

The Periodic Table: Into the 21st Century

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Chapter 2

The Short Happy Life of Mendeleev's Periodic Law

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1. INTRODUCTION

In Ernest Hemingway's short story, "The Short Happy Life of Francis Macomber," the title character is an American businessman on safari who finds, following a terrific display of public cowardice, that he becomes truly alive after he remedies his failing through an equally public display of bravery, only to be accidentally killed a few moments later. Hemingway's point is that "life" is defined by the full experience of one's existence, of realizing one's full potential. In this chapter, I shall expand on this notion of a "short happy life" to analyze the strange career of Mendeleev's Periodic Law. It may surprise the modern reader that Mendeleev's law, which still hangs in classrooms and laboratories around the world in one of its incarnations as the polychromatic icon of the Periodic Table, had only a short life. Dmitrii Ivanovich Mendeleev (1834–1907) developed his Periodic Law in the period from 1869 to 1871, at which point he made predictions of three yet-undiscovered elements and promptly abandoned any further research on his system. The Periodic system was certainly Mendeleev's at this point, but it was not yet — in his mind — a law. That would only come with the discovery of these three elements, particularly the third element, eka-silicon (germanium) in 1886. Now that it had met his personal test of prediction, the Periodic system had become a law, but it would not remain Mendeleev's for long. By 1897, just a decade after its coronation, the Periodic Law was beset by the three threats of inert gases, radioactivity, and the electron. While within a decade these three phenomena were generally accepted by chemists and physicists as spectacular confirmations of the patterns revealed by the Periodic Law, for Mendeleev all but the inert gases remained anathema, and his final attempt to salvage his interpretation of the Periodic Law ended lying atop the dustbin of history.

2. THE PATH TO PERIODICITY

Picture a historian searching for the origins of the Periodic Law. Knowing that it emerged in the late 1860s, he begins to scour the major chemical journals in English, French, and German. Eventually, this search pays off, and our historian

finds a lengthy article published in 1871 where it would be expected: in the most prominent of German chemical journals, the *Annalen der Chemie und Pharmacie*. A cursory glance at the footnotes, however, reveals that this is *not* the original publication: this Periodic system of chemical elements had appeared before in a rather obscure St. Petersburg chemical journal, published in Russian. In fact, in the very second issue of this journal — restricted from a broader European readership for linguistic reasons — one finds a rather casual description of a chemical classification. This is hardly the universal law of nature our historian had set out to find. But the quest does not stop there, for in the body of this first article, dated April 1869, it appears that the author of this law first published his scientific findings in a *textbook* — an introductory textbook for first-year college students at that. This law of nature, therefore, which has become so ubiquitous that it appears in every classroom and textbook of chemistry, actually first emerged in a classroom and a textbook of chemistry.

That much has long been known. The formulator of the Periodic system's most successful and widespread variant, D. I. Mendeleev, made no secret of its conceptual genesis during the writing of a chemical textbook. Yet the implications of taking this historical curiosity seriously — it is not everyday that our most fundamental concepts of the world stem from a basic exercise in pedagogy — have scarcely been realized. Let us consider Mendeleev's path towards the Periodic Law as a *path* — a historical movement through time, with all the contingencies that implies. The Periodic system was the product of twin pedagogical trajectories: Mendeleev's personal trajectory through the educational institutions of St. Petersburg in his attempt to solidify a scientific career; and an effort to introduce the totality of chemistry through a set of easily-understood basic principles. How the classification of elements became a Periodic system and then a law of nature was intimately tied with how Mendeleev became increasingly secure at St. Petersburg University.

One of the most striking aspects of Mendeleev's successful endeavors to provide a stable framework for both inorganic chemistry and his personal career is how haphazard the whole process was. When he returned to Petersburg from his two years' postdoctoral study abroad at Heidelberg, he was neither famous nor on the track of the Periodic Law. Little more than a cold breeze met Mendeleev as he disembarked from the international platform of the Vitebsk station in St. Petersburg on 14 February 1861. Mendeleev had few close friends to greet him in this city where he was still a relative outsider, his Siberian origins not quite washed away by a decade of schooling in Petersburg and Heidelberg. He arrived at a most auspicious time: within a few days, the centuries-long tradition of serfdom was to be abolished in the first and most prominent of Tsar Alexander II's Great Reforms.

Mendeleev, like his peers, bridled with anticipation. A young, bright newcomer, he arrived at precisely the moment when the Great Reforms provided

astounding upward mobility for professionals, especially those with technical expertise. The story of the creation of the Periodic Law is the story of Mendeleev finding his way in this culture of rapid transformation and developing local, stop-gap solutions to pressing personal crises. Mendeleev would take the University and elevate it as a symbolic citadel for technical expertise and develop his hasty Periodic system into a "law" that would undergird his adult worldview. Similarly, the Great Reforms themselves were a series of *ad hoc* measures, designed to bolster the fiscal and military stability of the Empire, which were retrospectively recast by their principal agents into a unified picture of a reformed Russia. Mendeleev was a product of the Great Reforms, and happily so. Long after the Reforms were curtailed or repealed, Mendeleev would continue to consider them the only cultural model that had partially succeeded in modernizing Russia.

Consider the personal transformation that took place in the 1860s. Mendeleev returned to Petersburg burdened by debt. He had to find an apartment, pay back a 1,000 ruble loan for the laboratory equipment he had purchased in Heidelberg, and locate resources for new research material. Arriving at the middle of the academic year, he was unlikely to find a speedy appointment at one of the capital's many teaching establishments. In less than a month after his return, he had already contacted a publisher about translating J. R. Wagner's German text on chemical technology and had obtained a contract for his own proposed organic chemistry textbook [1]. From these modest beginnings, flash ahead to the end of the decade. In 1871 he was professor of general chemistry at St. Petersburg University, the most important chemistry chair in the country, and had expanded the chemistry faculty into one of the strongest in Europe. He had also developed a Periodic system of chemical elements that he considered sufficiently "lawlike" to hazard the prediction of three undiscovered chemical elements. In addition, he had published two highly successful textbooks, joined the ranks of the Ministry of Finances as advisor on alcohol taxation and agricultural reform, and served as a private consultant for the burgeoning Baku oil industry. His star was on the rise, and he knew it.

