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DMITRII IVANOVICH MENDELEEV (1834–1907)

Michael D. Gordin

Russian chemist Dmitrii Ivanovich Mendeleev (1834–1907) is most widely known for his 1869 formulation of the periodic system of chemical elements. In addition to this achievement, he also explored a variety of topics in physics and chemistry over the course of a very active scientific and political career. Distinctive about Mendeleev's work was his close (although not systematic) attention to various philosophical topics relating to his chemical work. This entry briefly discusses Mendeleev's life, scientific research, and some of his views on the philosophy of chemistry.

1 INTRODUCTION

The figure of Russian chemist Dmitrii Ivanovich Mendeleev (1834–1907) has long inspired the fascination of both chemists and philosophers. His bearded visage, which peers from the margins of countless chemistry textbooks, seems to recall the magus of medieval lore, and the principal achievement for which he is recognized — his formulation of the periodic system of chemical elements[1] — hangs in every chemistry classroom in the world and might be the most ubiquitous icon of science today. Mendeleev's life and career contain enough drama in them to sustain a consistent interest from chemists, and the periodic system has served as a cornerstone generator of questions for the philosophy of chemistry ever since the field split off from philosophy of science in general.

Mendeleev's own positions on the philosophy of chemistry, mostly but not exclusively related to the periodic system, are of often-unrecognized importance to those interested in this area of inquiry. Not only does Mendeleev's career span across a series of impressive solidifications of the status of the periodic system, and thus enables a historical view of the evolution of certain philosophies of matter and chemistry, but Mendeleev's rather long life of contemplation of the periodic system and the questions it engendered — his first formulation was in 1869, and

[1]More commonly called the periodic *table*. Mendeleev himself never used this expression, although he would later in life consider it a periodic *law*. "System" struck him as more general, pointing to the fundamental periodic relation of chemical properties with atomic weight, independent of any particular tabular formulation.

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he reflected on and off about the system until his death as the senior member of a vibrant Russian chemical community — offers some potential insights into the philosophical problems of chemistry in an age before quantum theory changed the agenda of both science and philosophy.

2 BIOGRAPHY

Mendeleev's life began in the small city of Tobol'sk, Siberia, and ended in the Imperial capital of St. Petersburg; his entire career, outside of small research trips and one postdoctoral journey abroad, was bounded by the demands and concerns of technical specialists in the Russian Empire [Gordin, 2004; Figurovskii, 1961; Kedrov, 1980].

He was born in 1834 as the last child in a large family, and was brought by his mother in 1850 first to Moscow and then to St. Petersburg to obtain higher education. He enrolled at his father's *alma mater*, the Chief Pedagogical Institute in St. Petersburg, which shared many of the same faculty as the more prestigious St. Petersburg University. Mendeleev quickly began studying the natural sciences there, and obtained his first two degrees, candidate and masters, in 1856 in chemistry. (His doctorate, analogous to a German *Habilitationschrift*, was completed in 1864.) Following a few years teaching as an adjunct at St. Petersburg University and in secondary schools in Southern Ukraine, he was sent abroad as a postdoctoral student to Heidelberg University. While there, he attended few classes and engaged in his own research projects.

Upon his return to St. Petersburg in February 1861, he began to look for steady employment. His first position as an adjunct at St. Petersburg University proved short-lived as that university shut down in September 1861 due to student unrest. Mendeleev eventually obtained a post at the St. Petersburg Technological Institute in 1863. He obtained a professorship at St. Petersburg University in 1867 teaching inorganic (general) chemistry, and he maintained that post until 1890. It was at St. Petersburg University that his most significant contributions to chemistry, most notably the periodic system in 1869–1871, took place. The first edition of Mendeleev's important textbook, *Principles of Chemistry* (*Osnovy Khimii*) was published at the same time, and the textbook and the periodic system were intimately connected.

The most significant personal development in Mendeleev's career occurred in November 1880, when he was rejected for appointment to the chair in Technology at the Imperial St. Petersburg Academy of Sciences, the most prestigious institution in the Russian Empire. Following this event, which coincided with a disruption in his physics research and his divorce, Mendeleev began to devote his time much more intensively to consulting with the Ministry of Finances on topics of economic development and modernization, an activity he had been engaged in to some degree since the early 1860s. A particular topic of interest was the development of the petroleum fields of Baku.

