# MENDELEEV´S PERIODIC LAW AND THE 19$^{TH}$ CENTURY DEBATES ON ATOMISM

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## 1. Introduction and French Prelude

The heated debates and severe conflicts between the atomists and the anti-atomists of the latter half of the nineteenth century are well known to the historian of science.[123] Anti-atomism was advocated by a number of notorious scientists such as Marcellin Berthelot (1827–1907), Ernst Mach (1838–1916), Wilhelm Ostwald (1853–1932), František Wald (1861–1930), and Pierre Duhem (1861–1916), whereas the atomistic school included Julius Thomsen (1826–1909), Charles Marignac (1817–1894), Adolphe Wurtz (1817–1884), Auguste Laurent (1807–1853) and Charles Gerhardt (1816–1856) among others. The position of Dmitrii Ivanovich Mendeleev (1834–1907) towards these nineteenth century debates on atomism will be studied in this paper. A first attempt will thus be offered to reconcile Mendeleev's seemingly contradictory comments and ambiguous standpoints into one coherent view.

By way of introduction, this section proposes a brief summary of a paper from the French rare-earth specialist, Georges Urbain (1872–1938), who wrote about the reception of the periodic table in France, and who provided a lucid (and at first sight very convincing) account of Mendeleev's atomistic standpoints and the French response. Urbain noted that the ideas of Mendeleev had not always been generally admitted in France, and he compelled himself to offer his audience the reasons for this intriguing fact. "Longtemps deux tendances ont divisé les chimistes français", he said (Urbain 1934, 657). "Les uns étaient *équivalentistes* et récusaient la valeur de toute hypothèse moléculaire, les autres étaient *atomistes*, et affirmaient leur foi dans la réalité des atomes" (*Ibid*., 658).[124] Both the equivalentist and atomist schools were personified in France by an illustrious scientist: "l'une, celle des atomes, par *Wurtz*; l'autre, celle des équivalents, par *Berthelot*, qui traitait l'atomisme de *religion nouvelle*" (*Loc. cit*.).

It is indeed a well-known fact that whereas the atomic doctrine was generally accepted by the chemical community, a great majority of French chemists remained reluctant to adopt the atomic theory of John Dalton (1766–1844) in view of its hypothetical (if not metaphysical) character (see e.g. Bensaude-Vincent 1999). "Se refusant aux hypothèses, [les équivalentistes] ne voulaient entendre parler ni d'atomes, ni de poids atomiques," said Urbain, "mais seulement de nombres proportionnels et d'équivalents, parce que ce sont là des *données pures* de toute *considération métaphysique*" (Urbain 1934, 658). It is sufficient to recall the famous statement from Jean-Baptise Dumas (1800–1884) who exclaimed in his *Leçons sur la Philosophie Chimique* that "si j'en étais le maître, j'effacerais le mot *atome* de la science" (Dumas 1878, 315).

These were the French conditions in which Mendeleev's ideas first appeared in 1869. "Vous comprendrez, d'après cela," Urbain exclaimed, "que si [les idées de Mendéléeff] furent chaleureusement accueillies par les uns, elles devaient l'être très peu par les autres" (Urbain 1934, 658). Indeed, Urbain observed that "Wurtz et son école se hâtèrent d'incorporer le Système Périodique dans la doctrine atomique. Ils s'en firent les propagandistes zélés, et le défendirent contre les inévitables attaques dont ne manquèrent pas de le cribler leur adversaires" (*Loc. cit*.). While setting the scene for the nineteenth century debates between the atomists and the anti-atomists, Urbain's account moreover forms a useful background against which to analyse Mendeleev's position with regard to this thorny issue.

## 2. Mendeleev as an Atomist

The reason why the atomistic school of Wurtz adopted Mendeleev's table was self-evident. After all, "Les *poids atomiques*, et non pas les *équivalents*, formaient le pivot de ces idées", dixit Urbain (*Loc. cit*.). Indeed, Mendeleev never refrained from rejecting the utility of the equivalent weights as confusing at the least, and he frequently praised the atomic theory to the skies when extolling the labours of nineteenth century atomists.

Dmitrii Ivanovich Mendeleev had probably turned into this convinced atomist after attending the first *International Chemical Congress* of Karlsruhe in 1860. Not surprisingly, Mendeleev's admiration for the pioneering work of such great atomists as Avogadro (1776–1856), Ampère (1775–1836), Gerhardt (1816–1856) and Cannizzaro (1826–1910) came up quite frequently in his scientific publications. He thus emphasized at the beginning of his paper announcing the discovery of the periodic law in 1869 that "the procedure, according to which Gerhardt and Cannizzaro have determined the atomic weights of elements, is based upon such *unshakeable* and *indubitable methods* that, for the majority of substances […] there no longer exist any doubts about their atomic weights, as was the case several years earlier when the *atomic weight was so often confused with the equivalent weight*" (Mendeleev 1869, 25). Similar statements about the

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[123] There exists an extensive literature on the history of atomism and the nineteenth century atomic debates. Some of the more important studies include: Rocke (1984), Nye (1976 and 1981), Brock (1967), and Knight (1967).

[124] All emphasis in this text is the author's, unless otherwise noted.