The ambitious and energetic Mendeleev did not, at age 35 in 1869, believe his arrangement of elements to be the apex of career. He did not even recognize his "Periodic system" as a "Law." Why would he? He was no prophet — at least not until 1871. This section chronicles the emergence of periodicity out of the confluence of local concerns — professionalization, pedagogy, authorship — and how Mendeleev built up not just a "Periodic Law" out of his "Periodic system," but a notion of the rightful place of chemical experts in Great Reforms Russia out of the model of St. Petersburg University [2]. As Mendeleev became more convinced of the potential of his Periodic system, he transformed it into a law by invoking the power of prediction, a tactic he would continually employ to legitimize both the notion of chemical expertise and his own status as the archetypal expert. Mendeleev was not just building his own career as a scientist in Imperial Russia, he

was constructing what it *meant* to be a scientist in Imperial Russia. This process began with Mendeleev's path through the Petersburg educational network from the Chief Pedagogical Institute to professor of chemistry at St. Petersburg University and culminated in the codification of the Periodic Law. By the end of Mendeleev's first decade back in Petersburg, he had assembled what would become the elements of his utopia of chemical prophecy.

2.1 The Education of Dmitrii Mendeleev

Mendeleev first came to St. Petersburg in 1850 as a last resort. After his graduation from the local *gymnasium* in Tobolsk, Siberia, his mother brought him to European Russia to further his education. She first tried to enroll him at Moscow University, the nation's oldest and most prestigious institution, but was refused. The next option was to take young Dmitrii to St. Petersburg. When the University there did not take him, he eventually registered — through the help of a family friend — at the Chief Pedagogical Institute, his father's alma mater. The Institute that fostered Mendeleev from 1851 to 1855 was a transformed place since his father's days. Ivan Ivanovich Davydov, who directed the Institute from 1847 until 1858 (when it closed), shifted the school's focus from training teachers to independent research. The curriculum contained a standard backbone of theology, logic and psychology, pure mathematics, mathematical and general geography, physics, general history with ancient geography, Russian, Greek, Latin, German, and French. The students then broke off into three faculties: Philosophical-Juridical, Physical-Mathematical, and Historical-Philological. Mendeleev was enrolled in the second of these. All of the 100-200 students received free education in return for devoting two years of teaching in secondary *gymnasias* [3]. The sickly adolescent Mendeleev thrived in the environment, enjoying the attention of distinguished University faculty (who also taught at the Institute, located on University grounds): mathematician M. V. Ostrogradskii, mineralogist S. S. Kutorga, physicist Heinrich F. E. Lenz, and chemist A. A. Voskresenskii.

Mendeleev was encouraged to pursue his scientific interests. His early work explored organic isomerism, the phenomenon where two substances with different chemical composition express the same crystalline structure, discovered by Eilhard Mitscherlich in 1822. Mendeleev's 1856 candidate thesis, "Isomerism in Connection with Other Relations of Crystalline Form to Content," reflected an early interest in connecting internal properties to external structure. Heavily influenced by French chemist Charles Gerhardt, Mendeleev conducted what was essentially a broad literature review and concluded that specific volume was the best means to examine the influence of composition on form. He continued to explore specific volumes with a Gerhardtian emphasis in his master's thesis, also published in 1856 [4]. At the end of the 1860s, when formulating his Periodic system, Mendeleev would draw on certain aspects of this research: a concern with

ordering elements by *physical*, not chemical, properties, attention to classification, and a reconsideration of atomic-weight values [5].

On 14 April 1859, after an unpleasant stint teaching secondary school in the Crimea, Mendeleev left for Heidelberg on a subsidized trip to further his studies in chemistry. Upon arrival, he approached the distinguished German chemist Robert Bunsen for a spot in his laboratory, but the fumes and the noise so annoyed him that he instead transformed his apartment into a "very cute laboratory" that even had its own gas supply [6]. Mendeleev almost immediately threw himself into chemical researches on capillarity (the effect whereby liquid is drawn up in a narrow tube against the pull of gravity). He conducted a broad array of experiments with a variety of organic liquids, which eventually led both to his doctoral thesis on alcohol solutions and to his co-discovery of the "critical point" of liquids. Mendeleev was socially active among Russian students or travelers. Many of them have left accounts of their encounters with Mendeleev, and almost all remarked that his powerful personality formed the center of the Russian student community [7]. The time in Heidelberg was extremely important for the young Mendeleev, cementing bonds between fellow Russian chemistry students, and bringing him to the Karlsruhe Chemical Congress in September 1860, when Italian chemist Stanislao Cannizzaro revived Amedeo Avogadro's 1811 hypothesis for providing a consistent system of atomic-weight calculation, rationalizing what had become a veritable chaos of competing systems.

Poor and desperate for money back in Petersburg in February 1861, Mendeleev turned to publication. In a matter of months, he composed a textbook, *Organic Chemistry*, one of the last defenses of Gerhardt's style of organic chemistry, which was being eradicated by the rise of structure theory. Mendeleev submitted the manuscript to the Academy of Sciences in the hopes of winning their Demidov Prize. The committee, composed of two of his patrons, J. Fritzsche and N. N. Zinin, awarded Mendeleev the prize in early 1862, which he used to finance his marriage to Feozva N. Lesheva. Reception among students was enthusiastic. As N. A. Menshutkin, later professor of analytic chemistry at St. Petersburg University, recalled: "I remember with what interest we, still students, greeted the appearance in 1861 of his *Organic Chemistry*. At that time this book was the only one in Russia, standing at the height of science, even distinguished in comparison to foreign works in its interest, clarity of exposition, and completely unique integrity." [8]. Mendeleev could now use that reputation to build a career.

