton, ce qui a dû nécessairement contribuer à donner beaucoup plus de précision à l'analyse».

¹⁶ On Dalton, Davy and Thomson's attitude towards Prout's integral multiples weight hypothesis, see W. BROCK, *Dalton versus Prout: The Problem of Prout's Hypotheses*. In: D.S.L. CARDWELL (ed.), *John Dalton and the Progress of Science*, Manchester, Univ. Press, 1968, pp. 240-259.

¹⁷ ORFILA, *Eléments*, cit. (1), (1817), II, pp. 479-489. The chapter *Des Composés relativement à la proportion de leurs éléments* was changed in *Id.*, *Eléments*, cit. (1), (1819), I, pp. 8-13, to the following title *sur les lois qui président à la composition des corps*. Moreover, he established a chapter on «the laws on the composition of bodies», which were previously discussed in the fourth and final section on chemical analysis in the first edition.

¹⁸ *Ivi*, I, pp. 8-9: «La composition des corps formés de deux éléments est soumise à une loi remarquable, dont M. Berzelius a fait connaître toute la généralité par des expériences multipliées, et que l'on peut énoncer ainsi: lorsque deux corps sont susceptibles de s'unir en diverses proportions, ces proportions sont constamment le produit de la multiplication par 11/2, 2, 3, 4, etc. de la plus petite quantité d'un des corps, la quantité de l'autre corps». This text was also in *Id.*, *Eléments*, cit. (1), 1817, II, pp. 479-480.

¹⁹ *Ibid.*, «il y a des rapports simples entre les divers volumes du corps A, qui se combinent avec un volume du corps B, mais encore qu'il en existe entre les volumes respectifs de A et de B».

²⁰ *Ivi*, I, pp. 10-13. It was also in *ivi*, II, pp. 487-488. Orfila kept this discussion almost unchanged until his fifth edition. Cfr. *Id.*, *Eléments*, cit. (1), 1831, I, pp. 8-13.

²¹ *Id.*, *Eléments*, cit. (1), 1819, I, 13: «Nous croyons le faire connaître avec détail, parce que nous nous en servons souvent par la suite, et surtout parce qu'il est généralement admis, et que l'on peut en faire de nombreuses applications à l'analyse». *Id.*, *Eléments*, cit. (1), 1824, p. 13.

that the «Dalton system» was «completely hypothetical» but very useful for calculating chemical composition even in cases where no chemical analysis was available.²² These comments together with his choice of oxygen as the unit clearly show that Orfila was interested in atomic theory due to its advantages in chemical analysis and not by virtue of its theoretical consequences. He accordingly included a new paragraph with information about atomic weights in chapters dealing with the chemical properties of substances. The description of chemical composition was now expressed in quantitative terms using atomic theory.

A contemporary review of Orfila's textbook praised his new use of atomic theory to calculate the elemental composition of compounds, which was «almost the same» as that calculated by «direct [chemical] analysis» or the laws of volumes.²³ Orfila now offered far more quantitative data than in his previous first edition. For instance, whereas in 1817 Orfila described carbonic acid composition in just one brief sentence,²⁴ in 1819 he dedicated a long paragraph to the subject and introduced a new point on carbonic acid atomic weight:

Un volume de gaz acide carbonique est formé d'un volume de gaz oxygène et d'un volume [ou d'un atome] de vapeur de carbone condensés en un seul: il est donc évident que le poids d'un atome de gaz acide carbonique doit se composer de la somme des poids d'un volume d'oxygène et d'un volume de vapeur de carbone, ou de 72,624 [100] d'oxygène et de 27,376 [38,22] [37,50] de carbone: en effet, ces nombres sont exactement en rapport avec les densités de l'oxygène et de la vapeur de carbone, qui sont 1,10359 [1,1026] [1,111] pour l'oxygène, et 0,4160 [0,4214] [0,4166] pour la vapeur de carbone. En supposant l'acide carbonique

²² «Avant de terminer cet article, nous croyons devoir faire sentir que le système de M. Dalton est entièrement hypothétique, et qu'il est impossible d'en démontrer rigoureusement l'exactitude, mais qu'il peut être d'une très grande utilité pour parvenir à faire connaître la composition des corps; que déjà plusieurs chimistes célèbres l'ont employé avec le plus grand succès pour déterminer les proportions de plusieurs composés qui n'avaient pas été analysés; enfin, qu'il paraît être la source où M. Berzelius a puisé la première idée de sa belle théorie sur les lois qui président à la composition des corps». Cfr. *Id.*, *Eléments*, cit. (1), 1819, I, p. 17; *Id.*, *Eléments*, 1824, I, 17 and 1831, I, p. 17.

²³ «Des notions précises sur le système atomistique ou corpusculaire de M. Dalton, précédent l'histoire des faits particuliers, et en facilitent l'intelligence. On trouve à la fin de l'histoire de chacun des principaux corps, des détails sur leur composition, calculés tantôt d'après les lois et la théorie atomistique, tantôt d'après l'analyse directe, tantôt enfin d'après les lois qui président à la combinaison des corps qui a lieu par volume; et, ce que le plus souvent M. Orfila prouve que la composition des corps se trouve être à-peu-près la même, quelle que soit la méthode employée pour la découvrir. Cette partie essentielle manquait entièrement à la première édition». Cfr. J. CLOUET, *Eléments de chimie appliquée à la médecine et aux arts*. «Nouveau Journal de médecine, chirurgie, pharmacie», vol. VII, 1820, pp. 44-47, on p. 46.

²⁴ ORFILA, *Eléments*, cit. (1), 1817, I, p. 132: «Il est formé de 27,376 de carbone, et de 72,624 d'oxygène».

composé d'un atome de carbone (dont le poids est 0,75 [0,76] [0,75]) de deux atomes d'oxygène (dont le poids est 2), on le trouve formé de 72,624 (100) [100] d'oxygène et de 27,225 (38) [37,50] de carbone.

Poids d'un atome d'acide carbonique: Il est de 2,75, somme du poids d'un atome de carbone et de deux atomes d'oxygène dont il est composé²⁵

It should be borne in mind that in this passage Orfila used atomic theory to express the «weight of an atom of carbonic acid» and also to calculate the specific weights of vapours. The most evident case is carbon. While no empirical means of calculating the specific weight of carbon vapour were available at the time, its value could be obtained by using Gay-Lussac's law and additional hypotheses on ratio volumes. Orfila supposed that carbonic acid was made up of one volume of oxygen and one volume of carbon, so the vapour specific weight of carbon could be calculated as oxygen (1,10359) minus carbonic acid (1,5196) = 0,4160.²⁶ The other values of specific weights were also theory-laden, while not as evident as in the case of carbon vapour. In his second edition, both oxygen and carbonic acid values came from Biot and Arago's research, which was also used by Thenard in his textbook.²⁷ In 1824, and also following Thenard, Orfila adopted some of the new values obtained by Berzelius and Dulong (1820). However, in 1828 and 1831, and coinciding with the increasing importance of atomic theory, Orfila adopted new specific weights. Orfila took this new data from *An Attempt to Establish the First Principles of Chemistry by Experiment* by Thomas Thomson, which was published in 1825 and translated into French during the same year. In his book, Thomson included a broad discussion about the calculation of densities and atomic weights and, following Prout's ideas, claimed that a simple relation existed between both magnitudes. He subsequently aimed to obtain a consistent set of values and, in some cases, calculated densities by using atomistic hypotheses.²⁸

²⁵ Brackets show changes in subsequent editions: Id., *Elémens*, cit. (1), 1819, I, p. 189; { } = changes in 1824, I, p. 207, and [] = changes in 1828, I, p. 207 and 1831, I, p. 210.

²⁶ Obviously, other volume ratios were possible. For instance, Berzelius regarded two volumes of oxygen plus one volume of carbon condensed in two volumes of carbonic acid, so carbon vapour specific weight was approximately twice Orfila's.

²⁷ J.B. BIOT, F. ARAGO, *Mémoire sur les affinités des corps pour la lumière, et particulièrement sur les forces réfrigérentes des différens gaz*, «Mémoires de la classe des sciences mathématiques et physiques», vol. VI, 1806, pp. 301-387. See THENARD, *Traité*, cit. (1), 1813-16, I, p. 182.

²⁸ T. THOMSON, *Principes de la chimie établis par les expériences ou essai sur les proportions définies dans la composition des corps*, Paris, Crevot, 1825, t. I, pp. 226-228. See also, for instance, chapter III on the densities of oxygen and hydrogen, vol. I, pp. 45-72. In fact, some of

In the text quoted above, Orfila employed atomic theory to calculate the ratio of carbon in carbon oxide composition and showed that it was almost identical to the results obtained by chemical analysis. After adopting Thomson's values for specific weights, both values became completely identical.²⁹ The difference between experimental and theoretical values was more dramatic in other substances. For instance, when describing the composition of hydrochloric acid, Orfila employed volume ratio and specific weights in the calculation: two volumes of hydrochloric acid being made up of one volume of hydrogen and one of oxygen, so its composition (*i.e.*, the chlorine/hydrogen ratio) should be equal to the chlorine/hydrogen specific weight ratio (33,73/1), *i.e.*, 33,73 parts of chlorine and one part of hydrogen.³⁰ However, using atomic theory, an atom of hydrochloric acid was made up of one atom of hydrogen (0.125) and one atom of chlorine (4.5), so its composition was «one part hydrogen and 36 parts of chlorine». Why were the results of both methods so different? Orfila answered this question in a footnote:

Cette différence entre les proportions, calculés d'après les volumes ou d'après les atomes, tient uniquement à ce que les densités de l'hydrogène et du chlore, qui ont servi de base au calcul, ne sont pas les mêmes. M. Thomson admet que la densité de l'hydrogène est de 0,694 et celle du chlore 2,500; tandis que, suivant nous, la première est 0,7321, et la seconde 2,470.³¹

As in carbonic acid, these alarming differences could be avoided by adopting Thomson's specific weight values and Orfila duly proceeded to do so in his 1828 and 1831 editions.³² In other words, Thomsonian atomic weights compelled Orfila to correct some «empirical» data in order to adjust theoretical results. In this way, and following Thomson's *Principles of Chemistry*, Orfila was making a broader use of atomic theory than other French textbooks. For instance, compare Orfila's earlier description of carbonic acid with that of Thenard in his 1824 edition:

Thomson's values of densities came from an anonymous paper on specific weights which was published by Prout in «*Annals of Philosophy*», VI, pp. 321-330.

²⁹ Orfila calculated $72,624 \text{ of oxygen} / 2 * 0,75 = 27,225$ of carbon. In fact, the result of this mathematical equation is 27,234 and not 27,225. In 1828 and 1831, the text was almost identical but the values were changed, so atomic-calculated and chemical analysis values were identical. See text quoted *supra*.

³⁰ That is $\text{Cl} (= 2,470) \text{ H} (= 0,0731) / = 33,8$ parts of chlorine / 1 part of hydrogen (in weight).

³¹ ORFILA, *Elémens*, cit. (1), 1819 I, pp. 234-345.

³² For other examples, see *ivi*, I, p. 428 (ammonia).