"*indestructible solidity*" of the atomic weight concept appeared in Mendeleev's landmark paper of 1871 as well (see Mendeleev 1871, 40). Finally, during his *Faraday Lecture* of 1889, Mendeleev indicated the following group of elements, in which the gradual increase of atomic weight was "seen at once and is perfectly clear":

K = 39 Rb = 85 Cs = 133

Ca = 40 Sr = 87 Ba = 137

"Whereas with the *equivalents* then in use" –

K = 39 Rb = 85 Cs = 133

Ca = 20 Sr = 43.5 Ba = 68.5

"The […] change in atomic weight […] completely disappear[ed]" (Mendeleev 1889, 637). His belief that only "*real atomic weights* […] could afford a basis for generalisation" (*Loc. cit.*) seems therefore to be in agreement with Urbain's abovementioned account of Mendeleev's siding with the atomistic school.

### 3. Mendeleev as an Anti-atomist

However, numerous *anti-atomistic* statements which heavily contradict our first, preliminary conclusion are scattered throughout the Mendeleev corpus. In his groundbreaking paper of 1871 for instance, Dmitrii Ivanovich admitted that "the expression atomic weight implies the hypothesis of the atomic structure of matter" (Mendeleev 1871, 40). In order to "*avoid the concept of atoms* when speaking of elements", Mendeleev therefore suggested to "replace the term *atomic weight* by *elementary weight*" (*Ibid*., 106).

In his recent book *Dmitrii Mendeleev and the Shadow of the Periodic Table*, the renowned Mendeleev scholar, Michael Gordin, considered atomism to be the theory "Mendeleev was most loath to take literally" (Gordin 2004, 24). After a thorough analysis of Mendeleev's views on the atomic theory, and in sharp contrast with Urbain's account, Gordin concluded that Mendeleev must not necessarily have been thinking in terms of atomism when he constructed his periodic table (*Loc. cit.*). According to his opinion, "Mendeleev's scepticism toward atomism sharply emphasizes the difference between the present day interpretation of the periodic system and Mendeleev's view of 1869" (*Ibid*., 25). In the same way, Kaji (2003, 193) argued that "Mendeleev was always cautious about atomic theory."

### 4. Atomistic Confusion

The question naturally arises then of how Mendeleev's apparent scepticism towards atomism is to be reconciled with the paradoxical fact that his greatest discovery was after all entirely based on the atomic weight values of the chemical elements. Whatever may be the truth, it should be clear at this point that Mendeleev's viewpoints on atomism were far from clear-cut. As a philosopher of chemistry once noted, "there is clearly a *tension* between Mendeleev's various remarks, even on successive pages of *The Principles of Chemistry*" (Hendry 2006, 333). Not surprisingly, Mendeleev's ambiguous statements have often induced pronounced disagreements between various historians and philosophers of chemistry who tried to grapple with Mendeleev's seemingly schizophrenic behaviour towards atomism.

One such recent dispute for instance arose a few years ago between Eric Scerri (2006) and Robin Hendry (2005, 2006). Scerri (2006, 311) claimed that "there [was] considerable evidence to show that Mendeleev was rather *sceptical* of atomistic explanations," while Hendry (2006, 331) thought Scerri to be "mistaken to represent Mendeleev as an *anti-atomist*" – claiming in contrast that "Mendeleev inclined towards an *atomist interpretation* of the periodic law, and of other chemical phenomena." While Scerri agreed with Kaji and Gordin (among others) that Mendeleev was "*cautious*" about atomism – if not "*wary*" and even "*sceptical*" – Hendry on the other hand thought Mendeleev was "*overwhelmingly realist*" about atoms – "willing to bet on the *truth of atomism*" (*Ibid*., 332).[125]

Perhaps, as a way out of this chaos, one could consider Mendeleev a *practising atomist* who relied on the atomic weight values when working in the lab or building periodic tables, but who turned to *anti-atomistic ideas* whenever he was theorizing about chemistry. This stance is more consistent with an instrumentalist, rather than a realist, position (*vide infra*), and seems to be strengthened by a well-known statement of Alexander Williamson (1824–1904), president of

[125] According to Hendry's interpretation of Mendeleev's various statements, Dmitrii Ivanovich was "willing to take the epistemic risk of a commitment to the truth of atomism" (Hendry 2006, 333). Hendry admitted that this speculative interpretation was in need of "much more development and textual defense", but wondered how an anti-atomist interpretation of Mendeleev's statements could be squared with his more realist comments. This paper offers a first attempt to reconcile Mendeleev's seemingly contradictory comments into one coherent view (*vide infra*).

the *London Chemical Society*. In 1869 – the year when Mendeleev discovered his periodic law – Williamson (1869, 330-331) presented a paper on the atomic theory, and shockingly noted the fact that "on the one hand, all chemists *use* the atomic theory, [but] that on the other hand, a considerable number of them *view* it with mistrust, some with positive dislike."