That career was almost entirely bounded by St. Petersburg University. Upon returning to Petersburg, Mendeleev approached his undergraduate mentor, Aleksandr Voskresenskii, professor of chemistry at St. Petersburg University. Although Voskresenskii managed to find some job openings, Mendeleev was too occupied writing *Organic Chemistry* to take on heavy teaching commitments, and he worked on the book for the remainder of the summer, securing an adjunct

position at the University for the fall. This University, founded only in the second decade of the nineteenth century, would become — for political, demographic, and intellectual reasons — the apex of the Russian university system by the end of the century, a transformation in which Mendeleev figured centrally.

In 1867, Mendeleev obtained tenure at St. Petersburg University and could fully appreciate the benefits of professorial autonomy provided by the liberalizing University Statute of 1863, one of the Great Reforms. For the six years between the dislocations of student unrest at St. Petersburg University in 1861 and his tenure there, he circulated among a variety of local institutions. The Technological Institute in Petersburg, administered by the Ministry of Finances, hired him as extraordinary professor of chemistry on 19 December 1863. He had a relatively light teaching load (compared to the previous generation of Russian chemists) consisting of three lectures a week on organic chemistry for sophomores, one lecture a week on analytic chemistry for upperclassmen, and the supervision of laboratory exercises [9]. He became a tenured ordinary professor of technical chemistry in late 1865. In that same year he was elected extraordinary professor of general chemistry at St. Petersburg University, and he held both posts simultaneously, neglecting the Technological Institute even more after he was promoted to an ordinary professorship of general chemistry at the University in October 1867. He only resigned his post at the Institute in 1871, even after successfully petitioning to have his time-intensive laboratory teaching load eliminated or at least split with another professor. St. Petersburg University would provide the framework in which Mendeleev approached his classification of chemical elements.

2.2 *The Principles of Chemistry and the Periodic System*

The Periodic Law emerged out of the Periodic system of elements, the tabular classification that Mendeleev composed in early 1869 at St. Petersburg University. He created the Periodic system to address a specific set of demands required in the composition of a new inorganic chemistry textbook — pedagogical problems of classification and organization. The 1860 Karlsruhe Congress had made the problem of creating a consistent general chemistry textbook more acute. The reform of atomic weights meant that all prior textbooks needed to be heavily revised, supplemented by the array of new elements discovered in this decade due to the innovation of spectroscopy. But hidden within this population explosion in the elemental world was the seed of its own solution, for without those consistent atomic weights, the patterns of periodicity would have remained hidden. It is striking, in fact, that the six competing versions of the Periodic system, including Mendeleev's, emerged following the assimilation of Cannizzaro's resurrection of Avogadro's hypothesis. Karlsruhe set the stage for the Periodic system, and the Periodic Law returned the favor by furthering the post-Karlsruhe regime of atomic weights.

St. Petersburg University proved to be a fruitful setting. When Mendeleev took over his mentor Voskresenskii's post as professor of chemistry in October 1867, he assumed the large inorganic chemistry lecture course that was required of all students in the natural sciences faculty. In order to teach such a course, he had to find an appropriate textbook. With a few exceptions — including two important texts on organic chemistry (one Mendeleev's own) — Russian chemical textbooks in this period were adapted translations from Western European texts. With the rapid advances in chemistry, however, any new translation would be almost certainly out of date as soon as it appeared [10]. When Mendeleev began teaching at the University, there were 63 known elements, each identified by atomic weights newly determined by Avogadro's hypothesis. He had to develop some system of classification. The two basic methods for dividing the elements — into metals and metalloids (non-metals) or by using the new concept of valency — seemed unhelpful to Mendeleev. He chose to write his own textbook instead and work out the challenges of classification himself.

Textbooks are a much-maligned genre in today's science, seen as merely second-rate reiterations of "real" science. This grossly undervalues both the historical and pedagogical functions of these texts. Not only does a textbook stand as a codification of what is considered "universal" knowledge within a field at a given moment, but the application of these textbooks to teach a younger generation of scientists reinforces that universality. Particularly in the field of chemistry, which both at the beginning and middle of the nineteenth century underwent tremendous transformations even in the definitions of central terms (affinity, valency, atom, element, atomic weight, molecule), textbooks were used not only to codify what was standard knowledge, but to *create* the very set of standard concepts [11].

The text Mendeleev wrote for his introductory chemistry course, the *Principles of Chemistry* (*Osnovy Khimii*), was divided into two volumes, each with two parts. The two parts of volume one were largely written in 1868, and concluded in the first month of 1869 [12]. Rather than structuring the first volume of his textbook around a classification of the elements, Mendeleev described chemistry in terms of the *practices* by which one acquired knowledge of the chemical world. Early in volume 1, which was entirely written before the inception of the Periodic system, Mendeleev's definition of chemistry illustrated the text's structure: "[Chemistry] is a natural science which describes homogeneous bodies, studies the molecular phenomena by which these bodies undergo transformations into new homogeneous bodies, and as an exact science it strives... to attribute weight and measure to all bodies and phenomena, and to recognize the exact numerical laws which govern the variety of its studied forms." [13]. Notice that Mendeleev did not introduce elements, atoms, or any theory of chemical combination. Instead, volume 1 is littered with basic definitions, plans for chemical experiments, and natural-historical

information. The reader finds no direct hints of the forthcoming Periodic Law. The second volume of the *Principles*, however, which led to Mendeleev's initial formulation of the Periodic system, was integrated with chemical theory.

The theory that one would expect to be most connected to periodicity was also the one Mendeleev was most loath to take literally: atomism. Physical atomism — the belief that atoms are discrete physical bodies — was heavily contested in chemistry in the nineteenth century, and the Periodic Law eventually served as one of the strongest arguments in its favor [14]. It does not follow, however, that Mendeleev must have been thinking in terms of physical atomism when he conceived his system. Indeed, Mendeleev had long maintained a conflicted attitude to atomic theory. In his 1856 masters thesis, he explained that, while the atomic hypothesis was a useful explanation, 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], not even to mention Copernicus's theory, which one can no longer call a hypothesis.” [15]. In an 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.” [16]. Even as late as 1903, Mendeleev accepted atomism only as a pedagogically “superior generalization.” [17].