TABLE 1

Atomic weights	Thomson 1818-1822 (°)	M. ORFILA <i>Eléments de chimie appliquée à la médecine</i> , Paris, 1819 (2 nd ed.), 1824 (3 rd ed.), 1828 (4 th ed.), 1831 (5 th ed.), 1835-36 (6 th ed.), 1843 (7 th ed.) and 1851 (8 th ed.)					
		1819 and 1824	1828 and 1831	1835-36 atomes (°)	1835-36 prop. (°)	1843 (prop.) (°)	1851 (prop.) (°)
O	1	1	100	100	100	100	100
H	0.125	0.125	6.239	12.479	12.48	12.5	12.5
P	1.500	1.5-2'67	196.150	196.150	196.15	400	400
S	2.000	2	201.160	201.160	201.16	200	200
I	15.625	15.625	789.750	1579.500	1579.50	1578.2	1578.2
Cl	4.500	4.5	221.325	442.650	442.64	443.2	443.2
N	1.750	1.75	88.518	177.360	177.02	175	175
Ca	2.625	2.625	256.019	256.019	256.01	250	250
K	5.000	5	489.916	489.916	489.916	490	490
Na	3.000	3	290.897	290.897	290.89	287.2	287.2
Fe	3.500	3.5	339.210	339.210	339.21	350	350
Sn	7.375	7.375	735.294	735.294	735.29	735.3	735.3
As	4.750	4.75	470.120	479.120	470.12	937.5	937.5
Sb	5.625	5.625	806.452	1612.900	1612.90	806.5	806.5
Pb	13.000	13	1294.500	1294.500	1294.50	1294.5	1294.5
Cu	8.000	8	395.695	791.390	395.6	395.6	395.6
Ag	13.750	13.75	675.803	1350.000	1351.60	1350	1350

(°) In 1835-36, I, 52-53, «poids des atomes» and «poids des proportions». In 1843 and 1851, Orfila just offered data about the «poids des proportions».

(°) T. THOMSON, *Système de Chimie*, Paris, 1818 and *Supplement*, Paris, 1822

L'acide carbonique contient un volume égal au sien de gaz oxygène, or, comme la pesanteur spécifique de l'acide carbonique est de 1,5245, et que celle de l'oxygène est de 1,1026, il s'ensuit évidemment qu'il est composé de 27,67 de carbone et de 72,33 d'oxygène en poids, ou, d'après ce que nous avons dit de la vapeur de carbone (p. 199), de 1 volume de cette vapeur et de 1 volume d'oxygène.³³

There are several important differences: in this paragraph, Thenard used Berzelius's and Dulong's new research on specific weights and commented on the hypothetical character of carbon vapour density.³⁴ In contrast with Thomson and Orfila, Thenard did not offer any information about carbonic acid atomic weight, so he was not compelled to reconcile theoretical and empirical results. In fact, even though Thenard added new data on atomic theory at the beginning and end of his textbook between 1817 and 1824, he did not substantially use atomic theory in describing chemical composition until his fifth edition (1827). Orfila gave information on atomic theory in the introductory chapters of his second edition (1819) and these contents remained almost unchanged until the fourth edition (1828). Nevertheless, he substantially modified his chapters dealing with chemical composition by using atomic weights. Not only did Orfila describe new chemical composition in atomic terms but he also adapted empirical data to reconcile Thomson's atomic weights. As such, while largely employing Thenard's textbook classifications and contents, Orfila did not follow his path to atomic theory. In this regard, Orfila was relying on Thomson's textbooks, which he used as the principal source of his atomic weight and specific gravity data. Despite these important differences, both French textbooks writers regarded atomic theory as a useful tool for quantitative chemical analysis and calculating problematic vapour densities. The advent of Berzelian atomism and formulae drastically changed this scenario.

³³ THENARD, *Traité*, cit. (1), 1824, II, p. 146. Id., *Traité*, cit., 1821, I, p. 644.

³⁴ In his first editions (see Id., *Traité*, cit. (1), 1821, I, pp. 643-644), Thenard employed Arago and Biot's specific weights and he changed in 1824 to the new values which had been empirically calculated by J. BERZELIUS, P. DULONG, *Nouvelles déterminations des proportions de l'eau et de la densité de quelques fluides élastiques*, «Annales de chimie et de physique», vol. 15, 1820, pp. 386-395. See THENARD, *Traité*, cit. (1), 1824, I, p. 265. Concerning carbon vapour, Thenard (*lvi*, I, p. 199) offered Gay-Lussac's (0,4219) and Berzelius's (0,973) hypotheses about its specific weight.

2. INTRODUCING BERZELIAN FORMULAE IN FRENCH CHEMISTRY TEXTBOOKS, 1827-1836

Atomic theory gained maximum popularity in French chemistry textbooks from the time of the publication of Thenard's textbook's fifth edition (1827) and Dumas's famous lectures at the Collège de France (1836). The old versions (Dalton, Wollaston, Thomson) of atomic theory were replaced by Berzelian atomism, which was based on new methods of calculating atomic methods such as the Dulong-Petit law, the EVEN hypothesis and Mitscherlich's isomorphism. This then led to the introduction of an increasingly clear division between equivalent and atomic weights in French textbooks. While these words were employed with almost the same meaning in the first editions, separate tables of equivalents and atomic weights were subsequently included in Orfila's and Thenard's textbooks. At the same time, Berzelian formulae slowly gained ground in textbooks and contributed to various unforeseen applications of atomic theory. While atomic theory had previously been regarded as a tool for chemical analysis, Berzelian formulae were now being employed in order to reveal chemical binary composition, to explain chemical reactions and to classify chemical substances.³⁵

Berzelian formulae, which had been presented in 1813, were scarcely employed until the end of 1820s but were then rapidly introduced in textbooks and research publications. By the mid-1830s, they were broadly employed throughout Europe. By way of example, Thenard, who had described these formulae in his 1827 edition,³⁶ did not make widespread use of the same until the 1834-35 edition. In a similar fashion Orfila first mentioned the new formulae in his 1828 edition³⁷ but did not use them extensively until his 1835-36 edition.

The broader use of atomic theory raised a didactic problem. Atomic theory could not be regarded as specialized knowledge which only advanced students could understand – as was the case of Thenard until as late as 1824³⁸ – but as a preliminary subject to the study of chemistry.

³⁵ See U. KLEIN, *Paper tools in experimental cultures*, «Studies in History and Philosophy of Science», vol. 32 (2), 2001, pp. 265-302 and Id., *Experiments, Models, Paper Tools. Cultures of Organic Chemistry in the Nineteenth Century*, Stanford, Stanford University Press, 2003.

³⁶ THENARD, *Traité*, cit. (1), 1827, I, pp. 176-180.

³⁷ ORFILA, *Elémens*, cit. (1), 1828, II, pp. 579-180.

³⁸ After an introductory chapter on atomic theory, THENARD, *Traité*, cit. (1), 1824, I, p. 24 said: «Nous sommes loin d'avoir traité convenablement un sujet aussi étendu [dans les premiers chapitres]; nous n'avons dû qu'en exposer les bases: en allant plus loin, le lecteur qui commence

As the popular textbook writer Edward Turned realized in his fourth edition (1833), «chemical symbols are not only suitable as a convenient abbreviation for educated chemists, but may also serve as a powerful teaching tool for teachers of chemistry».³⁹ During the 1830s, several books were published which gave an introduction to chemistry through atomic theory. Alexandre Baudrimont (1806-1880), author of one of these textbooks, clearly recognised the new meaning of atomic theory in the classroom:

La théorie atomique appliquée à la chimie a fait tant de progrès depuis un petit nombre d'années, son utilité est si grande et ses résultats sont si nombreux, qu'il ne lui manque rien qu'elle devienne une science vulgaire. Cependant un préjugé s'y est opposé jusqu'à présent: on a pensé qu'elle ne pouvait être comprise que par ceux qui avaient déjà acquis des connaissances profondes en chimie. Une étude long-temps continuée de ce sujet et quelques essais m'ont appris, au contraire, qu'elle pouvait servir d'introduction à l'étude de cette science.⁴⁰

Substantial changes were introduced in French chemistry textbooks between 1827 and 1836. And once again Orfila and Thenard followed different paths when introducing the new Berzelian atomism. Orfila, who had written new introductory chapters on atomic theory as early as in 1819, added further chapters on the subject at the end of the section on chemical analysis in his fourth (1828) and fifth editions (1831).⁴¹ This was the strategy followed by Thenard between 1818 and 1827, when he extended his chapters on chemical analysis, mainly with excerpts from Berzelian texts. However, in his fifth edition (1827), Thenard decided to gather all the information on chemical theory that had previously been scattered in different parts of his textbook into just one introductory chapter. In the forewords, he explicitly pointed out the new role of atomic theory:

Ce qui distingue surtout cette nouvelle édition des précédentes, c'est le soin que l'on a mis à développer la théorie des atomes et celle des nombres proportionnels, lesquelles découlent du même principe. Une idée précise en a d'abord été

l'étude de la chimie n'aurait pas pu nous suivre, au lieu qu'il ne rencontrera plus de difficultés lorsque les propriétés des corps lui seront bien connues; c'est pourquoi tous les développements dont ce sujet est susceptible seront présentés dans la dernière partie de cet ouvrage». This sentence was also in Id., *Traité*, cit. (1), 1827, I, p. 176.

³⁹ E. TURNER, *Elements of Chemistry*, London, John Taylor, 1833, p. vii.

⁴⁰ A. BAUDRIMONT, *Introduction à l'étude de la chimie par la théorie atomique*, Paris, L. Colas, 1833, p. 1. Other similar books were published in France during late 1830s and early 1840s by Choron (1837), Liebig (1837) and Colin (1841).

⁴¹ ORFILA, *Elémens*, cit. (1), 1828, II, 574-581 and Id., *Elémens*, cit. (1), 1831, II, pp. 620-627.

In his textbook, he changed the name of the chapter *du système atomistique de Dalton* to *la théorie atomique*. Here he placed the chapters which he had added in his second volume in 1828 and 1831 and rewrote the first chapters about the laws of chemical combination and added a completely new chapter on atomic theory. He set out by discussing the laws of chemical composition which he divided in two parts: (a) «law of multiple proportions» (Berzelius's law and Gay-Lussac's law of combining volumes)⁵³ and (b) «law of equivalents and proportional numbers» in which Orfila explained the methods for calculating equivalents weights.⁵⁴ He then continued by discussing atomic theory and where the main problem, according to Orfila, was to figure out how many constituent atoms existed in a compound body and the weight of each atom.⁵⁵ Whereas in earlier editions he had included a brief description of Dalton's rules of greatest simplicity, these rules were now replaced by a more elaborate set including the EVEN hypothesis, chemical analogies and Dulong-Petit and Mitscherlich's laws.⁵⁶ Orfila explained how to calculate the atomic weights of (1) gaseous simple substances (by using the EVEN hypothesis) (2) liquid and solid substances which could react to produce gaseous substances (by using the EVEN hypothesis plus chemical analogies) (3) other substances (by using the Dulong-Petit law and isomorphism).⁵⁷ For the first time, Orfila included a table with both atomic and «proportions» weights and pointed out that their differences were generally limited to proportional numbers being double that of atomic weights.⁵⁸

Daremberg physique, minéralogie, chimie médicale, chimie minérale, botanique, géologie, etc. (1835-1836) fol. 65r. This text is after a table with formulae and atomic weights of acids.

⁵³ There were some significant changes in this paragraph. While in the first editions Orfila asserted that «lorsque deux corps sont susceptibles de s'unir en diverses proportions, ces proportions sont constamment le produit de la multiplication par 1 1/2, 2, 3, 4, etc., de la plus petite quantité d'un des corps, la quantité de l'autre corps restant toujours la même», in the sixth edition, he said he substituted «1 1/2, 2, 3, 4, etc.» by «1, 2, 3, 4, etc.». Cfr. ORFILA, *Elémens*, cit. (1), 1819, I, pp. 8-9; 1828, I, 8; 1831, I, p. 8; and 1835-36, I, p. 24. He added that cases such as «1 à 1 1/2», «ou de 2 à 3», de 4 à 5» were «assez rares» and that «on ne les observe probablement que parce que l'on ne connaît pas encore tous les composés que peuvent former les deux corps que l'on examine». *Ivi*, 1835-36, I, p. 25. Compare also THENARD, *Traité*, cit. (1), 1821, I, pp. 20-21; 1827, I, pp. 163-164; 1834-35, I, p. 30, for similar changes.