It was Friedrich August Kekulé (1829–1896) who first resolved the apparent ambiguity about the way chemists (Mendeleev included) dealt with the concept of atoms. "I have no hesitation in saying that, from a philosophical point of view, I do not believe in the *actual existence* of atoms," Kekulé (1867, 304) said, "taking the word in its *literal significance* of indivisible particles of matter […]. As a chemist, however, I regard the assumption of atoms, not only as advisable, but as *absolutely necessary* in chemistry. I will even go further, and declare my belief that *chemical atoms exist*, provided the term be understood to denote those particles of matter which undergo no further division in chemical metamorphoses. Should the progress of science lead to a theory of the constitution of chemical atoms – it would make but little alteration in chemistry itself. The chemical atoms will always remain the *chemical unit*; and for the specially chemical considerations we may always start from the constitution of atoms, and avail ourselves of the simplified expression thus obtained, that is to say, of the atomic hypothesis" (*Loc. cit.*).

## 5. Chemical versus Physical Atomism

Kekulé alluded to the crucial distinction between *chemical* and *physical atomism* – a distinction first proposed by the historian Alan Rocke (1984) when dealing with 19th century atomism. A concise summary of Rocke's main points will help to clarify Mendeleev's ambiguous position.

The stoichiometric laws of Lavoisier (1743–1794), Proust (1754–1826) and Dalton governed the relationships between the *equivalent weights* of substances undergoing chemical reactions. According to Rocke's opinion, these equivalent weights had three important characteristics: 1. they were empirical, 2. dependent on the compound analyzed (typically exhibiting a number of different values for one particular element), and 3. related to the atomic weight, i.e. $AW(X) = EW(X) \times V(X)$ (*Ibid.*, 11).The chemical atomic theory, first proposed by John Dalton during the early decades of the nineteenth century, suggested an explanation for these stoichiometric regularities. From a purely instrumentalist point of view, Dalton's atomic theory provided a conceptual basis for assigning unique, relative *atomic weight values* to the chemical elements. Dalton moreover claimed that these *chemically indivisible units* entered into combination with each other in small integral multiples in accordance with the laws of stoichiometry.

Lest any reader find himself identifying atomic weights with chemical equivalents, let me hasten to emphasize Rocke's list of characteristics distinguishing atomic weights from chemical equivalents: 1. atomic weights are theoretical (rather than operational), 2. presumed to be invariant, and 3. dependent on the assumed formulae for the simple oxides of the elements. Once chosen, atomic weights could of course be used to deduce the formulae of any other chemical substance (*Ibid.*, 12).

Even though Dalton and some other chemists assumed the atomic theory to refer to the ultimate physical atoms (i.e. *physical atomism*), most chemists advocated a less materialistic interpretation. They accepted Dalton's atomic theory epistemologically, rather than ontologically. Rocke termed this *chemical atomism* – a pragmatic chemical doctrine that avoided all reference to the true indivisible primary particles of matter.

## 6. Mendeleev as a Chemical Atomist and Physical Anti-atomist

Having established the difference between chemical and physical atomism, it will be (temporarily) claimed in the following paragraphs that Mendeleev acted as a *chemical atomist* on the one hand, and a *physical anti-atomist* on the other.[126] Some evidence for both assertions can be found on a more detailed examination of Mendeleev's papers and textbooks. For instance, Dmitrii Ivanovich repeatedly emphasized (cf. Mendeleev's renowned article in *Liebig's Annalen* and his 1889 *Faraday Lecture*) that he considered the atom as "the smallest portion of an element which enters into a molecule of its compound" (Mendeleev 1871, 40; Mendeleev 1889, 637).[127] This quotation from Mendeleev's hand sheds some light on his interpretation of the word *atom*. It seems that Mendeleev considered the atom as *a chemically indivisible unit* that entered into combination with similar units of other elements (i.e. chemical atomism), while refraining from any consideration about the physical reality of atoms (i.e. physical atomism).

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[126] This viewpoint is in accordance with Gordin who stated that "in his practical work Mendeleev, of course, used the notion that substances combine in defined ratios with each other ("chemical atomism") – it was practically impossible to be a chemist without doing so – but he had long maintained a conflicted attitude to the physical interpretation of atomic theory" (Gordin 2004, 24). In the same way, Hendry (2006, 330) argued that "in understanding the complex story of atomism in the nineteenth century, it helps to distinguish *chemical* atomism (atoms are the smallest units of the elements), and various versions of physical atomism."[emphasis in original] Surprisingly then, Hendry did not pursue this crucial line of thought any further in his defense against Scerri's abovementioned objections.

[127] A similar definition emerged as early as 1861 in his textbook on *Organic Chemistry* where he defined the atomic weight as "the minimum quantity of an element in the compound molecules of the element" (quoted in Kaji 2003, 193).

Indeed, in a footnote of the sixth edition of his *Osnovy Khimii* (his celebrated *Principles of Chemistry*), Mendeleev (1897, 216) compared the atomic doctrines of the ancient philosophers with the present atomic theory of Dalton – noting that they were "essentially different" (though historically connected). While the Greek atomists considered the atom as being *geometrically* and *mechanically* indivisible (a "metaphysical principle" by the way which had never been "ratified by fact"), Mendeleev considered Dalton's atoms as being "indivisible, not in the geometrical abstract sense, but only in a *physical* and *chemical* sense" (*Loc. cit.*). Therefore, the atoms of nineteenth century science formed the "*units* with which [chemists were] concerned in the investigation of the natural phenomena of matter" (*Loc. cit.*).