Mendeleev's skepticism sharply emphasizes the difference between the present-day interpretation of the Periodic system and Mendeleev's views of 1869. Today's Periodic system is widely understood as revealing periodic properties caused by the gradual filling of electron shells in individual atoms. Elements with one free electron in the outer shell will have similar propensities to combine in certain ratios, and thus have similar chemical properties. The primary ordering of today's system — atomic number — measures the number of protons in the nucleus of an atom, which in turn determines the electrons and thus the chemical properties. This entire concept is structured around *atoms*. For Mendeleev, any atoms that might exist had *absolutely no* substructure, and he resisted the notion of electrons (discovered in 1897) until his death. (He never even heard of protons.) Mendeleev's system had no notion of atomic number, and everything was ordered by atomic weights — or, as Mendeleev would prefer, “elemental weights.” This raises the crucial concept that underlay the entirety of the Periodic system, and that would serve as the chief warrant for Mendeleev's elevation of the convenient classification to a law: the abstraction of an “element.” There is, strictly speaking, no such thing as an element in nature; what exist instead are “simple substances,” a concept initially developed by Lavoisier. That is to say, no one (even after the advent of scanning-tunneling microscopes) has ever seen “carbon”, instead, they have seen diamond, or graphite, or other forms (and, today, carbon *atoms*). Oxygen is observable in nature as the oxygen molecule or ozone. We *infer* the notion of an “element” as the metaphysical basis that relates the various forms, much as Mendeleev later inferred

the Periodic Law as the metaphysical basis to explain the diversity of “elements.” [18].

This distinction would only come to Mendeleev halfway through writing his *Principles of Chemistry*. Instead, chemical practice and not chemical theory provided his initial organizing principle, which begins to transition into the origins of the Periodic system as the reader approaches Chapter 20: Table salt. Up to this point, Mendeleev had only treated four elements in any detail: oxygen, carbon, nitrogen, and hydrogen — the so-called “organogens.” Mendeleev began this chapter as usual by purifying sodium chloride from sources such as seawater. A discussion of sodium and chlorine followed in the next chapters, and finally the halogens appeared, the family of elements (bromine, iodine, fluorine) that were clearly related to chlorine. Thus ends volume 1, and the alkali metals (the sodium family) form the first chapter of volume 2.

Mendeleev faced a serious predicament in late January 1869. His textbook was pedagogically sound, and he had just sent volume 1 to the publishers, but had only dealt with 8 elements, relegating 55, fully seven-eighths of known elements, to the second volume [19]. Clearly, Mendeleev had to come up with a less rambling organizational method or he would never finish in the contractually agreed-upon time and space. As he recalled in April 1869:

Having undertaken the compilation of a guidebook to chemistry, called “The Principles of Chemistry,” I had to set up simple bodies in some kind of system so that their distribution was not governed by accidents, as if by instinctive guesses, but by some definite exact principle. Above we saw the almost complete absence of numerical relations in the establishment of a system of simple bodies; but any system based on exactly observed numbers, of course, will already in this fashion deserve preference over other systems which do not have numerical foundations, in which there remains little place for arbitrariness. [20]

Mendeleev's earlier system of pedagogically-useful organization — using laboratory practices to explain the common substances (water, ammonia, table salt) in which they are found — could no longer sustain the burden of exposition. He needed a new system that would still be pedagogically useful, and he hit on the idea of using a numerical marker for each element. Atomic weight seemed the most likely candidate for a system that would: a) account for all remaining elements; b) do so in limited space; and c) maintain some pedagogical merit. His solution, the Periodic system, remains one of the most useful teaching tools in chemistry.

Early in February 1869, while Mendeleev was writing Chapter 1 and Chapter 2 of volume 2 on sodium and the alkali metals, he listed these elements in order of increasing atomic weight and compared them with the halogens, similarly arranged [21]. By Chapter 4, on the alkaline earths, Mendeleev was entirely converted to the idea of organizing all of the elements according to a numerical system. He no longer enumerated the elements according to substances in which they could be found; instead, he began on the first page of this chapter to show that the arithmetical difference between rows followed a similar pattern in all three Groups: halogens, alkali metals, and alkaline earths [22]. In addition, these elements, with a valency of 2, succeeded the alkali metals, with a valency of one. While Mendeleev remained resistant to aspects of valency theory, his system followed the progression of combining power across the elements. Note that atomic weight was not yet of *dominant* importance. Atomic weight was used as a secondary quality that showed the hierarchical ordering within families. As volume 2 proceeded, Mendeleev would begin to emphasize atomic weights so much that they were listed even in chapter titles, and elements were always introduced along with their atomic weight.

It is extremely difficult to reconstruct the process by which Mendeleev came to his periodic organization of elements in terms of their atomic weights. He did not simply list them in order of increasing weight, but observed the periodic repetition of chemical properties, thus correlating two parameters. The problem from a historical perspective is that, while Mendeleev kept almost every document and draft that crossed his hands *after* he believed he would become famous, he did not do so *before* the Periodic Law. As a result, we have just *four* relevant documents that precede the first publication on the Periodic Law — and one of these is a fair copy of another. Thus we are forced to consider volume 1 of the *Principles* in conjunction with these documents and come to some informed speculations.