⁵⁴ This chapter was substantially enlarged from a former 1828 and 1831 chapter on «Equivalents chimiques». Cfr. ORFILA, *Elémens*, cit. (1), 1828, II, pp. 580-581. *Id.*, *Elémens*, cit. (1), 1831, II, pp. 626-627.

⁵⁵ *Ibid.*, «Combien existe-t-il d'atomes constituans dans un corps composé, et quel est le poids de chacun de ces atomes?».

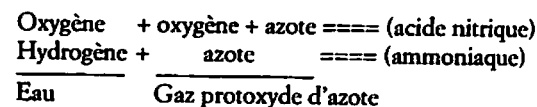
⁵⁶ ORFILA, *Elémens*, cit. (1), 1835-36, I, pp. 40-50. Some parts had already been included in a former chapter on «De la théorie atomistique, des signes algébriques employés par M. Berzelius et des équivalents chimiques». Cfr. *Id.*, *Elémens*, cit. (1), 1828, II, 574-581 and 1831, II, pp. 620-627.

⁵⁷ *Id.*, *Elémens*, cit. (1), (1835-36), I, pp. 40-50.

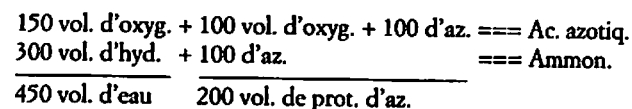
⁵⁸ «La proportion offre un poids double de celui de l'atome». *Ivi*, pp. 51-53. Orfila also

Orfila closed his chapter on atomic theory with a description of Berzelian formulae that he used for the first time in his inorganic chapters. Orfila praised the advantages of these symbols in that they offered an easy description of the results of chemical reactions and he remarked that the result of these equations should be exact whatever «the relative arrangement of atoms» might be.⁵⁹ However, he rarely employed these balances in his 1835-36 edition. In the first editions, Orfila had employed chemical reaction balances by using the names of substances instead of Berzelian formulae and just a few of these equations were transformed into Berzelian formula balances in his following editions. For instance, by using these balances, Orfila described the extraction of nitrogen protoxide by heating ammonium nitrate in a retort and explained it with the following equation:

Théorie. Nous pouvons représenter les éléments de ce sel [ammonium nitrate] par:



This equation expressed qualitative balance between chemical element reactants and products. In 1835-36, Orfila introduced volume ratios:



Finally, in 1843 Orfila used Berzelian (equivalent) formulae and expressed this balance in a more compact way:⁶⁰



mentioned other cases such as «bismuth, aluminium et de glucinium» whose atomic weights were one and a half times their proportions. «sont une fois et demi aussi considérables que ceux de leurs proportions». In the case of «bore», its atom «pèse quatre fois moins que sa proportion». Cfr. *Ibid.*

⁵⁹ «Il suffit que le même nombre d'atomes existe dans chaque membre d'une équation, pour qu'elle soit exacte, quel que soit d'ailleurs l'arrangement relatif des atomes». Cfr. *ivi*, I, pp. 51-58. Quoted in p. 56. Berzelius formulae have been already mentioned in 1828 (*ivi*, II, pp. 579-580) but Orfila did not employ them either in his 1828 or 1831 editions.

⁶⁰ *Id.*, *Elémens*, cit. (1), 1828, I, pp. 193-194; 1831, I, p. 196; 1835-36, I, p. 256; and 1843, I, pp. 165-166. The second and third balances express a quantitative relation whereas the first one does not. However, the first and second balances highlight the fact that water is formed by union of oxygen from nitric acid and hydrogen from ammoniac and nitrogen protoxide by oxygen and nitrogen of nitric acid plus nitrogen from ammonia.

Thus, even though atomic theory had reached its apex in Orfila's textbook by the mid-1830s, some of its main features, such as Berzelian formulae and equations, were not completely developed throughout the text until the 1840s editions. However, a wider use of atomic theory in the text compelled Orfila in 1836 to write a larger introduction, in which he described its main characteristics. Atomic weights were employed in almost every chapter dealing with inorganic chemistry in order to portray chemical composition and reactions. In other words, by the mid-1830s, atomic theory was a substantial part of both the theoretical and descriptive chapters in Orfila's textbook.

3. REMOVING ATOMS FROM THE CHEMICAL REALM

In 1843, Orfila erased the chapter on atomic theory from the introduction which he had just presented in the previous edition. He also dramatically reduced the number of pages of his chapter on the laws of chemical composition and on equivalents. Entire paragraphs were removed such as those dealing with Gay-Lussac's law and its application to chemical calculations⁶¹ or the advantages of equivalent weights in chemistry.⁶² As a result, the thirty-five-page introduction was reduced to just six pages.⁶³ Orfila only included one table with equivalent weights, without giving any information about their differences and their relationship with atomic weights. Finally, he included a brief description of Berzelian formulae, which he employed more broadly than he had in his former edition. However, Orfila pointed out that Berzelian formulae should not be confused with «what is called atomic theory», «an hypothesis» which he affirmed he would never deal with.⁶⁴ In the descriptive chapters, paragraphs on chemical composition were rewritten by using chemical equivalent weights and formulae. For instance, the

⁶¹ ORFILA, *Elémens*, cit. (1), 1835-36, I, pp. 27-29. Orfila mentioned three uses: calculation of (1) specific weights of a gas produced by two gases (2) Weight compositional ratios of gases by using densities produced by two gases (3) Weight composition of a gas produced by a solid and a gas (example: HS^2). The last two uses disappeared in 1843. *Id.*, *Elémens*, cit. (1), 1843, I, pp. 11-12.

⁶² *Id.*, *Elémens*, cit. (1), 1835-36, I, pp. 36-40. Orfila offered four advantages: First, it was possible to foresee without chemical analysis the composition of a binary body or a neutral salt. It was also possible to know the quantities of a substance replacing another in a compound and the amount of an acid which was necessary to use when decomposing salts. Only the first one was maintained in 1843. *Id.*, *Elémens*, cit. (1), 1843, I, pp. 14-16.

⁶³ *Id.*, *Elémens*, cit. (1), 1835-36, I, pp. 23-58 and *Id.*, *Elémens*, cit. (1), 1843, I, pp. 11-17.

⁶⁴ *Ivi*, 1843, I, p. 17: «il ne faut pas la confondre [Berzelius's formulae] avec ce que l'on appelle la théorie atomique, qui n'est qu'une hypothèse dont nous ne nous occuperons même pas».

chemical composition of ammonia was changed as follows (brackets include new information in 1843 edition):

Lorsqu'on décompose 100 parties en volume de gaz ammoniac par l'étincelle électrique, on obtient 150 parties de gaz hydrogène et 50 de gaz azote en volume: le gaz ammoniac est donc formé d'un volume et demi d'hydrogène, et d'un demi-volume d'azote condensés de manière à ne former qu'un volume: en déterminant le poids de ces volumes d'après le poids spécifique des deux gaz, on trouve le gaz ammoniac formé de 100 parties d'azote et de 21,15 d'hydrogène en poids. Si on calcule sa composition en admettant qu'il est formé d'un atome et demi [trois équivalents] d'hydrogène qui pèse 9,358 [37,44], et d'un demi-atome [un équivalent] d'azote dont le poids est 44,25 [177,02], on le trouvera composé de 100 d'azote et de 21,14 d'hydrogène en poids. L'atome [L'équivalent] d'ammoniaque pèsera donc 53,608 [214,46], et sa formule sera H^3Az .⁶⁵

Why did Orfila drastically erase atomic theory from his textbook? There is not a single answer to this question. In order to understand Orfila's decision, we should consider several different aspects. First of all, we shall discuss the most widely employed explanation: Did the emergence of positivist philosophy give rise to an anti-metaphysical attitude among chemists, which led them to eliminate atoms from their textbooks? During those years, a clear divide was established between equivalents and atomic weights, these being two concepts which had practically been treated as synonyms in previous years. We shall then analyse whether equivalents were regarded as empirical data in opposition to hypothetical atomic weights and go on to consider Orfila's reaction against new organic chemistry, a growing subfield in which atomic theory made its most dramatic progress during the 1840s and 1850s. As the contents and structure of a textbook do not simply depend on the personal decisions of the writer, we should also discuss the targeted audience as well as the institutional constraints of Orfila's book.

3.1. Positivist constraints? «Physical atoms» in French textbooks in Comte's times

Alan Rocke has remarked that microscopic interpretations of chemical processes in terms of atoms («physical atomism») were not broadly accepted by nineteenth-century chemists. The main problem for atomists

⁶⁵ *Id.*, *Elémens*, cit. (1), 1835-36, I, p. 379. Changes introduced in 1843 are between []. Cfr. *Id.*, *Elémens*, cit. (1), 1843, I, p. 219. In 1851, there were just some changes in figures. Cfr. *Id.*, *Elémens*, cit. (1), 1851, I, p. 264: hydrogen (37,5), nitrogen (175) and ammonium (212,50).

was the absence of any decisive empirical evidence about the physical existence of atoms at that time. In this context, anti-atomists such as Jean Baptiste Dumas asserted that atoms «went beyond the realm of experiment» and doubt could easily be cast regarding their physical existence. They could also employ these plausible doubts to argue against atomic weight and to support equivalent weights, which were regarded as empirical values without any arbitrary assumption. In the case of France, this historical trend seems to be in consonance with the emergence of Auguste Comte's philosophical system, which gave added weight to the rejection of unverified hypothesis in science.

As we have mentioned above, this scenario, was recently questioned by Bernadette Bensaude-Vincent who called it «a legend of French chemistry». Bensaude-Vincent has suggested that «textbook positivism» – and not Comte's philosophical ideas – could well be the reason for the rejection of atoms from the chemical realm. This «variety of positivism» conveyed an image of experimental knowledge uncontaminated by hypotheses. As Fremy and Pelouze put it, a textbook should just summarize «what can be called the most positive and verified part of science, namely facts, and [to] reject what is only conjecture».⁶⁶ In the following paragraphs, we will argue that «textbook positivism» was not in opposition to the acceptance of physical atoms in French chemistry textbooks during the 1830s and 1840s. In other words, physical atoms (or molecules) were commonly regarded as a part of the «positive and verified part of science» and they were subsequently included in almost every chemistry textbook published in France over these years. The problem was not the physical existence of atoms but how to ascertain the number of atoms combined in a chemical compound. As Thenard stated in 1827:

Sans doute il paraît démontré que toutes les combinaisons se font d'atomes à atomes, et qu'elles n'ont ordinairement lieu qu'entre quelques-uns; mais entre combien? c'est ce qu'on ne saurait dire. Le choix, il est vrai, se trouve borné, même très limité; mais enfin on est obligé de choisir, et, en choisissant, on court le risque de se tromper.⁶⁷

⁶⁶ E. FREMY, J. PELOUZE, *Cours de chimie générale*, Paris, Masson, 1848, I, p. 1. Quoted by BENSAUDE-VINCENT, *Atomism and Positivism*, cit. (4), p. 89. For other examples about similar statements, see A. MANAVIT, *Précis élémentaire de chimie, à l'usage des élèves des collèges royaux*, Paris, L. Hachette, 1828.