One understands now that when Mendeleev was praising the work of Cannizzaro and Gerhardt, he actually referred to their pioneering work in the field of chemical atomism (i.e. atomic weight determinations), rather than physical atomism. As a convinced chemical atomist, Mendeleev was moreover enabled to rely on the atomic weight values of the elements when building his periodic table – without therefore making any reference or claim about the actual existence of physical atoms.

All this should not be very surprising. Alan Rocke (1984, xiii) has argued that "virtually all chemists after Dalton were chemical atomists." Indeed, chemical atomism was "universally (if implicitly and often unknowingly) accepted throughout the course of the nineteenth century" (*Ibid.*, 10). The Karlsruhe conference of 1860 significantly aided chemists in achieving this uniform consensus with regard to chemical atomism, and Rocke therefore boldly referred to the periodic law "as more a *result* than a cause of that *consensus*" (*Ibid.*, xii).

However, "the chemical theory was as successful and as uncontroversial as the physical theory was reviled and often rejected," dixit Rocke (*Loc. cit.*). Physical atomism was far from universally accepted and many chemists considered it a rather controversial theory about the ultimate physical nature of chemical substances. Mendeleev shared this opinion and kept arguing that the atom should be treated as a *convention*, rather than to be taken *realistically* (e.g. Mendeleev 1871, 40). He thus argued that "the atomism of our day must first of all be regarded merely as a *convenient method* for the investigation of ponderable matter" (Mendeleev 1897, 217). This *instrumentalist* attitude towards atomism plainly follows from his saying that "as a geometrician in reasoning about curves represents them as formed of a succession of right lines, because such a method enables him to analyse the subject under investigation, so the scientific man applies the atomic theory as a method of analysing the phenomena of nature" (*Loc. cit.*). According to Mendeleev's opinion, Dalton's atomic theory was therefore "exclusively applied to explaining *the phenomena of the external world*" (*Loc. cit.*).

Whereas physical atomism could be used as a model of representation, this was certainly not compulsory for Mendeleev. He thus exclaimed that "there [was] a simplicity of representation in atoms, but […] no *absolute necessity* to have recourse to them" (*Ibid.*, 221). Mendeleev warned his students not to "apply reality to imagination" and he disliked the "atomists of extreme views" who still believed in the geometrical indivisibility of the atom (*Ibid.*, 217).

*The Atom as a Chemical Individual*

In order to keep his distance from the "metaphysical reasonings of the ancients" and in an attempt to remain with both feet on the sure foundations of chemical atomism, Mendeleev considered it "better to call the atoms *indivisible individuals*" (*Ibid.*, 216–217). He thus stated that "all masses are nothing but aggregations, or additions, of *chemical atoms* [!] which would best be described as *chemical individuals*" (Mendeleev 1889, 640). He admitted that "the Greek atom" and "the Latin individual" were equal "according to the etymology and original sense of the words," but noted that they had acquired a "different meaning" in the course of time (Mendeleev 1897, 216). Mendeleev explained that an individual was "mechanically and geometrically divisible, and only indivisible in a special sense" (*Loc. cit.*). For instance, "the earth, the sun, a man or a fly are individuals, although geometrically divisible" (*Loc. cit.*). Just as a man represented the "*indivisible unit*" in sociology, and as the planets served as units in astronomy, so the atom formed the unit of chemical experimentation. This shift in terminology from "atom" to "individual" clearly emphasizes Mendeleev's desire to remain *agnostic* about physical atomism. Indeed, Mendeleev espoused the term chemical individual "in order to avoid *recourse to the atom*" (quoted in Scerri 2006, 312). The fundamental importance Mendeleev attached to the conception of a chemical individual will be discussed further on.

## 7. Nineteenth Century Criticism about the Periodic Law

Recent studies by Nekoval-Chikhaoui (1994) and others have shown that the relationship between atomism and the reception of the periodic law was not as clear-cut as Urbain had fooled us into believing (*vide supra*). It appears that both atomists *and* anti-atomists accepted the periodic system as a valid teaching aid or a useful paper tool for chemical research. "It appealed to the positivist respect for empirical facts [i.e. chemical atomism], while at the same time offering new opportunities for theoretical speculation [i.e. physical atomism]", Brush remarked (1996, 614). Michael Gordin (2004, 24) explicitly noted that "the periodic law eventually served as one of the *strongest arguments* in […] favour [of] physical atomism." Although Mendeleev never considered his elementary table as providing even the slightest indication for the existence and compound nature of physical atoms, many of his colleagues apparently did. *Prout's hypothesis* for example – which stated that all elements were aggregates of hydrogen or some other primary matter – gained new impetus after the appearance of Mendeleev's periodic law. Even Lothar Meyer (1830–1895) and John

Newlands (1837–1898) – two precursors of the periodic table and both ardent advocates of physical atomism – saw proof in the periodic table for the physical reality of atoms (see e.g. Spronsen 1969). According to Brush (1996, 616), Mendeleev's periodic system was considered "a doorway to deeper knowledge of atomic structure."