There are two ways Mendeleev could have moved from a recognition of the importance of atomic weight as a good classifying tool to a draft of a Periodic system: either he wrote out the elements by order of atomic weight and noticed periodic repetition; or he assembled several “natural groups” of elements, like the halogens and the alkali metals, and noticed a pattern of increasing atomic weight. Most analyses of Mendeleev stand dogmatically on either the “row” or “group” version. Mendeleev’s only direct statement on this matter, however, shows a middle way. He wrote in April 1869 that he “gathered the elements with the lowest atomic weights and placed them by order of their increase in atomic weight” [23]. This produced what he called his “first try,” marking elements with their atomic weights:

Li = 7;	Be = 9.4;	B = 11;	C = 12;	N = 14;	O = 16;	F = 19
Na = 23;	Mg = 24;	Al = 27.4;	Si = 28;	P = 31;	S = 32;	Cl = 35.5
K = 39;	Ca = 40;	—	Ti = 50;	V = 51. [24]		

I will return shortly to the “—” underneath aluminum. For the moment, however, consider Mendeleev’s list. These are most of what Mendeleev called the “typical elements” — the set of elements up to chlorine that provide the nearest encapsulation of the Periodic system [25]. The list also emphasizes elements treated in volume 1 and the first chapter of volume 2 of the *Principles*: the “organogens” (minus hydrogen), the halogens, and the alkali metals. Here Mendeleev built “groups” and “rows” simultaneously. He took the highest elements, which most sharply showed the differences in properties, and listed them by rising atomic weight, building a row; but each of the “typical elements” in the top row *encoded as typical* the properties of the elements below. They stood in for their group, and thus Mendeleev saw both patterns at once.

This realization happened sometime early in 1869. After considerable work to make a system that contained all of the elements, he sent a draft of a single sheet to the printers on 17 February 1869. This draft was printed in both Russian (150 copies) and French (50 copies), and the sheet, entitled, “An Attempt at a System of Elements, Based on Their Atomic Weight and Chemical Affinity,” was sent off to various chemists (Figure 1). The fact that he had more printed up in Russian indicates that his primary audience at this point was local and not international. This “Attempt (*Opyt*)” was not the final version of the Periodic system — it contains many errors, and Mendeleev spent the better part of the next two years reinventing it. In order to begin to transform it into a developed form of the system similar to today’s representation, one must rotate it clockwise by 90° and reflect it across the vertical axis. Even then, the alkali metals and the halogens are next to each other, which is counter-intuitive if you organize the elements according to any physical property — atomic volume, electronegativity, electron shells, etc. Mendeleev’s “Attempt” was a draft. He would keep tinkering with the system until he found a chemical property that monotonically separated each group: the degrees of oxidation in a saturated chemical compound of the element [26]. The quality of a first draft can be seen in the title of the “Attempt.” In a rough draft, Mendeleev crossed out in both French and Russian the word “classification” (*classification, raspredelenie*) and replaced it with “system” (*système, sistema*), once he became convinced that his organization was not arbitrary. But in the French title, he forgot to change the gender of the indefinite article from feminine to masculine (*une* to *un*). The version he sent out thus bears the traces of Mendeleev’s gradual process of construction [27].

This system, then, emerged out of a pedagogical “classification” that answered the specific needs of presenting material to beginning chemistry students. The pedagogic utility of Mendeleev’s Periodic system would later be universally recognized, even by its critics. Mendeleev repeatedly invoked the system’s pedagogical origins: “I note also that the outlining for beginners of the facts of chemistry and their generalization benefits very much from the use of the Periodic Law, as I became convinced not only in lectures in the last two years, but also

By August of 1869 Mendeleev had developed a stricter conception of what it took to be a law of nature. In an article published that month on the variation of atomic volumes over the Periodic system, he shied away from the word "law" and called it a "regularity (*pravil'nost'*)" [33]. This retreat was motivated by the existence of exceptions to strict ordering by physical properties. Yet, by October 1869 Mendeleev found that ordering the elements by the quantity of oxygen in their oxides revealed how "natural" his system was, by showing the evolution from the alkali metals to the halogens. That is, taking R to be a generic element, the alkali metals combined as R_2O , the alkaline earths as RO (or R_2O_2), all the way to the halogens, which combined as R_2O_7 . This provided a neat ordering of Groups from 1 to 7, based on the oxygen subscript [34].

Over the next year, Mendeleev conducted broad-ranging investigations into aspects of his scheme, trying to account for the problems that beset the rare earths, indium, and other irregularities in his system. By November 1870, Mendeleev was utterly convinced of the "naturalness" and the lawlike character of his Periodic system. That month, he published a Russian article which predicted the discovery of new elements, proposed changes in the atomic weights of current elements, and formed the framework for his more detailed German article the following year that would eventually create his European reputation. This grandeur is foreshadowed in the title: "The Natural System of Elements and Its Application for the Indication of the Properties of Undiscovered Elements." In this piece one sees the first usage of "law" in the strict sense as referring to periodicity: "I propose also that the law of periodicity (i.e. the periodic dependence in the change of properties of the elements on their atomic weight) gives us a new means to determine the magnitudes of the atomic weight of elements, because here already in two examples, namely with indium and cerium, the propositions which were drawn from the foundation of the law of periodicity, were affirmed." [35].

In this article (and in its German successor), Mendeleev recapitulated the process by which he came to the Periodic Law. First he surveyed current systems; then he created his own conventional system; then he tested it on items about which we have stable knowledge (such as the typical elements); then he tried it on less stable elements and corrected their properties (such as doubling the atomic weight of uranium); and next on extremely doubtful objects (indium and cerium). Building incrementally on these foundations, he moved to the prediction of new elements. He called the system "*a natural system of elements*," because "not in a single instance does one meet any essential obstacles for the application of this system for the study of the properties of elements and their compounds..." [36]. This cautious transition from convention to broader and broader claims about less and less stable knowledge is a recurrent pattern for Mendeleev that transcended the boundaries between science, politics, and culture.