Mendeleev resigned his post at the university in Spring 1890 in the wake of a dispute over student rights. He soon thereafter began work for the Navy Department developing a form of smokeless gunpowder he dubbed pyrocollodion [Gordin, 2003]. From 1893 to his death in January 1907 he served as Director of the Chief Bureau of Weights and Measures, deputed with standardizing the Russian system of weights and measures and facilitating the introduction of the metric system on a non-obligatory basis. When he died, he had achieved level IV of the Table of Ranks, the highest rank achieved by a scientist in the Russian Empire.

3 RESEARCH TOPICS

As can be inferred from Mendeleev's diverse career, he had opportunities to engage with a broad variety of research topics, opportunities he took care to take full advantage of. For the purposes of this volume, the questions of interest relate to Mendeleev's research in the physical sciences, and those will be the topics addressed here. His extensive work on economics and other aspects of the social sciences — including his policy advice to the modernizing Tsarist state — as well as his thoughts on aesthetics and ethics, will not be discussed.[2]

Mendeleev's early research projects, beginning in the mid-1850s, dealt largely with organic chemistry, the largest and most dynamic branch of chemistry at the time, particularly among the younger generation of Russian chemists. His early work in his candidate and masters theses was theoretical, relating to type theory and specific volumes. While at Heidelberg, Mendeleev shifted from a more theoretical set of concerns to empirical testing of them through a series of experiments on the capillarity of organic solutions. (He would later claim that this work on the "temperature of absolute ebullition" prefigured Thomas Andrews's discovery of the "critical point.") Upon his return from Heidelberg, his research slowed due to the more mundane concerns of employment and family life, although he completed his doctoral dissertation in 1864 on the contraction of alcohol-water mixtures, an interest in "indeterminate chemical compounds" (e.g. solutions, alloys), that would return in the 1880s.

In the context of writing his *Principles of Chemistry* textbook, Mendeleev formulated his first version of the periodic system of chemical elements in the first two months of 1869. He would spend the next two years elaborating upon this system, expanding the scope and utility of the system in a variety of ways: classification of peroxides, the properties of rare earth metals, and, especially, the detailed prediction of properties of three yet-undiscovered chemical elements, which he named eka-aluminum, eka-boron, and eka-silicon. After the publication of these predictions in his most detailed article on the chemistry of the periodic system in 1871 [Mendelejew, 1871],[3] Mendeleev attempted briefly to experimentally discover these elements himself, but quickly abandoned the project by the end of that calendar year.

[2]The interested reader can turn to [Gordin, 2004, Chapters 6–7; Stackenwalt, 1976; Almgren, 1968].

[3]Translated into English, among other articles, in [Jensen, 2005].

He spent the 1870s largely elaborating an experimental project on the physics of gas expansion at very low and very high pressures, funded by an unusual (for the time) government grant from the Russian Technical Society and the Ministry of Finances. The purpose of this research was ostensibly to investigate gases at high pressures for the purposes of ballistics and industrial processes, but Mendeleev's own primary interest was to discover in the laboratory, under regimes of extremely low pressure, the substance of the luminiferous ether. In the course of this project Mendeleev developed some interesting physical instruments for the precision weighing of gases, as well as a form of highly articulated laboratory organization that would become typical of the labor management of larger laboratories in Imperial Russia and then the West. This project collapsed by January 1881 after the failure to obtain enough useful results to satisfy his patrons. Mendeleev's interest in the physics of aeronautics, which includes a detailed analysis of Book II of Isaac Newton's *Principia* (on the nature of vortices), stems from this period of intense interest in the physics of gases.

The 1880s represented a retreat for Mendeleev to a more chemical and less physical topic: the properties of solutions as a category of indeterminate chemical compounds, the set of questions that had motivated his doctoral dissertation of 1864. This research project — surpassing gases to become the longest single sustained research project of his career — systematically explored the solubility and properties of solutions of differing concentrations. Mendeleev interpreted the evidence to argue for a chemical vision of solution that emphasized the equilibrium of solution and solvent and rejected the now commonplace notion that certain compounds break into ionized component parts when dissolved. This theory gained some currency in England, before being eclipsed by the dissociationist claims that are at the bedrock of modern physical chemistry [Dolby, 1976, p. 327–331]. When Mendeleev left St. Petersburg University in 1890, his interest in this area seems to have faded.

For two and a half years, Mendeleev worked actively for the Russian Navy to develop a form of smokeless gunpowder. Mendeleev did not hesitate to discuss the implications of his gunpowder for naval procedures and organization, but he did not extend the work's philosophical implications into the realm of solutions and colloid theory from which it clearly emerged.