Not surprisingly, physical anti-atomists responded heavily and the periodic table had to endure many severe criticisms during the latter half of the nineteenth century. Since very few chemists clearly distinguished between chemical and physical atomism, Rocke (1984, 10) noted that "every attack on physical atomism impugned, by association, the scientific worth of chemical atomism." As a result, those chemists who disapproved of physical atomism, felt forced to reject the periodic law in its entirety – not noting the possibility of retaining the periodic table in the light of chemical atomism alone. This point of view will be substantiated in the following paragraphs by looking at two critiques against the periodic law from the renowned anti-atomists Marcellin Berthelot and Wilhelm Ostwald.

*Berthelot's Criticism*

Marcellin Berthelot was a French chemist and a well-known personality in scientific circles for his anti-atomistic views on matters chemical and physical (see e.g. Nye 1981).[128] Somewhat strangely, Berthelot's piercing critique against the periodic law first appeared in 1885 in his work *Les Origines de l'Alchimie.* In the last chapter on *Alchemical Theories and Modern Theories*, Berthelot (1885, 302) considered the periodic table as "une tentative hardie, touchant peut-être à la chimère". The chemical groups in Mendeleev's elementary classification were only artificial constructs ("des assemblages artificiels") based on vague numerical relationships of an approximate nature (e.g. atomic weight triads). "Ce sont donc là des à peu près", he said, "[résultant] du jeu équivoque des combinaisons numériques. […] Tout ceci touche à la fantaisie" (*Ibid*., 301–310). Indeed, chemists who took the approximate for real would soon divert to the arbitrary fantasies of their imagination, Berthelot proclaimed. The only certain criteria of modern science were the empirical results, rooted in the solid ground of chemical experience: "c'est la seule barrière qui nous garantisse contre le retour des rêveries mystiques d'autrefois" (*Ibid*., 297).

From a purely epistemological point of view, theoretical systems such as Mendeleev's classification could of course be very useful in science. "Ils servent à exciter et à soutenir l'imagination des chercheurs" said Berthelot (*Ibid*., 312). But they did not necessarily reflect nature's ontology. "Quelle que soit la séduction exercée par ces rêves," wrote Berthelot, "il faudrait se garder d'y voir les lois fondamentales de notre science et la base de sa certitude, sous peine de retomber dans un *enthousiasme mystique* pareil à celui des *alchimistes*" (*Loc. cit*.).

Interestingly enough, the approximate character of the elements' numerical relationships was not the only reason why Berthelot discarded the periodic table. "Au fond," Berthelot concluded, "ceux qui invoquent les *multiples de l'hydrogène* et les *séries périodiques* rattachent tout à la conception de certains *atomes*, plus petits à la vérité que ceux des corps réputés simples" (*Ibid*., 313). It is apparent that Berthelot referred to Prout's hypothesis and Mendeleev's table in one and the same breath as "des interprétations aussi hypothétiques […] que l'existence même des atomes absolus" (*Ibid*., 291). Once linked with physical atomism, both these *a priori* conceptions ("analogues à celles des Pythagoriciens") were thus rejected as a logical consequence.

*Ostwald's Criticism*

A second criticism came from Wilhelm Ostwald in the second decade after Mendeleev's initial announcement of the periodic law. Ostwald was one of the leading critics of atomism during the early twentieth century, who boldly proclaimed in 1906 that "atoms are only hypothetical things" (Ostwald 1906, 41). It seems therefore plausible that Ostwald would have opposed the periodic law for that very same reason. His critique against the periodic law appeared in 1885, the same year as Berthelot's publication of *Les Origines de l'Alchimie*, and ran along the same lines. In his *Lehrbuch der allgemeinen Chemie* Ostwald (1885, 115) initiated his critique with the statement that "the numerous and unexpected developments which the Periodic Law has given us as to the relations of the atoms, one to another, should not make us blind to certain *difficulties* which have arisen in its full application."

"In reflecting upon the causes of the Periodic Law, the same *metaphysical consequences* press forward which have served as starting points for the *hypothesis of Prout*", Ostwald continued (*Ibid*., 116–117) – thus linking Prout's (physical atomistic) hypothesis with Mendeleev's (chemical atomistic) classification. "If the properties of the elements prove to be functions of the atomic weights, […] the assumption of a *primal matter*, whose different states of condensation define the differences of the elements, can hardly be set aside. These hypotheses are *far reaching* and *far removed from sure foundation* […]" (*Ibid*., 117). Once again, the periodic law was dismissed because of its supposed links with physical

[128] In an influential paper, Mary Jo Nye (1981) has identified the twofold roots of Berthelot's anti-atomism. First of all, Berthelot spoke against the physical realistic interpretation of Dalton's atomic theory, while acknowledging atomism as a useful system of conventions. Secondly, Berthelot's stubborn resistance to physical reductionism made him argue for the classification of chemistry among the traditions of natural history.

atomism. Ostwald (as Berthelot) did not note the possibility of retaining the periodic table in the light of chemical atomism.[129]