⁶⁷ THENARD, *Traité*, cit. (1), 1827, I, pp. 173-174.

We have already indicated that chemical reactions were discussed in French textbooks in molecular terms long before the advent of Dalton's atomic theory. Following the eighteenth-century usage, the chapters on affinity forces employed the words «molecules integrantes» and «molecules constituantes». The relation between this approach and Daltonian atomism is controversial. The differences between 'British chemical-atomism' and 'French physical-molecularist approaches' has been forwarded as the main reason for the rejection of Avogadro's ideas, which were expressed in molecular terms.⁶⁸

However, chemical textbooks offered a very different picture. At the beginning of the nineteenth century, atoms and molecules were used in separate chapters, the former when dealing with chemical proportions and chemical analysis and the latter when explaining affinity forces.⁶⁹ However, when new introductory chapters on atomic theory were created just after dealing with affinity forces, some authors introduced the word atom as a synonym of molecule. During the 1820s, these words were used in the first chapters with very slight differences of meaning, if any. Along with the spread of atomic theory, the word «atom» gained ground and, in some cases, replaced the word «molecule». The replacement was a gradual and silent change. For example, in his first edition (1813), Thenard only employed the word «molecule» and introduced the word «atom» as a synonym in his fourth edition (1824).⁷⁰ In the following edition (1827), the word «atom» was clearly preferred to «molecule»⁷¹ and, finally, in the last edition (1835-36), Thenard employed the word «atom» almost exclusively. Expressions such as «molécules integrantes» and «molécules constituantes» were replaced by «atomes intégrants» and «atomes constituants».⁷² Orfila followed a similar path. Even though he introduced atomic theory in 1819, he only used the word molecule when asserting that both elementary and compound bodies were made up of «very small,

⁶⁸ For a recent critical discussion of this issue see M. CIARDI, *Amedeo Avogadro's Concept of the Atom: Some New Remarks*, «Ambix», vol. 48 (1), 2001, 17-24. See also J.B. BROOKE, *Avogadro's hypothesis and its fate: A case-study in the failure of case-studies*, «History of Science», vol. 19, 1981, pp. 235-273; N.W. FISHER, *Avogadro, the Chemists and the Historians*, «History of Science», vol. 20, 1982, pp. 77-102; 212-231; M. CIARDI, *L'atomo fantasma. Genesi storica dell'ipotesi di Avogadro*, Firenze, Olschki, 1995.

⁶⁹ For an analysis of the uses of «atoms» and «molecules» in first half of nineteenth century France see M. GYUNG KIM, *The Layers of Chemical Language, II: Stabilizing Atoms and Molecules in the Practice of Organic Chemistry*, «History of Science», vol. 20, 1992, pp. 396-437.

⁷⁰ THENARD, *Traité*, cit. (1), 1813-16, I, pp. 2-3 and *Id.*, *Traité*, cit. (1), 1824, I, p. 3.

⁷¹ Compare *ibid.* and *Id.*, *Traité*, cit. (1), 1827, I, p. 3.

⁷² ORFILA, *Eléments*, cit. (1), 1834-35, I, pp. 2-3.

similar or homogeneous, invisible parts which are designated by the name of integrand molecules or particles». ⁷³ In 1824, he just added the word «atom» as a synonym of molecule and he kept this sentence during 1828 and 1831. ⁷⁴ In 1835-36, and coinciding with the maximum use of atomic theory, Orfila clearly preferred the word «atom» to «molecule» even though he continued to use both words:

Un corps élémentaire doit être considéré comme étant formé d'une multitude de très petites parties semblables ou homogènes et invisibles, que l'on désigne sous le nom de *molécules intégrantes*, de *particules*, ou d'*atomes* [d'atomes intégrants]. Il en est de même d'un corps composé: ainsi par exemple, le composé d'or et de plomb, dont nous avons parlé, résulte de l'assemblage d'un très grand nombre de molécules intégrantes [d'atomes intégrants]; mais chacune de ces molécules [atomes] en renferme deux autres de différente nature, l'une d'or, l'autre de plomb, que l'on désigne sous le nom de constituantes [atomes constituants]. ⁷⁵

Moreover, Orfila extended this paragraph by describing the way atoms were combined to each other «by juxtaposition» and, for the first time, defined the atom as «the excessively small particle of a body that does not suffer any alteration during chemical reactions». ⁷⁶ Surprisingly enough, the new definition was kept in the following edition in which Orfila claimed that he would never again mention atomic theory. He now only employed the word «molecule» instead of «atom». Indeed, he went on using the word atom as a synonym of molecule but now preferred the word molecule to the word atom, and was compelled to make changes in the opposite direction from the one he had followed in the first editions. The word atom was now substituted by molecule but the definitions and general microscopic approach to chemical reactions were still there:

Un corps élémentaire doit être considéré comme étant formé d'une multitude de très petites parties semblables ou homogène et invisibles, que l'on désigne sous le nom de *molécules intégrantes*, de *particules*, ou d'*atomes intégrants*. Il en est de même d'un corps composé: ainsi par exemple, le composé d'or et de plomb, dont

⁷³ *Id.*, *Elémens*, cit. (1), 1817, I, p. 2 and *Id.*, *Elémens*, cit. (1), 1819, I, pp. 2-3: «très-petites parties semblables ou homogènes et invisibles, que l'on désigne sous le nom de molécules intégrantes ou de particules».

⁷⁴ *Id.*, *Elémens*, cit. (1), 1824, I, p. 3: «très-petites parties semblables ou homogènes et invisibles, que l'on désigne sous le nom de molécules intégrantes ou de particules ou d'atomes».

⁷⁵ *Id.*, *Elémens*, cit. (1), 1828, I, p. 3 and 1831, I, p. 3. Brackets [] indicate changes in *id.* 1835-36, I, p. 3.

⁷⁶ *Id.*, *Elémens*, cit. (1), 1835-36, I, p. 3: «On peut, d'après ce qui précède, définir l'atome, la particule excessivement petite d'un corps qui n'éprouve plus d'altération dans les réactions chimiques».

nous avons parlé, résulte de l'assemblage d'un très grand nombre d'*atomes intégrants* [de *molécules intégrantes*]; mais chacun de ces *atomes* [molécules] en renferme deux autres de différente nature, l'une d'or, l'autre de plomb, que l'on désigne sous le nom d'*atomes constituants* [de *molécules constituantes*]: ces *atomes* [molécules] en se combinant ne se pénètrent pas, il ne sont que juxtaposés; ils n'éprouvent donc, par la combinaison, aucune altération réelle, en sorte que si le composé (l'or et le plomb, par exemple) vient à être détruit, les *atomes constituants* [les molécules constituantes] se trouvent isolés, jouissant de toutes leurs propriétés, et probablement de leur forme et de leur dimension. On peut, d'après ce qui précède, définir l'*atome* [la *molécule*], la particule excessivement petite d'un corps qui n'éprouve plus d'altération dans les réactions chimiques. ⁷⁷

The replacement of the word «atom» by the word «molecule» took place in other textbooks in different ways. During the late 1830s and early 1840s, some secondary school textbooks employed both words with a similar meaning whereas other books preferred to use the word «atom». ⁷⁸ In 1842, a very popular textbook published by A. Bouchardat, which came out in three editions over the 1840s, asserted that bodies were made up of small parts that «could be named molecules, atoms or particles». Even so, Bouchardat distinguished two kinds of molecules which he referred to as «atomes intégrants» and «atomes constituants». ⁷⁹ These latter expressions were also used by authors such as Grosourdy (1838-39), Guérin (1840) or Favrot (1841), whose books were intended for medical and pharmaceutical students. However, Jean Lassaigne, a chemistry lecturer at the Alfort Veterinary School, went on using «molécules intégrantes» and «molécules constituantes» while largely employing atomic theory in his textbook during the 1840s. In technological oriented lectures at the Conservatoire des Arts et Métiers, Anselme Payen distinguished between «molécules intégrantes ou atomes physiques» and «molécules constituantes ou atomes chimiques» during the early 1830s. ⁸⁰ In contrast, Jean Jacques Colin, chemistry lecturer at the military school of Sant Cyr,

⁷⁷ *Ibid.* Between brackets [] are the changes made in *Id.*, *Elémens*, cit. (1), 1843, I, p. 3 and *Id.*, *Elémens*, cit. (1), 1851, I, pp. 2-3. There are also other minor amendments (commas, periods, etc). Similar changes were introduced in chapters dealing with affinity forces. Compare *Id.*, *Elémens*, cit. (1), 1835-36, I, p. 5 and *Id.*, *Elémens*, cit. (1), 1843, I, pp. 3-4.

⁷⁸ See J. TYRAT, *Nouveau manuel complet et méthodique des aspirants au baccalauréat ès sciences*, Paris, J. Delalaine, 1837, for an example of the first case and E. BURNOUF, *Nouveaux Cahiers de chimie*, Paris, Roret, 1840 for the second one.

⁷⁹ A. BOUCHARDAT, *Cours des sciences physiques, à l'usage des élèves de philosophie*, Paris, G. Baillière, 1842, Paris, 1845, 2nd ed.; *Id.* Paris, 1848, 3rd ed. Quoted from the second edition, (1842) p. 2.

⁸⁰ A. PAYEN, *Cours de chimie élémentaire et industrielle*, Paris, Thomine, 1832, I, p. 50.

preferred the word «molecule» and developed a particular molecular approach that he published in an introductory book aimed at his students. During the 1840s, Colin argued that «atoms grouped each other to give birth to molecules and the latter to particules» and asserted that chemical phenomena happened at the molecular level. He then employed the expression «weight of each sort of molecule» instead of atomic weight and, by way of example, described «iron peroxide» composition as «two iron molecules» and «three oxygen molecules».⁸¹

These examples clearly show the great diversity of uses of the words «atoms» and «molecules» in chemistry textbooks during the 1830s and the 1840s. Most chemistry textbooks writers did not regard molecular and atomic approaches as incompatible or incommensurable but integrated both approaches in their opening chapters. Some of them used atom and molecule as synonyms or quasi-synonyms, whereas others employed these words with clearly different meanings. In Orfila's successive editions, the word «atom», which was introduced at the end of the 1810s had almost completely replaced the word «molecule» by the middle of the 1830s. During the 1840s, there was a tendency in the opposite direction and the word «molecule» regained lost ground in chemistry textbooks. These changes were probably motivated by his dissatisfaction with the idea of indivisibility conveyed by the word atom. Orfila remarked in his textbook that, in some cases, the EVEN hypothesis made it necessary to employ expressions such as «half an atom». As one volume of chlorine plus one volume of hydrogen yields two volumes of hydrochloric acid, an atom of hydrochloric acid should be regarded as half an atom of chlorine and half an atom of hydrogen.⁸² Orfila pointed out this surprising situation:

Il résulte de ce qui précède, que la théorie atomique serait insuffisante pour expliquer les faits, si l'on n'admettait pas que *les atomes des corps gazeux sont susceptibles de se diviser en entrant dans les combinaisons*.⁸³

⁸¹ J.J. COLIN, *Cours de chimie*, 3rd ed. Paris, Gaultier-Languionie, 1841, pp. 24-25 and Id., 4th ed. 1845, pp. 23-24. See also his book on atomic theory: Id., *Considérations élémentaires sur les proportions chimiques, les équivalents et les atomes, pour servir d'introduction à l'étude de la chimie*, (Paris, Versailles, G. Laguionie, 1841). He employed the expression «poids de chaque espèce de molécules» and «2 molécules de fer [...] et de 3 molécules d'oxygène».