Mendeleev's final fourteen years, from 1893 until his death, were spent as the Director of the Chief Bureau of Weights and Measures, which was charged with putting the metrological affairs of the Russian Empire in order, and to facilitate the introduction of the metric system into Russia. In this post, he also conducted some significant research on the techniques of precision weighing, such as how to use the oscillations of a scale to provide for more accurate error correction terms [Brooks, 1998]. The most significant chemical research of this period was a theoretical interpolation and extrapolation from the periodic system's newly-added (and for a time strongly resisted by Mendeleev) family of inert gases to allow for two new elements: coronium and the chemical ether (tentatively dubbed newtonium). Newtonium was meant to explain the effects of radioactivity and electron discharge that suggested there was an atomic substructure by attributing those effects as epiphenomena of ether-matter interactions (which were, naturally, matter-matter interactions in Mendeleev's picture). He died shortly after abandoning this picture of subatomic interactions as unworkable, although he did not in turn accept the existence or conventional interpretations of radioactivity and atomic disintegration [Gordin, 1998; Gordin, 2004, chapter 8; Bensaude-Vincent, 1982].

4 PHILOSOPHICAL VIEWS

Mendeleev's philosophical views relating to the philosophy of chemistry can be broken down into three general areas: questions of ontology concerning fundamental entities in chemistry; questions of reductionism and the relation between physics and chemistry; and questions of the character of natural laws. The categorizations and language used throughout this section, unless specified otherwise, are the present author's and not Mendeleev's.

4.1 Ontology

Perhaps unsurprisingly, since he was a practicing chemist and not a philosopher by training or temperament, Mendeleev was often inconsistent concerning his attitude toward the existence of fundamental entities in chemistry, vacillating between strict realism in some areas, through instrumentalism to anti-realism in others. The entities he assigned to the three categories in many ways defy conventional interpretations of matter theory or chemistry.

Mendeleev was most strictly realist when considering a topic that is now considered a conventional construct: that of the chemical element [Bensaude-Vincent, 1986]. There is, strictly speaking, no such thing as an element in nature; what exist instead, as Mendeleev noted, were Antoine Lavoisier's "simple substances." No one, even today, has ever seen "carbon"; instead, they have seen diamond, or graphite, or carbon *atoms.* Oxygen, for example, appears in nature either as oxygen molecules or ozone. One infers the notion of "element" as the metaphysical basis that relates the various forms. For Mendeleev, this notion of element was fundamentally real. Elements, even though they were abstractions and unobservable, were strictly speaking "real": they were what was classified in the periodic system. Substances found in nature were merely instantiations of the abstract notion of an element which was truly the organizing principle of matter. Mendeleev's instrumental and anti-realist views about various entities all stemmed from this specific understanding of the reality of chemical *elements.*

Atoms, for example, were merely an instrumental convention for Mendeleev, a heuristic useful for talking about the combinations of chemicals, but not necessarily to be understood as real, a relatively common attitude in mid-nineteenth-century chemistry dubbed "chemical atomism" by historian of chemistry Alan Rocke [1984]. Mendeleev of course used the notion that substances combine in defined rations with each other while doing his practical work, but he had long maintained a conflicted attitude toward the physical interpretation of atomic theory. In his 1856 candidate thesis, he explained that, while the atomic hypothesis was useful, it "does not possess even now a part of that tangible visualizability, that experimental reliability, which has been achieved, for example, by the wave hypothesis [of light]." In an 1864 lecture, Mendeleev argued that "one should not seek in chemistry the foundations for the creation of the atomic system," since indefinite chemical compounds (like solutions) argued against definite ratios as much as stoichiometry argued for it. As late as 1903, Mendeleev continued to accept atomism only as a pedagogically "superior generalization" [Gordin, 2004, pp. 24–25]. Atoms were useful and could be treated with a realist stance, while at the same time they should not be taken too seriously. This was partially an attempt to reconcile his study of solutions with the atomist theories then current in theoretical chemistry.

Entities Mendeleev believed could not exist were ones that contravened his realist attitude to chemical elements. Matter, according to Mendeleev, had three essential properties: It was "integral" (atoms, should they exist, must be assumed to be integral and without substructure); it was immutable (transmutation between elements was impossible, an extension of the quasi-Platonic picture of chemical elements); and each element had a specified valency. Mendeleev's often-noted early resistance to inert gases stemmed from a contravention of the third principle. His opposition to electrons (first principle) and radioactivity (second principle) sustained itself until his death [Gordin, 2004, chapter 8; 1998]. Similarly, ionized elements could not exist in the abstract, and thus could certainly not be present in any solutions.