*Mendeleev's Response*

Mendeleev was forced to react if he was to save the periodic law from these severe critiques. In his Faraday Lecture of 1889, he admitted that "the periodic law [had] opened for natural philosophy a new and wide field for *speculation*" by contributing "to again revive an old but remarkably long lived hope – that of discovering, if not by experiment, at least, by a mental effort, the *primary matter*" (Mendeleev 1889, 642–643). But Mendeleev convincingly countered Berthelot's criticism and he broke off all relations with Prout's hypothesis. "The modern promoters [of the Pythagorean conception] are so bent upon its being confirmed by the periodic law, that the illustrious Berthelot, in his work *Les Origines de l'Alchimie* […] has simply mixed up the fundamental idea of the law of periodicity with the ideas of Prout, the alchemists, and Democritus about primary matter", Mendeleev began (*Ibid*., 644). "But the periodic law, based as it is on the solid and wholesome ground of *experimental research*, has been evolved independently of any conception as to the *nature* of the elements [i.e. physical atomism]; it does not in the least originate in the idea of an *unique matter*; and it has no historical connection with that relic of the *torments of classical thought*, and therefore it affords no […] indication of the unity of matter or of the compound character of our elements […]" (*Loc. cit*.).

**8. Mendeleev as a Physical Atomist**

Although some of the ambiguity surrounding Mendeleev's (anti)atomistic statements has been eliminated at this point (e.g. by showing that 1. Mendeleev relied on the atomic weight values of the elements when constructing his classification schemes as a *chemical atomist*, and that 2. Dmitrii Ivanovich rejected Prout's hypothesis and the complexity of the elements as a *physical anti-atomist*) this does not resolve the whole issue. It appears for instance that Mendeleev did not always reside with the physical anti-atomists; neither did he always act as a chemical atomist![130]

It will be claimed in the following paragraphs that Mendeleev was prepared to adopt some form of *physical atomism* whenever the universality of his periodic law was threatened by new discoveries. Two examples will be mentioned in order to substantiate this viewpoint. The first one is connected with the *rare-earth crisis* of 1869 and the seeming impossibility of characterizing the rare-earth metals by their atomic weights (see also Thyssen and Binnemans 2010). The second one comes from Mendeleev's *Attempt towards a Chemical Conception of the Ether* – an intriguing response by the father of the periodic law to the discoveries of *radioactive elements* early in 1902 (see e.g. Bensaude-Vincent 1982 and chapter 8 in Gordin 2004).

*The Rare-Earth Crisis*

In order to understand the first illustration of Mendeleev's physical atomistic viewpoints, a thorough understanding of the *dual sense of the epistemological concept of chemical elements* and Mendeleev's philosophical approach with regard to the characteristic properties of the elements will be necessary (see e.g. Paneth 1962a, 1962b, 1965; Bensaude-Vincent 1986; and Scerri 2000, 2005, 2007). Summarizing Dmitrii Ivanovich's perspective, one could state that Mendeleev clearly recognised this dual sense of the nature of chemical elements. He thus distinguished between the elements as *simple substances* and as *basic substances*. Simple substances could be characterised by the plethora of secondary properties (i.e. colour, taste, smell, etc.), and were therefore observable and isolable. Basic substances on the other hand were completely unobservable to our senses. This did not imply however that they were *devoid of properties*. Mendeleev was of the opinion that the more abstract, basic substances were characterized by the atomic weight, and he therefore used this property in accommodating all the chemical elements in his system. "In the proposed system the *atomic weight* of an element serves to *determine its place*", Mendeleev (1869, 26) explained. He concluded for that reason that "the magnitude of the *atomic weight determines the character of an element* to the same extent that the molecular weight determines the properties and many of the reactions of a compound substance" (*Ibid*., 27).

[129] It must be mentioned that Oswald (1885, 116) commuted his criticism by observing that "these objections are not raised to *refute* the Periodic Law." "They are too few in number for that," he said, "and they stand opposed to too many favouring circumstances. They serve only to show that the law in its present form is only the beginning of a most promising line of thought" (*Loc. cit*.). After Winkler's discovery of germanium in 1886, even Ostwald found it hard to remain sceptical about the periodic law, and he admitted that Mendeleev's periodic system had now "stood the test both in the prediction of the properties of elements at the time undiscovered, and in the indication of errors in the atomic weights previously accepted" (quoted in Brush 1996, 614).

[130] Kaji (2003) recently emphasized that Mendeleev's doctoral thesis *On Compounds of Alcohol with Water* of 1865 arose from his interest in indefinite compounds, whose composition was difficult to explain in terms of chemical atomic theory since chemical atomism was based on compounds showing only definite proportions. Kaji (2003, 194) cites Mendeleev further as saying: "In fact, while the atomic theory was strongly supported by the law of definite chemical compounds, it was also challenged by the so called indefinite compounds." And as Gordin (2004, 25) further concluded: "In a 1864 lecture Mendeleev argued that since definite compounds pointed towards atomic theory and indefinite compounds (like solutions) pointed away from it, "one should not seek in chemistry the foundations for the creation of the atomic system.""

An important consequence of taking the atomic weight as the characteristic property of basic substances was the possibility of distinguishing between the (chemically and physically very similar) congeners of a certain elementary group in the periodic table. The natural group of alkali metals, for example:

Li = 7 Na = 23 K = 39 Rb = 85.4 Cs = 133

consisted of five metals which shared a number of similar properties – their metallic lustre, their low melting points and densities, their pronounced reactivity with respect to water, their rapidly oxidizing character (tarnishing the metallic surface in a dull and grey colour), etc. It thus seemed as if the atomic weight differences were the only possible way to differentiate between these analogous elements. "Similar elements [in chemical and physical properties] possess different atomic weights", wrote Mendeleev (*Ibid.*, 31).