So far, there has been nothing to distinguish this process of reasoning from that which produced the less rigorous "regularities." After he had moved the reader to extremely doubtful elements and showed the application of periodicity, he now moved to *completely* doubtful elements, i.e., those that did not even exist:

With the pointing out of the periodic and atomological dependence between the atomic weight and the properties of all elements, it appears possible not only to point to the absence of certain of them [elements], but also to determine with greater certainty and likelihood for success the properties of these still unknown elements; one can point to their atomic weight, density in free form or in the form of an oxide, the acidity or basicity of their degrees of oxidation, the possibility of reduction and the formation of double salts, to decide with this the properties of metalloorganic and chlorine compounds of the given element — there is even the possibility to describe the properties of certain compounds of the still undiscovered elements with very great detail. I decide to do this for the sake of having the possibility, when with time one of these substances I predict will be discovered, of finally assuring myself and other chemists of the justification of the propositions which lay at the foundation of my system I propose. For me personally these propositions were finally solidified from the moment when these propositions, which were based on the periodic law (*zakonnost'*), which lies at the basis of all this research, were justified for indium. [37]

Mendeleev's famous November 1871 article takes this thinking into a great deal more detail. This article was written in July and translated into German by Felix Wreden [38]. Mendeleev was now convinced that his system was superior to those of his predecessors, and even hinted that there might be a mathematical function underlying the pattern produced by the atomic weights. It was, after all, from the mathematical concept of a periodic function that Mendeleev had borrowed the term "periodicity" in the first place, a term not used by any of the other proponents of systems of elements [39]. At the basis of this relation was the importance of prediction:

That is the essence of the law of periodicity. Each natural law (*estestvennyi zakon*), however, only acquires scientific significance when there is the possibility of drawing from it practical, if one can put it that way, consequences, that is, those logical conclusions which explain what is not yet explained, point to phenomena not yet known, and especially when it gives the possibility to make such predictions which can be confirmed by

experiment. Then the utility of the law becomes obvious and one has the possibility to test its validity. [40]

It was at this point that he declared that the system "has a significance not just pedagogical, not only easing the study of various facts, bringing them into order and connection, but it also has a purely scientific significance, discovering analogies and pointing through them to new paths for the study of elements." [41]. He had moved from pedagogy to pure science through prediction.

2.4 The Eka-Elements

Clearly, the crux of Mendeleev's attitude toward what made the Periodic system into a "law" was the role of prediction. It was this capacity for prediction that convinced him of the "naturalness" of his system of elements, and it was the discovery of new elements that would eventually astonish chemists internationally.[42] For Mendeleev, following mainstream philosophies of the scientific method in the nineteenth century, prediction was what made a science "scientific," as he expressed in his notes for a public lecture in the early 1870s: "A theory is a connection of the internal with an entire worldview: beginning as an hypothesis, it ends with the theoretical discovery of new phenomena, drawing everything from one proposition. This corresponds to the prediction of phenomena in their complete accuracy, the discovery of new unprecedented phenomena. Astronomy [and] physics are in this situation, chemistry still isn't." [43].

It is important to stress that prediction was *not* what Mendeleev was after when he first began constructing his Periodic system, as the "Attempt" (Figure 1) demonstrates. He had been trying to assemble a teaching tool, and he used question marks as placeholders for elements that were needed to keep the system viable. The atomic weights offered were educated guesses, and would fluctuate as he moved beyond this first draft to a complete revision of the system. But the question marks are there all the same, and they (as well as the "—" in his "first try") indicate the moment at which Mendeleev began to think of his system as something scientific — as something that could predict. The first explicit mention of prediction was in his April 1869 article, which Mendeleev concluded with a list of eight advantages of his system over the competing classifications of his day. The sixth point read: "One should expect the discovery of many yet *unknown* simple bodies, for example, elements with affinity to Al and Si, with atomic weights 65-75." [44]. Notice the weakness of this prediction: it is only the *sixth* point in his list, and it is remarkably vague (he did not even specify the number of elements). In fact, it is apparent from his notes that he tried to fill the blanks at first with existing elements on the grounds of chemical consistency, to see if perhaps their atomic weights had been inaccurately measured [45]. By late August 1869, in his article on atomic volumes, he had abandoned this approach and some of his earlier vagueness: "Therefore it is possible to say, that the two elements which are not yet

in the system and which should display affinity with aluminum and silicon and have atomic weight of about 70, will display an atomic volume around 10 or 15, i.e. will have specific weight of about 6 and, thus, will occupy exactly in all relations the average or will comprise the transition in properties from zinc to arsenic." [46].

But prediction was not emphasized as a primary function of the system for over a year, until Mendeleev's extensive Russian article of November 1870, and repeated more intensely in the German expansion of 1871. During this period, Mendeleev tinkered with aspects of the system, especially the problematic rare earths, such as indium and cerium [47]. Once again he displayed a characteristic of his prophetic work: if an idea was promising, he would retreat from some his bolder claims and comprehensively study of the minutiae of the project, making sure that all easily answerable questions were resolved before using these as a stable platform to leap into the undiscovered.

By November 1870 Mendeleev was persuaded that the major difficulties posed by the rare earths and other problematic elements had been resolved (as with uranium or indium), or contained (as with the cerite metals) so that substantial revisions were unlikely. It was at this point that he publicly articulated the process of prediction. He began by displaying a revised system, what would come to be called the "short-form" Periodic system (Figure 2). These systems are built as direct analogies from the list of typical elements — those elements with sharp characteristics that stand at the top of the twin peaks of today's long-form Periodic systems. Short-form systems compress the "long" periods that contain the transition elements (the valleys) into a second "little period" that folds underneath the first, so those periods with sixteen elements are shown in two rows of eight. The advantage of this form from Mendeleev's perspective was that it expanded the analogies one could draw between an element and its neighbors by increasing the number of neighbors, as well as simplifying the progression of levels of oxidation indicated in the headings of the groups. (The electron-shell interpretation of the system has today completely eradicated the viability of Mendeleev's short form.)