⁸² Avogadro had already discussed this problem in his famous *Essai* (1811) (see M. MORSELLI, *Amedeo Avogadro. A Scientific Biography*, Dordrecht, Riedel, 1982, pp. 162-163). However, it seems more probable that Orfila took this example from J.B. DUMAS, *Sur quelques points de la théorie atomistique*, «Annales de chimie», vol. 33 (2), 1826, pp. 337-391, on p. 339 or from Dumas's textbook. Cfr. Id., *Traité de chimie appliquée aux arts*, Paris, Bechet, 1828-1845, I, pp. XXXVIII-XXXIX. See also ROCKE, *Chemical Atomism*, cit. (3), pp. 116-117 for a discussion of Dumas's ideas concerning the EVEN hypothesis.

⁸³ ORFILA, *Elémens*, cit. (1), 1835-36, I, pp. 44, «point qui a dû frapper le lecteur». One

This claim was at odds with the Greek etymology of the word atom which Orfila quoted in a footnote in 1835-36. While Orfila continued to use the word «atomes intégrants» in 1843, he removed this footnote.⁸⁴ Perhaps Orfila was convinced that no limit could be established to the divisibility of matter and felt more comfortable using the word molecule. His lectures at the Paris Medical Faculty during 1844 shed further evidence. Here he employed a definition of the «corps simple» which was slightly but significantly different from that used in his textbook:

Un corps simple résulte de l'agrégation de particules infiniment petites que l'on peut concevoir divisibles à l'infini, toutes ces particules ont reçu le nom d'atomes ou molécules.⁸⁵

In his classroom Orfila affirmed something that he never included in his textbook, i.e., that «atoms or molecules» could be regarded as «divisibles à l'infini». That perhaps explains why he replaced the term atom with molecule in his textbook. Orfila's changes do not seem to have been caused by a strong anti-metaphysical tendency because, despite word changes, he maintained his picture of chemical reaction in microscopic particles terms. Whether using the word «atom» or «molecule», this image was widely conveyed in other contemporary French chemistry textbooks.

3.2. *Metaphysical atoms vs. empirical equivalents?*

The concern about atoms was not associated with their physical existence but to the calculation of atomic weights. It has been argued that chemists preferred equivalents to atomic weights on the assumption that the notion of equivalent was based on experimental and theory-free data. However, modern historical research has questioned this contraposition between «metaphysical atoms» and «empirical equivalents». As Alan Rocke has highlighted, it was impossible to derive chemical formulae and atomic weights from stoichiometric laws alone and several assumptions were necessary to calculate equivalents as well as atomic weights.⁸⁶ In the

volume of hydrogen plus one volume of chlorine yielded two volumes of hydrochloric acid. If the EVEN hypothesis was accepted, then each atom of hydrochloric acid must be formed by a half-atom of chlorine and a half-atom of hydrogen. Orfila mentioned this example as well as the case of arsine which involved similar problems. Cfr. *ibid*.

⁸⁴ Id., *Elémens*, cit. (1), 1843, I, p. 3. Id., *Elémens*, cit. (1), 1851, I, p. 3. See text quoted above.

⁸⁵ Archives de la Bibliothèque Interuniversitaire de Pharmacie, Paris, Ms. 154. *Cours de chimie minérale par Mr. Orfila*. 1844-1845, fol. 1, November, 6, 1844.

⁸⁶ ROCKE, *Chemical Atomism*, cit. (3), pp. 10-15.

following paragraph, we will discuss whether Orfila and Thenard were aware of these assumptions or not. Since our answer is in the affirmative, we shall go on to discuss why they decided to use equivalents instead of atomic weights.

During the 1810s and early 1820s, the words atom, equivalent and proportion were used with a similar macroscopic meaning, namely, the discrete quantities in which bodies combine in chemical reactions. Adolphe Wurtz clearly described this situation in his well-known discussion about atomic theory:

The atomic weights established by Dalton were really proportional numbers; they represented the proportion in which bodies combine, expressed by the relative weights of their ultimate particles. The atoms of simple bodies are equivalent to each other. We may, therefore, consider the terms *atomic weights*, *proportional numbers*, and *equivalents* as at this time synonymous.⁸⁷

There was no sharp distinction between atomic and equivalent weights or proportions in Orfila's text until his sixth edition. The development of the Berzelian system, which relied on physical properties such as gas specific weights or specific heat, introduced new possibilities of calculating atomic weights. As we discussed above, these new methods made chemists such as Thenard or Orfila more confident of the possibilities of calculating atomic weights. At the same time, the new methods also created differences between equivalent and atomic weight. While the second values were calculated by the said Berzelian methods, equivalents were mostly defined as the amount of an element which combines with oxygen in order to form the first protoxide. In some cases, equivalent and atomic weights were different and several textbooks of the early 1830s reproduced tables with both values. During the 1840s, tables with only equivalent figures were prevalent. Why did Orfila also follow this method? In 1835-36, when atomic theory reached its culmination in his textbook, Orfila added a quotation from the *Introduction à l'étude de la chimie par la théorie atomique* by Alexandre Baudrimont:

Ces déterminations [des poids relatifs des atomes] sont bien vagues, et il suffirait peut-être d'une seule découverte pour les renverser toutes. Toutefois, ces découvertes n'auront pas d'influence sur les proportions des combinaisons, mais simplement sur la manière dont on devra les considérer; car au lieu d'un atome,

⁸⁷ A. WURTZ, *La théorie atomique*, Paris, F. Alcan, 1886, 4th ed. Quoted from the English translation. London, 1898, p. 33. On Wurtz, see A. CARNEIRO, *The research school of chemistry of Adolphe Wurtz*, Paris, 1853-1884, Kent, University, Ph.D., 1992, and A. ROCKE, *Nationalizing Science*, cit. (3).

il pourra y avoir deux, trois, quatre, etc.; les poids de ces atomes seront alors deux fois, trois fois, quatre fois moins lourds.⁸⁸

As we have indicated above, the uncertainty associated with atomic weights was also mentioned by other textbook writers such as Thenard.⁸⁹ The study of vapour densities introduced new problems and perhaps it was this «single discovery» («seule découverte») which Baudrimont thought was able to «reverse atomic weights». As Hermann Kopp remarked in 1844, Dumas's and Mitscherlich's new research undermined trust in using specific weights to calculate atomic weights, even if a simple (but undetermined) relation was accepted to exist between the two quantities.⁹⁰ Orfila had relied on Thomson's densities and atomic weights during the 1820s and it is then possible that the new research on vapour densities led to serious problems in his textbook. Let us explore to what extent Orfila was acquainted with Dumas's and Mitscherlich's research.

Dumas did not question Avogadro-Ampère's hypothesis in his paper published in 1826 and which Orfila mentioned in his fourth edition (1828). By using a new experimental method, Dumas offered the densities of two elements (iodine and mercury) and compounds of phosphorus, arsenic, silicon, boron, tin and titanium. He calculated the density of these latter elements by using their chemical analogies, that is, by adopting similar suppositions to those described by Orfila in his textbook. Only in the case of mercury did Dumas recognize an important difference between his experimental results and those predicted by atomic theory. He did not discuss the «consequences of this fact» and announced that he would provide «a detailed study of mercury compounds».⁹¹ He also studied the sulphur density but did not publish his results because they were very different from those predicted by calculations and Dumas was worried

⁸⁸ ORFILA, *Eléments*, cit. (1), 1835-36, I, pp. 49-50. BAUDRIMONT, *Introduction*, cit. (40), p. 108. If Orfila read this book, he could also know Baudrimont's pessimistic views about the future of atomic theory: Cfr. *ivi*, p. 203.

⁸⁹ Compare THENARD, *Traité*, cit. (1), 1817-1818, I, pp. 23-24; *Id.*, *Traité*, cit. (1), 1824, I, pp. 21-23 and *Id.*, *Traité*, cit. (1), 1827, I, pp. 173-174 quoted *supra*.

⁹⁰ H. KOPP, *Geschichte der Chemie*, Brunswick, F. Vieweg und Sohn, 1843-47, II, pp. 397-398. Alan Rocke, however, has recently argued that even authors such as Dumas, who substantially contributed to obtaining the new data about densities, continued to use the EVEN hypothesis thereafter. See ROCKE, *Chemical Atomism*, cit. (3), pp. 115-118.

⁹¹ DUMAS, *Sur quelques points*, cit. (82), p. 353. See also table on p. 391. It should be remarked that Dumas attempted to attain a «natural classification» of chemical elements. See *ivi*, pp. 340-341. See T.M. COLEY, *Early Atomic Speculations of Marc Antoine Gaudin: Avogadro's Hypothesis and the Periodic System*, «Isis», vol. 66, 1975, pp. 334-360, p. 339 for a discussion about Dumas's calculations of the density of phosphorus vapour.

about some possible experimental mistakes.⁹² Finally, in 1832, Dumas, encouraged by Mitscherlich, who was visiting Paris at that time, published his research on the vapour density of phosphor and sulphur. In his first paper, he simply suggested halving the atomic weight of phosphor, that is, returning to the old value but announced the deeper consequences of his research on sulphur density.⁹³ Sulphur densities were three times greater than those expected by theoretical calculations and Dumas suggested that this result could unveil «some new molecular modification» connected with «fundamental ideas» of atomic theory («système atomique»). He wondered whether liquefied sulphur molecules could be grouped in «composed atoms» («atomes composés») which could «resist» the passage to the gaseous state. However, he did not make a clear assertion about the number of molecules that were grouped in these composed atoms.⁹⁴

Orfila largely used papers published in the «Annales de Chimie» as a source of information for his textbooks, so he probably read Dumas's papers. In fact, Orfila employed Dumas's experimental density of phosphor vapour (4.355) but did not realize its theoretical consequences: he did not change phosphor atomic weight as Dumas suggested in his 1832 paper⁹⁵ and went on using atomic theory and chemical analogies to calculate densities as late as his sixth edition, which was published between 1835 and 1836. He even argued that these methods could be applied to calculate vapour densities of «phosphor, sulphur and arsenic» and, by way of example, calculated the latter in the first pages of his textbook.⁹⁶ It seems quite probable that Orfila did not realize the

⁹² J.B. DUMAS, *Dissertation sur la Densité de la Vapeur de quelques corps simples*, «Annales de chimie», vol. 50, 1832, pp. 170-178, pp. 173-176 and J.L. GAY-LUSSAC, J. THENARD, *Rapport sur un Mémoire de M. Dumas, ayant pour titre: Sur la Densité de la Vapeur de quelques corps simples*, «Annales de Chimie», vol. 50, 1832, pp. 178-181, 180.

⁹³ J.B. DUMAS, *Sur la Densité de la Vapeur du Phosphore*, «Annales de Chimie et de Physique», vol. 49, 1832, pp. 210-214, 214.

⁹⁴ *Id.*, *Dissertation*, cit. (92), p. 177.

⁹⁵ Orfila mentioned 4,355 as phosphor vapour density at 500° C. He also said that phosphor atomic weight was «196,15» (Cf. ORFILA, *Eléments*, cit. (1), 1835-36, I, pp. 150-157) whereas DUMAS, *Sur la densité*, cit. (93), pp. 213-214 offered 4,355 as phosphor vapour density and he remarked that this density was at odds with its current atomic weight (196, 142).