But in the case of the rare-earth elements, such as the cerium group {*Ce* = 92, *La* = 94, *Di* = 95}, the difference in atomic weights was scarcely noticeable. As Mendeleev explained in the first edition of his *Osnovy khimii*: "In spite of the great similarity existing at present [between the chemical and physical properties of the congeners of the cerium group], there are no differences, or to speak precisely, there are *no considerable differences in the values of atomic weights* of [these] similar elements" (quoted in Trifonov 1970, 38). There are more examples of this kind. "Such are nickel and cobalt, whose *atomic weights are very close to each other*; rhodium, ruthenium and palladium on the one hand, iridium, osmium and platinum on the other are also elements which closely resemble one another, and which have *very similar atomic weights*. Iron and manganese have similar properties and their *atomic weights are also very similar*" (quoted in Trifonov 1966, 27).

This implied that, in the case of these elements, no differentiation between the congeners was possible anymore on the basis of their atomic weights. Worded somewhat differently, the rare-earth elements seemed to undermine the hope of characterizing the elements as basic substances on the sole basis of their atomic weight values. As a result, the question naturally presented itself as to how the differentiation between rare-earth elements should be pursued. According to Mendeleev, these elements were characterized by "*internal differences of matter*" (Trifonov 1970, 38). The reason for the differences "is no longer the size and the weight of the atom," he said, "but obviously some other *internal differences in the matter*, constituting the atoms of these similar elements" (Trifonov 1966, 28). This was comparable in some respects with *isomeric substances*, as well as with *metameric compounds*, which were defined by Mendeleev as having "the same weight of particle [i.e. molecular weight] but in which the distribution of parts or atoms inside the particle is undoubtedly not identical" (*Loc. cit.*). Clearly, during the period 1869–1870, Mendeleev was still giving his thoughts about the periodic system free rein. The rare-earth crisis had forced Mendeleev to accept the physical underpinnings of Dalton's atomic hypothesis, and he even seemed prepared to postulate about the compound nature of these elementary atoms.

*Mendeleev's Attempt towards a Chemical Conception of the Ether*

A second illustration of Mendeleev's use of physical atomism comes from a much later period in 1902 when Dmitrii Ivanovich wrote his *Attempt towards a Chemical Conception of the Ether*. According to Mendeleev's opinion, the "earnest investigator" had to seek "the reality of *truth*, and not the image of *fantasy*" (Mendeleev 1904, 7). Having said this, Mendeleev (*Ibid.*, 6) likened the atoms to "the heavenly bodies, the stars, sun, planets, satellites, comets, &c." According to this physical atomistic point of view, "the building up of molecules from atoms, and of substances from molecules, [resembled] the building up of systems, such as the solar system, or that of twin stars or constellations, from these individual bodies" (*Loc. cit.*). It would be tempting to consider this a useful model for chemistry, but Mendeleev emphasized that this was not "a simple *play of words* in modern chemistry, nor a mere *analogy*" (*Loc. cit.*). Chemistry being an "*archi-real science*", this naïvely realistic picture of atoms and molecules was "a *reality* which [directed] the course of all chemical research, analysis, and synthesis" (*Loc. cit.*). The reason why Mendeleev adopted this form of physical atomism will be outlined in the final section.

## 9. The Chemical Individuality of the Elements

In an attempt to answer the question as to whether Mendeleev was an atomist or an anti-atomist, a distinction has first been drawn between the two faces of atomism (chemical vs. physical). But even this distinction has shown its limits. Although some of the ambiguity surrounding Mendeleev's (anti)atomistic opinions has been removed by claiming that Dmitrii Ivanovich was a *chemical atomist* and *physical anti-atomist*, this characterisation of Mendeleev has not always been in accordance with his various statements on atomism (*vide supra*). It has been shown for instance that Mendeleev was forced to act as a *physical atomist* from time to time.

I do not consider it therefore possible (or even useful) to pigeonhole Mendeleev as either an atomist or an anti-atomist. Mendeleev's viewpoints clearly fluctuated over the course of time and he adopted both atomistic and anti-atomistic interpretations of his periodic law. From the vagueness of his statements and the inconstancy of his opinions, it seems to me that Mendeleev was not gravely concerned with the nineteenth century debates on atomism.

I would argue on the other hand that the all-important constant throughout Mendeleev's life was his unremitting belief in the *individuality of the elements*. Indeed, "the conception of the *individuality* of the parts of matter exhibited in chemical elements only is *necessary and trustworthy*", Mendeleev (1897, 221) said. The "peculiar individualities" of the elements, "the infinite multiplicity of [these] individuals," and their submission to "the general harmony of Nature" were all central to Mendeleev's conception of nature (Mendeleev 1889, 642–643). The fundamental principles of chemistry were therefore "the indestructibility of matter" and the "immutability of the atoms forming the elements" (Mendeleev 1904, 9). It would thus be better to characterise Mendeleev as an *individualist* (or a *pluralist*) about the chemical elements. As will be outlined in the last part of this paper, this philosophical point of view may be the key towards an understanding of the reasons behind Mendeleev's apparently schizophrenic position – oscillating between physical atomism and physical anti-atomism. It also puts a different complexion on Mendeleev's critical attitude towards Prout's hypothesis and the phenomena of radioactivity.