Mendeleev began by noticing that there were not enough analogs of aluminum and boron. Most groups seemed to have six analogs down to the fifth row, whereas the third Group only had four. That is, when you go to the third column (Group), there were two spaces that seemed unoccupied after boron (B) and aluminum (Al) before one hit the next element. Put another way, that meant that immediately after potassium (K) and calcium (Ca) in the second row, there was a gap, and immediately after copper (Cu) and zinc (Zn) in the next row there was a similar gap. Mendeleev began with the first of these. Since these elements had atomic weights close to 40, and then next one, titanium, was close to fifty, he opted for an "average" 44. (This is not an exact average of the atomic weights of K, Ca, Ti, and V, which would be 45 — Mendeleev modified the mathematics to suit his intuition.) [48]. Since this element was in an even row, it should have more alkali

properties than lighter elements in the same Group (boron and aluminum), and its oxide R_2O_3 should be a more energetic base. Mendeleev developed this point through a strong analogy to titanium, comparing TiO_2 and its lighter analogs. As with titanium, this element's oxide should have a sharper basic character and thus it should form alkali compounds insoluble in water, although it ought to form stable acidic salts. He also went into detail on its chloride and atomic volume. While some of these predictions displayed remarkable virtuosity, many others were repetitive (forms of compounds which are merely functions of the valency). Mendeleev chose to call the element eka-boron, "creating the name from the fact that it follows boron, as the first element of the even group, and the prefix *eka* comes from the Sanskrit word for *one*. $Eb = 44$." [49].

(31)	Группа I	Группа II	Группа III	Группа IV	Группа V	Группа VI	Группа VII	Группа VIII. Дефект в группе 1
Титанека титан	H = 1 Li = 7	Be = 9, 4	B = 11	C = 12	N = 14	O = 16	F = 19	
Ванадиека ванадий	Na = 23	Mg = 24	Al = 27, 3	Si = 28	P = 31	S = 32	Cl = 35, 5	
Хромека хром	K = 39	Ca = 40	Ti = 50?	V = 51	Cr = 52	Mn = 55	Pg = 56, Co = 59, Ni = 59, Cu = 63	
Манганека манган	(Ca = 63)	Zn = 65	— = 63	— = 72	As = 75	Se = 78	Br = 80	
Железака железо	(Nb = 83)	Sr = 87	(Yt = 89?)	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 104, Ag = 108
Кобальтака кобальт	(Ag = 108)	Cd = 112	In = 113	Sb = 118	Sb = 122	Te = 128?	I = 127	
Никелека никель	Cs = 133	Ba = 137	— = 137	Co = 138?	—	—	—	
Медьнека медь	— = 74	—	—	—	—	—	—	
Цинкака цинк	— = 83	—	—	—	—	—	—	
Оловака олово	— = 94 (Au = 197)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	Os = 193?, Ir = 198? Pt = 197?, Au = 197
Ртутека ртуть	— = 104	—	—	Tb = 232	—	U = 240	—	
Барманека барман	R3O	R2O2 или R2O	R2O3 (R3H3?)	R2O4 или R2O3	R2O5 или R2O3	R2O6 или R2O3	R2O7 или R2O3	R2O8 или R2O3
Двадцать второй период элементы	—	—	—	RH4	RH3	RH2	RH	—

Figure 2. Short-form Periodic system from Mendeleev's November 1870 article.

Note: Mendeleev used the system shown in Figure 2 to calculate the properties of his three eka-elements, which are located in Groups III and IV. The "long periods" (represented here by the brackets at the left) have been collapsed into two individually numbered rows — after excluding the first two rows of "typical elements." Thus, an element in row 2 in the short-form is in the fourth period of the long-form system. The staggering of the elements within columns allows the

determination of secondary chemical analogies. The degrees of oxidation and hydrogenation are indicated at the bottom of the columns. [50]

After treating eka-boron in great detail, he made similar arguments for eka-aluminum ($E1 = 68$). This element was immediately above indium in the short-form table, and Mendeleev had recently successfully re-classified this element, which enabled him to give an extended account of its properties [51]. He devoted less space to it, however, than to eka-boron. Finally, Mendeleev considered the "most interesting" of his elements to be eka-silicon (or eka-silicium, $Es = 72$). Unlike the other two cases, Mendeleev actually suggested in which minerals chemists might begin to search for this new element [52]. He especially valued this element because it occupied the center of the short-form table: the fourth element in the fourth row. In that sense, it was the centerpiece of the whole system [53].

Yet, in both the Russian and the German articles, Mendeleev set off eka-boron from the other two elements, not eka-silicon. In a contemporary Russian review, this separation was seen as marking eka-boron as the most important eka-element [54]. Mendeleev was following the logic I traced in the last section, beginning with the most stable knowledge and then moving to less and less reliable claims. The prediction of eka-boron may not have been the best, since it only had four elements near it (K, Ca, Ti, and V) that could serve as analogs, but those analogs were extremely well studied. In the 1871 article, Mendeleev again would place eka-boron first, and spend the same amount of space on both it and eka-silicon, leaving eka-aluminum with only a third of the attention [55].

Even though Mendeleev clearly believed that his ability to make such claims transformed his system into a law of nature, he was well aware that chemists — with little experience of such laws — might dismiss the possibility of his new elements. After such a bold departure, he immediately retreated and expressed the vague hope that one of these three would eventually be discovered. And then he retreated yet again, saying that even if these predictions did not work at all, at least he had managed to correct several atomic weights and determine the properties of poorly studied elements [56]. The image of a sage utterly confident in his predictions, experiment and community consensus be damned, is belied by the text. He concluded his 1871 article:

Not getting carried away with the immediately apparent advantages of such a system, one will have to, however, recognize its justification finally, at least, when the properties derived on its foundation for the yet unknown elements are justified by the actual discovery of them, because, one must confess, up till now chemistry has had no means to predict the existence of new simple substances, and they were only discovered via direct observation. When the periodic dependence

of properties on atomic weight and atomological relation of elements will be able to be attributed to exact laws, then we will approach even more the comprehension of the very essence of the difference of elements among themselves and then, of course, chemistry will be already in a state to leave the hypothetical field of static concepts which dominate it now, and then the possibility will appear of delivering it to a dynamical direction, already so fruitfully employed in the study of the majority of physical phenomena. [57]

Even though Mendeleev's article appeared in German, his Periodic system received little attention aside from brief flutters of a priority dispute with John Newlands in England and Lothar Meyer in Germany [58]. After the predictions of both gallium (eka-aluminum) and scandium (eka-boron) were confirmed, however, it was translated into French, and then into English from this French version, making Mendeleev a household name in scientific Europe.