⁹⁶ Orfila asserted in 1835 that atomic theory could be applied to calculate vapour densities of substances such as «phosphor, sulphur or arsenic». As an example, Orfila calculated the specific weight of arsenic by using arsine (2,695) and hydrogen (0,0688) densities. The result was 5,1836. Cf. ORFILA, *Eléments*, cit. (1), I, pp. 42-43. Arsenic vapour density was calculated by admitting that «un volume de gaz arsénhydrique résulte d'un volume et demi d'hydrogène, et d'un demi-volume de vapeur d'arsenic condensés en un seul». This assumption was based on the similarities between arsine and ammonia. Thus, the density of a «demi-volume de vapeur d'arsenic» was $2,695 \cdot 1.5 \cdot 0,0688 = 2,5918$ and «one volume» 5,1836.

problems connected with these calculations until he had read a paper which was published by Mitscherlich at the start of 1834. By using new apparatus, Mitscherlich offered evidence that arsenic density was 10.6, that is, around twice the calculated value reported by Orfila in his textbook.⁹⁷ But, more importantly, Mitscherlich clearly showed that similar problems arose with phosphor, sulphur and mercury, and he suggested that these elements had double, a third and a half the number of atoms, respectively, as an equal volume of oxygen. Orfila probably read Mitscherlich's paper some time after his first volume went into print, so he was compelled to add a supplement with a large note on atomic theory at the end of the volume. He explicitly recognized that new empirical data threatened the methods of calculation of atomic weights as well as vapour densities:

Nous avons établi qu'à volume égal, les gaz simples contiennent le même nombre d'atomes, et que ceux-ci sont à égale distance les uns des autres; d'où nous avons conclu que dans ces gaz les poids des atomes sont proportionnels aux densités. Cette loi ne doit pas être admise sans restriction; en effet les travaux plus récents de Mm. Dumas et Mitscherlich démontrent: 1° que le soufre gazeux dont la densité est de 6,65415 contient trois fois plus d'atomes qu'un égal volume d'oxygène; 2° que le phosphore gazeux, dont la densité est de 4,32562 en renferme deux fois plus; 3° que l'arsenic gazeux dont la densité est de 10,36536 en contient également deux fois plus; 4° enfin que le mercure gazeux dont la densité est de 6,97848, en renferme moitié moins qu'un égal volume d'oxygène.⁹⁸

After recognizing these mistakes, Orfila offered some guidelines about the amendments which readers should make in order to adapt several passages of the textbook to the new empirical evidence.⁹⁹ He also said that the new empirical data would not introduce deep changes in chapters dealing with atomic theory:

Les modifications apportées aux densités du soufre, du phosphore, de l'arsenic et du mercure en vapeur, ainsi qu'au nombre d'atomes contenus dans un volume de chacun de ces corps, doivent nécessairement en introduire dans certains

⁹⁷ E. MITSCHERLICH, *Sur le Rapport de la Densité des gaz à leur poids atomique*, «Annales de Chimie et de Physique», vol. 55, 1833, p. 541, on pp. 32-33. See H.W. SCHÜTT, *Eilhard Mitscherlich. Prince of Prussian Chemistry*, Philadelphia, American Chemical Society, 1987, pp. 127-128.

⁹⁸ ORFILA, *Eléments*, cit. (1), 1835-36, I, p. 579. [Curs. by Orfila].

⁹⁹ For example, in a previous chapter (*ivi*, I, 293) he had claimed that «il y a donc dans l'acide sulfurique décomposé, 100 volumes de soufre ou 1 atome, et 300 volumes d'oxygène ou 3 atomes». That assertion was clearly at odds with the new empirical density of sulphur vapour. Thus, Orfila suggested to his readers that they replace the former sentence with the following one: «6 volumes d'acide sulfurique anhydre ... [est formé] d'un volume de soufre (3 at.) et de 6 volumes d'hydrogène (6 at.)». *Id.*, *Eléments*, cit. (1), 1835-36, I, p. 579.

passages des tomes Ire et Iie de cet ouvrage; les pages 41, 42, 43 et 44 du tome Ire nécessiteront surtout quelques rectifications de calcul, qui porteront plutôt sur la forme que sur le fond.¹⁰⁰

Perhaps at this time Orfila still thought that the new data was not a serious threat to atomic theory or perhaps this last statement was a way of minimizing the consequences of the new data. In any event, in spite of Orfila's former assertion, the pages dealing with calculations of vapour densities were completely removed from the textbook in the following editions together with other chapters dealing with atomic theory. In fact, the Berzelian system of atomic weights, which Orfila and Thenard introduced in their textbooks between 1827 and 1836, was seriously affected. Of course, several possible reactions were left at that time ranging from a total rejection of Berzelian methods and atomic weights to the introduction of minor corrections in the system such as Berzelius's double atoms. Moreover, the new research on vapour densities were not completely incompatible with the EVEN hypothesis and some authors such as Marc A. Gaudin developed Ampère's ideas on submolecularity which accorded new data with the EVEN hypothesis. It seems quite possible that Orfila knew the Ampère-Gaudin hypothesis on submolecularity through Gaudin's paper in «Annales de chimie» or through Baudrimont's book that Orfila quoted in his textbook.¹⁰¹

Orfila followed a similar path to other French chemists: he replaced atomic weights with equivalents, as shown in table 1. In some cases, the changes were limited to the introduction of integral multiples of older values. Many Berzelian formulae remained identical or underwent minor changes. What was then the difference between atomic weights and equivalents according to Orfila and other French textbook writers? As we have said above, Alan Rocke has shown that, in spite of their empiricist rhetoric, equivalentists were compelled to make some arbitrary decisions when choosing their «equivalent» weights. Even Wollaston was compelled to choose between several formulae of one oxide in order to establish his equivalent scale.¹⁰² Equivalents were not raw empirical data and atomic weights were not purely speculative figures. However, Rocke has

¹⁰⁰ *Ivi*, I, p. 580.

¹⁰¹ See text quoted in note (86). See also, for instance, BAUDRIMONT, *Introduction*, cit. (40), p. 134 on mercury density. Orfila relied largely on papers published in «Annales de Chimie» in order to update his textbook. Thus, he probably read M.A. GAUDIN, *Nouvelle manière d'ensaisager les corps gazeux, avec son application à la détermination du poids relatif des atomes*, «Annales de Chimie et de Physique», vol. 52, 1833, pp. 113-133.

¹⁰² ROCKE, *Chemical Atomism*, cit. (3), (1984), pp. 63-64.

suggested that most nineteenth-century chemists were «led astray» by the names of equivalents and atoms, the former being regarded as empirical and the latter as theoretical-metaphysical quantities.¹⁰³

That does not seem to be the case of Thenard and Orfila. The difference between atomic and equivalents weights was only introduced at the same time as Berzelian atomism gained ground in Orfila's and Thenard's textbooks. In 1835-36, Orfila included different tables with atomic and equivalent weights for the first time. Whereas atomic weights were calculated through Berzelian methods (the EVEN hypothesis, densities, the Dulong-Petit law and isomorphism), equivalents were defined as the quantity of one element which combines with 100 parts of oxygen in order to yield the protoxide, that is, the oxide with the minimum proportion of oxygen:

on est convenu de représenter par 100, le nombre proportionnel ou l'équivalent chimique de l'oxygène, et de comparer à ce chiffre les nombres proportionnels des autres corps. Il a été également convenu pour trancher toutes les difficultés, que le nombre proportionnel d'un corps quelconque, serait la quantité de ce corps en poids, qui, en se combinant avec 100 parties de l'oxygène, donnerait naissance au premier oxyde de ce corps, c'est-à-dire à celui qui est le moins oxydé.¹⁰⁴

This apparently empirical definition was, however, based on some risky assumptions. While equivalent weights were defined by referring to the first oxide or protoxide, its value was exposed to changes if new oxides were discovered in the future. In fact, this situation was regarded as very probable in cases such as halogens, phosphor, antimony or arsenic. As a result, the rule of protoxide could not be applied and other methods had to be employed to calculate their equivalent weight:

On objectera, peut-être, qu'il eût été plus simple de déterminer les nombres proportionnels de cette seconde classe de corps par la première méthode. Sans doute; et si on ne l'a pas fait, c'est que tout porte à croire qu'il existe des protoxydes de ces corps, que l'on ne connaît pas encore, ou du moins si l'on en connaît quelques-uns on ne les a pas encore obtenus à l'état de pureté.¹⁰⁵

¹⁰³ See *Id.*, *Nationalizing Science*, cit. (3), (2001), pp. 317-323, for a recent discussion.

¹⁰⁴ ORFILA, *Eléments*, cit. (1), 1835-36, I, p. 32. A similar definition in *Id.*, *Eléments*, cit. (1), 1828, II; pp. 580-581 and *Id.*, *Eléments*, cit. (1), 1831, II, pp. 626-627. However, in these two last editions Orfila did not mention the differences between equivalents and atomic weights.

¹⁰⁵ *Id.*, *Eléments*, cit. (1), 1835-36, I, pp. 34-35. In those cases, Orfila defined equivalents as «la quantité du corps contenu dans une proportion d'acide, capable de saturer une quantité d'oxyde métallique, renfermant 100 parties d'oxygène». These exceptions were kept in the following editions after relinquishing atomic theory. See *Id.*, *Eléments*, cit. (1), 1852, I, pp. 16-17.

Why did Orfila accept this presumption? Why did he offer a different method in order to calculate equivalent weights for those substances? While Orfila did not answer these questions in his textbook, Thenard offered an interesting discussion in his *Philosophie Chimique*.¹⁰⁶ According to Thenard, if equivalents were always defined as those quantities combined with 100 parts in order to form the first oxide, then substances with similar properties would be represented by very different Berzelian formulae. For instance, when applying this definition to the first oxides of chlorine and iodine, equivalents of chlorine and iodine were 442.64 and 315.9 respectively. With these values, HCl and HI³ were the Berzelian formulae of hydrochloric and hydrobromic acids. Obviously, these formulae did not reflect the outstanding similarities between the two substances. It was then necessary to accept the existence of an unknown iodine oxide and to calculate iodine equivalent by using other methods.¹⁰⁷

Thenard was aware that in doing so he was accepting «more or less vague suppositions». These assumptions were, however, valuable for chemistry because they produced a set of equivalent weights yielding similar Berzelian formulae for analogous compounds.¹⁰⁸ Following this path, Thenard recognized that equivalents were as hypothetical as atomic weights:

Qu'ainsi modifiés [with those assumptions], les équivalents prennent le nom de *poids atomiques* ou tout autre qu'on voudra, cela importe peu, si on ne veut pas aller au-delà de ce qu'on vient d'exprimer; si, en un mot, on n'a pas la prétention de saisir la relation qui existe entre les équivalents et le nombre de molécules des corps. Mais des que cette prétention intervient, la théorie des équivalents s'arrête, et la théorie atomique commence.¹⁰⁹

According to Thenard, the major difference between atoms and equivalents was that, in the first case, chemists endeavoured to estimate the «number of molecules» by using physical laws.¹¹⁰ In some cases these laws yielded different values for atomic weights... so which one should be

¹⁰⁶ In his first editions, Thenard argued that those methods made the use of equivalent weights in chemical analysis easier and more convenient. See Cfr. THIENARD, *Traité*, cit. (1), 1824, V, pp. 259-260 and *Id.*, *Traité*, cit. (1), 1827, V, pp. 245-262.

¹⁰⁷ *Id.*, *Traité*, cit. (1), (1834-36), V, p. 417. Thenard had already employed this iodine equivalent weight in *Id.*, *Traité*, cit. (1), 1824, I, p. 251.