4.2 Reductionism

Mendeleev's career has occasionally been pointed to as evidence of a desire to reduce chemistry to physics, or to marshal chemistry to resist the onslaught of physics [Kargon, 1965]. Much of this stems from a retrospective evaluation of the periodic system: since physicists and philosophers have occasionally attempted to reduce the properties of that system to the principles of quantum mechanics or microphysics, there is an assumption that Mendeleev would have done so as well. The evidence points in the opposite direction. On each of the major reductionist debates of the late nineteenth-century — the physical existence of atoms, the reduction of chemical attraction to electric force, the substructure of atoms, the behavior of solutions — Mendeleev consistently argued for a fundamentally *chemical* way of looking at the world, leaving physics to an alternate domain. Mendeleev did not understand work on the borderlands of physics and chemistry, such as his physical experimentation on the expansion of gases, to be an issue of reduction, but more accurately a deployment of physical tools to solve chemical problems. He was familiar with the ether speculations of British physicists like James C. Maxwell and William Thomson, but he did not see the point of matter speculation that did not recognize that matter behaved *chemically*. His understanding of the border between chemistry and physics thus had more in common with a pragmatic attitude to the utility of results than to a fundamental reductionism or anti-reductionism [Gordin, 2004, chapters 3 and 8].

He even attempted to offer some more thorough philosophical speculations on this matter late in his life, a philosophy that he confusingly called "realism," to distinguish it from idealism and materialism. In September 1905, Mendeleev composed a piece called "Worldview (*Mirovozzrenie*)," which was intended to be an epilogue to his *profession de foi*, *Cherished Thoughts*, a book that mostly ranged across social and political matters [Mendeleev, 1995] (1903–1905).[4] According to Mendeleev's "realism," there were three basic components of nature: matter (substance), force (energy), and spirit (soul). Everything was composed of all three in some measure, and one could not reduce any one category to another. For example, the simple substance of ozone was composed of matter (measured by atomic weight), energy (its valency), and "spirit" (its property of belonging to the abstract chemical element of oxygen, as discussed above). The notion of spirit/soul is something like an Aristotelian final cause, but Mendeleev personally would have resisted any attempt to identify it with a classical notion. In any event, this philosophy of nature is far removed from the positivist notions scholars have occasionally attributed to Mendeleev [Bensaude-Vincent, 1986; Stackenwalt, 1976].

4.3 Laws of Nature

Mendeleev's views of the character of laws of nature changed dramatically over the course of his career as he came to see his legacy as linked to the lawlike status of the periodic system. The more it seemed that his major contribution to chemistry would remain the periodic system he had developed as a relatively young man — that is, as the gas and solutions programs came to naught in their quest for a yet more fundamental law, such as the behaviors of the ether — he gradually interpreted the periodic system as an increasingly rigorous law. Whereas immediately after its formulation Mendeleev held to a fairly expansive understanding of natural laws as general regularities like the rules of grammar, he modified his understanding to become *explainable* regularities, and then *invariant* regularities (although the mathematization of the periodic regularities, long the Holy Grail for Mendeleev, proved elusive) [Gordin, 2004, pp. 182–189]. Mendeleev's vision of laws of nature was never fully fleshed out, but the comparison seemed to more clearly emphasize *prediction* as a crucial feature of a natural law, patterning the concept on Newton's laws and their ability to predict unknown planets.

[4] Many of the ideas echoed an earlier piece, "The Unit," which he composed under a pseudonym as Popov [Mendeleev, 1877]; see also [Gordin, 2004, p. 229].

5 CONCLUSION

Although Mendeleev did not frame most of his thoughts about nature or chemistry in philosophical terms, it is productive to reflect on what can be retrospectively termed his "philosophy of chemistry (or science)." Even with the important exclusion of his thoughts on the social sciences (particularly economics), which Mendeleev himself did not differentiate sharply from his work in the physical sciences, one can see that his career, roughly around the time of the formulation of the periodic system of chemical elements, began to cohere around questions that he understood to have philosophical significance, and he regarded them as important questions in large part *because* of that significance, instead of for reasons of internal chemical or scientific interest. The somewhat foreign feel of his ideas in the light of post-positivist philosophy of science by no means points to the idiosyncracy of his views. Although most philosophically-inclined chemists of his period would not have held to all of his views, each individual tenet was not unusual. Distinctive about Mendeleev is rather the persistence by which he pursued questions of this nature and attempted to integrate them into an ordered system.

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