Starting with Prout's hypothesis, it seems to me that Mendeleev was not so much concerned about the physical atomistic character of this hypothesis, as he was about the possible reduction of the multiplicity of the elements to one primary matter (*proto hyle*). "While we admit unity in many things, we none the less must also explain the individuality and the apparent diversity which we cannot fail to trace everywhere", Mendeleev (1889, 645) said. The periodic table emphasized this elemental diversity and precluded any reduction towards one unique matter. Whereas the Greek philosophers had been compelled to adopt "the idea of unity in the formative material, because they were not able to evolve the conception of *any other possible unity* in order to connect the multifarious relations of matter," natural science had now discovered a "unity of plan throughout the universe" which obviated the necessity of adopting such metaphysical beliefs about the existence of a primordial matter (*Loc. cit.*). Dmitrii Ivanovich thus explained in his *Faraday Lecture* how "the conception of many elements" could be retained and understood by submitting them "to the discipline of a general law" (*Loc. cit.*). Indeed, Mendeleev argued that the periodic law (as embodied in his periodic system) represented the "*unity* [undergirding] the immense *diversity* of [chemical] individualities" (*Ibid.*, 644). One thus understands Mendeleev's violent reaction towards "the illustrious Berthelot" who "mixed up the fundamental idea of the law of periodicity with the ideas of Prout, the alchemists, and Democritus about primary matter" which had to be classed "amongst mere *utopias*" (*Ibid.*, 644-647).

The discovery of radioactivity (and the apparent transmutation of the elements) at the turn of the twentieth century also undermined Mendeleev's conception of a chemical element as an *integral, immutable, chemical unit*. In his *Attempt towards a Chemical Conception of the Ether*, Mendeleev (1904, 17) dismissed the idea of radioactively disintegrating elements – claiming that all this "talk about the division of atoms" was "contrary to the scientific conception of the present day." In order to get rid of all this "metaphysical" and "metachemical" mumbo-jumbo, Mendeleev (*Loc. cit.*) argued that "those phenomena in which a division of atoms is recognised would be better understood as a separation or emission of the generally recognised and all-permeating ether." He therefore had to consider the weighty elements uranium and thorium as real, physical bodies being "endowed with the highest degree of that individualised attractive capacity" (*Ibid.*, 45). Conceiving the ether as the lightest of gases, Mendeleev explained that it would naturally accumulate about the heaviest atoms of uranium and thorium. The "emissive flow […] from the radio-active substance" (i.e. radioactive radiation) was then assumed to be emitted ether (*Ibid.*, 48).

Thus, whereas Mendeleev (*Loc. cit.*) had discarded Prout's hypothesis from a *physical anti-atomistic* point of view (claiming that "the periodic law […] evolved independently of any conception as to the nature of the elements"), he now espoused a form of *physical atomism* in trying to save the periodic table from the dangers of radioactivity.[131] It thus appears that (while being predominantly physical anti-atomistic) Mendeleev was ready to adopt any kind of atomism or anti-atomism whatsoever whenever the sacred individuality of the elements was threatened.

## 10. Conclusion

Due to his *empiristic attitude*, Mendeleev attempted to dissociate himself from the nineteenth century debates on atomism and the farfetched, *hypothetical* speculations about the compound nature of physically real atoms, by holding fast to the phenomenologically apparent *diversity* of the elements. As a consequence, the key towards a coherent understanding of

[131] Mendeleev's response towards the rare-earth crisis was very similar. Since the rare-earth elements could no longer be characterized on the basis of their atomic weight, these elements lost their individuality. In order to save the individuality of this group of elements, Mendeleev postulated about the internal structure of their atoms. Also, when Bohuslav Brauner (1855–1935) – a close friend of Mendeleev and a renowned rare-earth specialist – proposed his *asteroid hypothesis* in 1902 according to which the rare-earth elements had to be clustered together in one case of the periodic system, Dmitrii Ivanovich remained sceptical because this accommodation methodology was once more undermining the chemical individuality of the elements (see Brauner 1902 and Thyssen and Binnemans 2010).

Mendeleev's viewpoints is not so much about the distinction between *atomism* and *anti-atomism* (or even between the two faces of (anti)atomism – *chemical* versus *physical*), but rather Mendeleev's conception of the elements as *chemical individuals*. While Mendeleev's continuously varying viewpoints – running back and forth between atomism and anti-atomism – may appear rather whimsical at first sight, they all become rational and comprehensible when set against the background of his unremitting belief in the individuality of the elements. Out of this positive conviction about the irreducible individuality of the elements, Mendeleev abhorred the idea of a primary matter (thus opposing Prout's hypothesis, Thomson's discovery of the electron, and the radioactive decay of the elements). The unity of the universe was not to be sought in a modern *proto hyle* constituting the chemical elements, but in a unique periodic law of nature, underlying the "immense diversity of elemental individualities", and harmoniously connecting the "multifarious relations of matter" (Mendeleev 1889, 644-645).

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