¹⁰⁸ *Ivi*, V, p. 417 «Que si l'on veut, au contraire, modifier les équivalents ou les corriger, pour se conformer aux analogies que la comparaison des corps nous fait reconnaître, on retombera dans l'écueil que nous cherchions à éviter; on sera forcé de mêler aux faits des suppositions plus ou moins vagues»

¹⁰⁹ *Ibid.*

¹¹⁰ *Ivi*, p. 415.

chosen? Thenard stated that this should refer to those yielding similar formulae for substances with analogous chemical properties. Thenard preferred the blind attempts («tâtonnements») of chemists to methods based on «physical laws» such as specific heats, gas densities, and other «physical properties of molecules». These latter methods could be useful in some cases but should be avoided when they offered results opposing chemical facts.¹¹¹

S'agit-il des besoins de la chimie? Les poids atomiques fondés sur l'isomorphisme sont ceux qui conviennent le mieux, en ce qu'ils attribuent les mêmes formules à des corps qui sont en général, doués de propriétés communes, et qu'il est essentiel de rapprocher sous tous les rapports. Ne perdons pas de vue, en effet, que les poids atomiques des chimistes, formés par tâtonnement et sans aucune règle, n'ont subi presque aucune altération, quand on est venu les contrôler par des lois physiques. Ainsi, rien ne nous oblige à nous départir de cette méthode.¹¹²

These statements of Thenard clearly show a new meaning of atomic theory. In contrast with his first editions, in which atomic theory was portrayed as an useful tool for chemical analysis, by the middle of the 1830s Thenard argued that a set of atomic weights should offer similar Berzelian formulae for analogous substances. Thenard claimed that «compounds with analogous chemical properties should be represented by an equal number of elementary equivalents».¹¹³ In other words, groups of substances with similar chemical properties had to be represented by similar formulae. Thus, atomic (or equivalent) weights should provide Berzelian formulae in consonance with chemical classifications. These new uses of atomic theory were especially useful in the new organic chemistry developed during the 1830s and 1840s. The increasing number of synthetic organic substances raised a problem of classification and Berzelian formulae were especially suitable for this task. The development of radical theory and the theory of types made it necessary to find a set of atomic weights that offered similar formulae for analogous substances. As a result, major progress of atomic theory was made in organic chemistry during the 1840s and the 1850s.

¹¹¹ *Ivi*, p. 448.

¹¹² *Ibid.*

¹¹³ *Ibid.*, «des composés analogues par leurs propriétés soient représentés par un nombre égal d'équivalents élémentaires».

3.3. Institutional constraints? Official syllabus, textbooks and teaching practices

Orfila never integrated new organic chemistry in his textbook. His targeted audience was deeply interested in important topics of animal and vegetal chemistry which were not part of the new culture of organic chemistry. In his chemical lectures at the Faculty of Medicine in mid-1836, Orfila passed over these new synthetic substances arguing that they were of no interest to medicine. When discussing the acids which «were always artificially produced», Orfila only mentioned two of the twenty-seven acids described in his textbook¹¹⁴ and said that it was «useless» to know the other acids.¹¹⁵ During the 1840s and the 1850s, new organic products were not so interesting to medicine as animal and plant immediate principles such as alkaloids. That was a major constraint to the transformation of this part of Orfila's textbook. The importance of natural immediate principles in therapeutics as well as chemical analysis in medical diagnosis favoured the old subculture of plant and animal chemistry instead of the new experimental culture of organic chemistry. In this old subculture, atomic theory was never employed in such a profound way as in the new organic chemistry. Thus, Orfila's targeted audience partially explains why he was not as concerned with atomic theory as Gerhardt, Laurent and other organic chemists.¹¹⁶

Orfila was not, however, compelled to give atoms up for this sole reason. This seems evident if we examine other chemistry textbooks aimed at similar medical and pharmaceutical audiences. A good example is Jean Lassaigne's textbook. He was a chemistry professor at the Alfort Veterinary School and, like Orfila, a prominent member of the Société de Chimie Médicale. Lassaigne wrote a large volume on animal and vegetal chemistry and kept this division until his last edition in 1848. And, just like Orfila, by the mid 1830s, Jean Lassaigne transferred his chapter on atomic theory to the first introductory chapters, adding new paragraphs on Berzelian formulae.¹¹⁷

¹¹⁴ ORFILA, *Elémens*, cit. (1), (1835-36), II, pp. 446-471. *Acides de la 3e section: Des acides qui sont toujours le produit de l'art.*

¹¹⁵ See the above mentioned Daremberg's *cahier de notes*, quoted in note (52), f. 141: «Tous les autres acides de la 3e section sont inutiles à connaître. Il suffit de dire que ceux qu'on appelle pyrogénés proviennent des acides des végétaux traités par le feu».

¹¹⁶ On plant and animal chemistry vs. organic chemistry see the recent work of Ursula Klein, cit. (5) and (35), which also deals with the uses of Berzelian formulae in early organic chemistry. On Orfila and organic chemistry, see BERTOMEU, *Mateu Orfila*, cit. (1).

¹¹⁷ J.-L. LASSAIGNE, *Abregé élémentaire de chimie*, Paris, Béchet jeune, 1829; Paris, 1836, 2nd ed.; Id. Paris, 1842, 3rd ed.; Id. Paris, 1846, 4th ed. In the first edition, Lassaigne included a

However, in contrast to Orfila, Lassaigne never omitted atomic theory from his textbook, which was edited on four occasions between 1829 and 1848. In his third edition, he broadly employed «atomic formulae» – as he called them – to describe the chemical composition of compounds.¹¹⁸ For example, in the case of nitrogen oxides, he used atomic notation such as Az^2O , AzO , Az^2O^3 , ... instead of AzO , AzO^2 , AzO^3 ... that were used by equivalentists. Lassaigne not only used atomic theory to show chemical composition, as Orfila did, but also to describe chemical reactions in atomic terms. Lassaigne generally represented atoms with circles (O), placed reagents on the left side and, by using dotted lines, he showed the way in which products were formed. He said that he had employed this method in his lectures at the Veterinary School of Alfort with excellent results.¹¹⁹ Were these graphic equations sufficient justification to keep using atomic theory when other French chemists had already given it up? Why did Lassaigne continue to do so while Orfila did not? Perhaps the answer lies in the fact that Lassaigne was not as constrained by secondary school programmes as Orfila was. After the 1830s, Orfila's medical students were required to have *bac-es-sciences physiques* before being accepted in medical schools. In contrast, veterinary students were only needed to know 'orthography' and how to forge a horseshoe to be accepted in a Veterinary School.¹²⁰ Therefore, changes in secondary school syllabuses affected Orfila more than Lassaigne. Let us follow the rise and fall of atomic theory in these official syllabuses and its consequences on secondary education textbooks.

In 1828, an official syllabus, which established the contents of scientific courses at the *collèges royaux*, for the first time included an explicit reference to atomic theory.¹²¹ In contrast, the official syllabus of *bac-es-sciences*

chapter on *proportional numbers and atomic theory* just after dealing with metalloids and before describing metals. (Cfr. 1829, I, pp. 298-308). In 1836, the chapter was enlarged and placed at the beginning of the book (Cfr. 1836, I, pp. 38-42). As early as 1829, Lassaigne was already using atomic theory in his publications: Cfr. LASSAIGNE *Note sur un composé solide de cyanogène et de soufre et à proportions définies (cyanure de soufre)*, «Journal de Chimie Médicale», vol. 5, 1829, pp. 1-7.

¹¹⁸ In his third edition, Lassaigne remarked that one of the most important changes from the later edition was precisely the introduction of Berzelian formulae in almost every chapter in order to describe chemical composition. Id., *Abregé* (1842), cit., I, pp. viii-ix.

¹¹⁹ Id., *Abregé* (1836), cit., I, p. ix and *Abregé* (1846), I, p. ix.

¹²⁰ *Ordonnance du roi portant l'organisation des écoles vétérinaires*, 1 de septembre 1825 in T. CHARMASOON *et al.* (1992), *L'enseignement agricole et vétérinaire de la Révolution à la Libération*, Paris, INRP, 1992, pp. 21-24. The students had to be between 16 and 25 years old and a «suitable constitution to practise the veterinary art». After four years at the veterinary school, students could take an exam and get the «diplôme de vétérinaire».

¹²¹ *Programme du cours des sciences physiques pour les élèves des deux années de philosophie*,

published in 1837 included a chapter on «proportional numbers» but none on atomic theory.¹²² As such, this latter syllabus, which appeared just one year after Dumas's famous lectures at the *Collège de France*, has been regarded as a major factor in the transition from atoms to equivalents in France. This conclusion, however, relies on a questionable assumption: the existence of a straightforward relationship between the official syllabus and teaching practice.

As was the case with other authors, Guerin, who wrote books aimed at developing this syllabus and who employed atomic theory in the first edition of his textbook (1833), erased chapters on atoms in his 1840 edition. He explicitly said in his foreword that atomic formulae had been replaced by equivalent ones.¹²³ However, other secondary school chemistry textbooks, which were written after the 1837 syllabus, continued to use atomic weights. This was the case of the textbooks written by Tyrat (1837),¹²⁴ Saigey (1837)¹²⁵ or Burnouf (1840), even though they did not use atomic theory to the same degree. Whereas the first two did not employ Berzelian formulae, Eugène Ferdinand Burnouf (b. 1818), a secondary school teacher, not only used them to describe chemical composition but also to explain chemical reactions. After dealing with a paragraph on «proportional numbers» in the 1837 syllabus, Burnouf added a new part on «atomic theory», in which he discussed the laws of combination «atome à atome», the EVEN law («volumes égaux = même nombre d'atomes») as well as Dulong and Petit's law and Mitscherlich's isomorphism.¹²⁶ Burnouf argued that atomic formulae were

1 avril 1828, in B. BELHOSTE, *Les sciences dans l'enseignement secondaire français*, Paris, INRP, 1995, pp. 115-121.

¹²² *Programme des baccalauréat ès sciences mathématiques et ès sciences physiques*, 3 février 1837, in B. BELHOSTE, *Les Sciences*, cit. (121), pp. 139-147: «lois suivant lesquelles les corps se combinent; nombres proportionnels».

¹²³ R.T. GUERIN, *Nouveaux éléments de chimie théorique et pratique*, Paris, F.G. Levrault, 1833; Id. Paris, Hachette, 1840, 2nd ed. Cfr. *ivi*, pp. v-vii: «des formules atomiques [...] ont été remplacées par celles des équivalents». He also said that chemical reactions had been expressed by using equivalents as far as possible: «des réactions des corps les uns sur les autres ont été exprimées en équivalents, toutes les fois que cela a été possible» (*ivi*, p. vi).

¹²⁴ TYRAT, *Nouveau manuel*, cit. (78), *passim*. He broadly used atomic theory in this textbook.

¹²⁵ J.F. SAIGEY, *Manuel des aspirants au baccalauréat ès sciences*, Paris, Hachette, 1837, was almost identical to Tyrat's textbook. He employed less atomic theory when describing chemical composition which he displayed by using mostly volumetric or weight ratios. Neither Saigey nor Tyrat used Berzelian formulae.

¹²⁶ E. BURNOUF, *Nouveaux Cahiers de chimie*, Paris, Roret, 1840, pp. 31-35. Interestingly enough, Burnouf quoted *Philosophie Chimique* by Thenard as suggested reading for those students who wished to receive more information about atomic theory.

useful for abridging information regarding chemical composition. These symbols were also suitable for representing chemical reactions because students could «follow and take in at a glance what happened in these combinations», and could then «easily engrave [this information] on their memory».¹²⁷ Another secondary school textbook published by the Alsatian teacher Rodolphe Kaepelin (1810-1871) also included a chapter on atomic theory and used Berzelian formulae in its two editions between 1837 and 1841. He also used atoms to make balance sheets between atoms «employed» and «produced» during a chemical process.¹²⁸

These four textbooks, aimed at a similar public and syllabus, offer evidence regarding the gap between the official syllabus and chemistry textbooks. Another example is offered by Apollinaire Bouchardat's popular textbook that was edited three times between 1842 and 1848. Bouchardat aimed to offer a suitable book for the *baccalauréat ès-lettres* official syllabus of 1840. This syllabus did not include any reference to atomic theory and only referred to equivalents on one occasion.¹²⁹ Bouchardat, however, included a chapter on «atomic theory» when answering this question in his textbook and he discussed how many elemental atoms were included in a compound body.¹³⁰ In 1845, Bouchardat continued to use atomic theory but recognised that several authors used another notation.¹³¹ As late as 1848, he changed to equivalent formulae although he kept his former chapter on atomic theory.¹³²

¹²⁷ *Ivi*, p. III: «Suivre et embrasser d'un seul coup d'oeil ce qui se passe dans ces combinaisons, et se le graver plus facilement dans la mémoire».

¹²⁸ He used the terms «atomes employés» and «atomes produits». Cfr. R. KAEPELIN, *Cours élémentaire des sciences physiques. Cours de chimie théorique et pratique*, Colmar, Z. Kaepelin, 1838, Colmar, 1841, 2nd ed. Kaepelin wrote Berzelian formulae in the following way: «o^z az^z + o ag» («nitrate argentique»), «cl^z h^z» and «az^z h^z» (ammonia).

¹²⁹ *Questions de mathématiques et de physique au baccalauréat ès lettres*, 14 juillet 1840, in: B. BELHOSTE, *Les sciences*, cit. (121), pp. 152-159. The question mentioned is number 38: «Qu'est-ce l'affinité chimique? En quoi diffère-t-elle de la cohésion? Définir l'analyse et la synthèse. Qu'entend-on par équivalents chimiques?». Cfr. *ivi*, p. 159. The next syllabus *Programmes de physique et de chimie en classe de philosophie* (24 février 1843) included a similar question: Chimie, question 2: «De l'affinité chimique. De la cohésion. Définition de l'analyse et de la synthèse. Des équivalents chimiques». Cfr. *ivi*, pp. 198.

¹³⁰ «Combien une combinaison donnée renferme-t-elle d'atomes des éléments qu'elle contient?». Cfr. A. BOUCHARDAT, *Cours*, cit. (79), (1842), p. 22. Bouchardat also remarked the problems surrounding the calculation of atomic weights.

¹³¹ Id., *Cours*, cit., (1845) p. 21: «quelques chimistes admettent pour certains atomes des valeurs différentes, mais qui sont nécessairement des multiples simples de celles que nous avons données; ainsi l'hydrogène, au lieu d'être 6,24 est 12,5. Quand on prend 6,24 pour le poids de l'hydrogène, l'eau est représentée par H^oO; quand, au contraire, on prend 12,5, sa formule devient HO». This text was not in his first edition.

¹³² Id., *Cours*, cit., (1848), p. XI: «dans les précédentes éditions, j'avais adopté les poids

Alan Rocke has recently claimed that «for a period of 40 years beginning about 1837 French *lycée* students learned only one kind of chemistry: that based on equivalents and suffused with theoretical caution, if not outright positivism».¹³³ The former analysis suggests a more complicated scenario. Chemistry textbook writers adopted a broad range of attitudes regarding atomic theory between the middle of the 1830s and the end of the 1840s.¹³⁴ These different positions cannot be grasped by analysing official syllabuses alone and other historical sources should be taken into account. Even though official secondary schools syllabuses did not mention atomic theory, contemporary chemistry textbooks did, so it seems quite possible that atomic theory was employed in secondary schools as well as in other chemistry lectures during those years.¹³⁵ Moreover, references to atoms or molecules were included in the first chapters and chemical reactions were portrayed in terms of particles acting under the influence of affinity forces.

CONCLUSIONS

As Peter Galison has remarked, scientists work «within a multiplicity of constraints, any one of which can be violated, but at a cost».¹³⁶ There is no single constraint to explain why chemistry textbook writers gave up (or retained) atoms in their textbooks. To understand chemistry textbooks we must pay attention to the wide range of situations in which they were written, sold and read. Insofar as these writers and teachers had to face multiple and different constraints, we might understand that some of them decided to continue using atoms whereas others preferred to give them up. There was no such thing as a «national rejection» of atoms during the 1840s in France.

When focussing on Orfila's textbook, some constraints seem to have played a more important role than others. We have shown that he

atomiques; dans celle-ci, je les ai remplacés par les équivalents. L'exposition de la science est ainsi plus claire, plus facile et convient mieux à des commençants». Nevertheless, a chapter on atomic theory was included in *ivi*, pp. 17-19.

¹³³ ROCKE, *Nationalizing Science*, cit. (3), p. 385.

¹³⁴ For more examples, see B. BENSUADE-VINCENT et al. *L'émergence d'une science des manuels*, cit. (1), pp. 203-222.

¹³⁵ A deeper analysis of secondary school notebooks will offer additional evidence. For a discussion about that question see A. GARCÍA BELMAR, J.R. BERTOMEU SÁNCHEZ, *Motivi, fonti e domande per una storia dei contenuti e delle pratiche dell'Insegnamento della Chimica*, in F. ABBRI, M. CIARDI (eds.), *Atti dell'VIII Convegno Nazionale di Storia e Fondamenti della Chimica*, Arezzo, SISFC, 2000, pp. 3-22. For a recent overview of historical studies on scientific pedagogy, see D. KAISER (ed.), *Pedagogy and the Practice of Science, 1800-2000*, Cambridge, MIT Press, forthcoming.

¹³⁶ P. GALISON, *Image and Logic*, Chicago, University Press, 1997, p. 15.

introduced atoms in his textbook as a tool for chemical analysis – as other French authors did. In his first chapters, he conveyed a theory of matter based on molecules and affinity forces, so atoms were easily integrated into this picture without major changes. Like Thenard, Orfila regarded atomic theory as a useful paper tool for quantitative chemical analysis. However, unlike Thenard's, Orfila's version of chemical atomism was shaped by Thomson's textbooks, which he probably used as the main source of his data. Between 1819 and 1831, Orfila used Thomson's rounded atomic weights and adopted specific weights which suited atomic theory values. He did not make major changes in his textbook regarding atomic theory until 1828. Then he added a new chapter on atomic theory with information about Berzelian formulae.

The height of atomic theory, however, was reached in the 6th edition (1835-36). Not only did he substantially increase his theoretical chapter but also extensively employed Berzelian formulae in his inorganic volume and stopped using Thomsonian rounded atomic weights. In Orfila's following edition, and while indicating that he would never again mention atomic theory in his textbook, he expanded the use of Berzelian formulae to the organic chemistry chapters and maintained the word «atom» as a synonym of molecule in his first theoretical chapters. However, like other chemistry textbook writers, he never abandoned the corpuscular image of chemical processes. As Thenard put it, by the early 1830s, «almost all physicists and chemists accepted that matter is made up of atoms». Even though it may come as a surprise to the modern reader, Orfila never really doubted the existence of microscopic particles. In the first chapters of his book, he changed the word «molecule» – which had been taken from eighteenth-century French chemistry – to the word «atom» during the late 1820s and 1830s but then went back to «molecules» during the 1840s and 1850s, perhaps because of a hesitance regarding the indivisible character of these particles, as may be revealed by his lecture notes of 1840s. Thus epistemological-positivist constraints did not seem to play a major role in Orfila's «rejection» of atoms. Or, like other chemistry textbook authors, Orfila regarded this particulate approach as belonging to the «positive part of science» which should be included in a textbook.

There were different and changing «layers of meaning» related to atomic theory, as Ursula Klein has shown when analysing Berzelius's formulae. During the 1810s and 1820s, Thenard and Orfila were interested in atomic weight due to its use in organizing the results of chemical analysis. The spread of Berzelian formulae in chemistry textbooks during the late 1820s and the 1830s introduced new meanings connected with atomic theory. As

Thenard discussed in his *Philosophie chimique*, atomic formulae were now regarded as a powerful instrument for chemical classification: compounds with similar properties should have similar formulae. This new meaning was particularly developed in organic chemistry, a new experimental area that Orfila never introduced in his textbook. He went on using plant and animal chemistry classifications as well as regarding atomic theory as a tool for chemical analysis. He never integrated the new meaning of atomic formulae in his textbook.

On the contrary, Orfila was concerned with the contradictions which appeared when using the Dulong and Petit law, the EVEN hypothesis and new vapour densities as calculated by Dumas and Mitscherlich during the 1830s. These problems questioned calculations of atomic weights, not the physical existence of atoms (or molecules after the 1840s). Orfila preferred equivalent weights because they were defined with a set of rules which could be clearly determined. Rather than portraying it as «raw empirical data», Orfila mentioned several assumptions related to equivalent weight calculations, namely the hypothesis about unknown protoxides. Equivalent and atomic weight have their own assumptions but atomic theory implied an additional idea: the existence of indivisible particles whose weights could be univocally calculated. And Orfila was not sure about the indivisibility of particles. Moreover, atomic weights turned out to be very useful for new organic chemistry classifications, a realm almost unknown to Orfila. His medical and pharmaceutical audience was more interested in some chapters of old plant and animal chemistry than in new synthesized products or radical or type theory formulae. Finally, it is not sure whether Orfila's students were only trained in equivalent weights at secondary school. The analysis of secondary chemistry textbooks published between 1836 and 1845 hints at a range of situations regarding atomic theory, a diversity that perhaps also took place in French classrooms. Institutional constraints probably encouraged – but definitely did not force – Orfila to relinquish atomic theory.

The analysis above shows that the study of scientific textbooks may well reveal additional aspects regarding some of the historical topics on nineteenth century atomic theory. Teaching and the writing of textbooks were and continue to be crucial activities in most scientists' careers and these pedagogical practices substantially shape subsequent generations of scientists. As such, if we really wish to gain a broader image of scientific activity, we must follow scientists both in the laboratory and in the classroom without taking for granted a priori images about these two spaces of scientific creativity.

SUMMARY

The *Éléments de chimie médicale* by Mateu Orfila i Rotger (1787-1853) is an excellent historical source for a reappraisal of the rise and fall of French atomic theory over the first half of nineteenth century. The book was edited eight times between 1817 and 1851. Several abridged versions were also published in English, Spanish, German, Italian and Dutch translations. We shall first analyse how atomic theory was received in French chemistry textbooks during the 1810s and 1820s. Atoms were regarded by French authors as a practical tool and not as a theoretical novelty. We shall follow atomic theory through the first editions of Orfila's and Thenard's textbooks. At the end of the 1820s, new methods for calculating atomic weights were introduced in textbooks as well as Berzelian formulae. We shall then study how and why atomic theory reached its apex in Thenard's and Orfila's textbooks between 1827 and 1835. Finally, we shall discuss why Orfila gave up atomic weight in his seventh edition (1843). We shall analyse Orfila's epistemological concerns, his views about the differences between atoms and equivalents, his interest for plant and animal chemistry and the institutional constraints (official syllabus) related to atomic theory. No single reason can be used to explain Orfila's rejection of atomic weights in the 1840s. He, indeed, chose a particular attitude among the many positions on atomic theory adopted by French chemistry textbook writers over these years.