2.5 The Eka-Discoveries

The first of these elements to be found was the very one to which Mendeleev had paid the least attention in his predictions — eka-aluminum — discovered in France in 1875 as gallium by Paul Émile (François) Lecoq de Boisbaudran. Lecoq de Boisbaudran was trained as a physical chemist, and in the late 1860s he became one of the foremost practitioners of the relatively new technique of spectroscopy. Using this method he discovered not only gallium, but also samarium (1879), gadolinium (1886), dysprosium (1886), and europium (1892). His discovery of gallium — so named in a burst of patriotism after his native France (Gallia) — earned him the cross of the Legion of Honor in 1876. In 1879, the English awarded him the Davy Medal for his discovery, three years before Mendeleev and Lothar Meyer would share one for the Periodic system [59].

Lecoq de Boisbaudran made his discovery on Friday, 27 August 1875 (N.S.), between 3 and 4 in the afternoon, when he noted a distinctive spectral line in a metal from Pierrefitte, a mine in the Pyrenees. Over the course of the next year, he published a series of articles which explicated the various properties of this new element [60]. It is clear that Lecoq de Boisbaudran had no prior knowledge of Mendeleev's predictions of eka-aluminum, but that does not imply that he was also an empiricist blindly searching for new elements. Rather, he had some years earlier produced his own classification of the elements, based on spectral lines. Using those regularities, he made a prediction of the atomic weight of an analog of aluminum that was actually fairly close to Mendeleev's value (and closer to today's accepted value) [61].

Two features of the discovery of gallium make it distinctive among the eka-elements. It was the first, and the obvious similarity of this element with eka-aluminum drew substantial attention to Mendeleev's 1871 system. Second, this was the only case among the three where Mendeleev scoured the foreign literature for possible confirmations of his predictions, and made the connection himself. In the cases of eka-boron and eka-silicon, intermediaries stepped in, although they extended full credit to Mendeleev.

At the 6 (18) November 1875 meeting of the Russian Chemical Society, Mendeleev observed that the properties of gallium looked a great deal like eka-aluminum, and he hoped that this would be further confirmed [62]. The article that truly made Mendeleev's name was published in the French *Comptes Rendus*, the same journal where Lecoq de Boisbaudran had announced his findings. Mendeleev published a short-form Periodic system, which showed a space for "68?" in the center. He then recounted the cases in which he had corrected atomic weights and been confirmed before moving into a much more detailed account of his prediction of eka-aluminum than he had in either 1870 or 1871:

The properties of eka-aluminum, following the periodic law, should be the following. Its atomic weight will be $EI=68$; its oxide will have the formula EI^2O^3 , its salts will display the formula EIX^3 . Thus, for example, the (unique?) chloride of eka-aluminum will be $EICl^3$, it will give in analysis 39 out of 100 of metal and 61 of 100 of chlorine and will be more volatile than $ZnCl^2$. The sulfide EI_2S^3 , or oxy-sulfide $EI^2(S,O)^3$, should be precipitated by hydrogen sulfide and will be insoluble in ammonium sulfide. The metal will be obtained easily by reduction; its density will be 5.9; therefore, its atomic volume will be 11.5, it will be almost fixed, and will melt at a rather low temperature. On contact with air, it won't oxidize; heated to red, it will decompose water. The pure and molten metal will be attacked by acids and bases only slowly. The oxide EI^2O^3 will have specific weight around 5.5; it should be soluble in energetic acids, forming an amorphous hydrate insoluble in water, it will dissolve in acids and bases. The oxide of eka-aluminum will form neutral and basic salts $EI^2(OH,X)^6$, but not acidic salts; the alum $EIK(SO_4)^2 \cdot 12H^2O$ will be more soluble than the corresponding aluminum salt and less crystallizable. The basic properties of EI^2O^3 being more pronounced than those of Al^2O^3 and less than those of ZnO , one must expect that it will be precipitated by carbonate of barite. The volatility, as well as the other properties of saline combinations of eka-aluminum, present the average between those of aluminum and those of indium, it is probable that the metal in question will be discovered by spectral analysis, as were indium and thallium. [63]

Lecq de Boisbaudran had received a letter from Mendeleev almost immediately after publishing his first account of the discovery, and said he would not comment on Mendeleev's corrections of his data (specifically the density findings) until he did more work [64]. After further research, Lecq de Boisbaudran found that the density of the metal was 5.935, which was strikingly close to Mendeleev's predicted value of 5.9, but not at all close to the average of 4.8 of indium and aluminum, which once again shows how much chemical intuition was built into Mendeleev's predictions to correct the simple averages [65].

There was an understandable reluctance among contemporaries to accept the two other predictions on the basis of one, possibly lucky, guess. When the second eka-element was discovered in 1879, Mendeleev's case was much more than twice as strong; it seemed as if there were really some deep regularity reflected in his system. This element, scandium (eka-boron) was a rather complicated case, since it was more similar to the rare earths than either of Mendeleev's other two eka-elements, and these elements were very close to each other both in atomic weight and chemical properties, and thus proved hard to isolate. This is a large part of why Mendeleev chose to rely on calcium and titanium to make his predictions [66]. This element was discovered among various rare earths by L. F. Nilson of Sweden. In his original publication announcing this (once again) patriotically-named element, Nilson made no mention of the correspondence with Mendeleev's eka-boron; Mendeleev, for his part, could not read Swedish and make the connection himself [67]. It was Nilson's countryman, Per Cleve, who did so.

Cleve wrote to Mendeleev on 19 August 1879: "I have the honor to inform you that your element eka-boron has been isolated. It is scandium, discovered by Nilson this spring..." [68]. Much more important was his article to the *Comptes Rendus*, where he drew out the similarities in detail. After chronicling the properties of scandium (Sc), he wrote: "What makes the discovery of scandium interesting is that its existence had been announced in advance. In his article on the Periodic Law, Mr. Mendeleev predicted the existence of a metal with atomic weight 44. He called it *eka-boron*. The characteristics of eka-boron correspond rather well with those of scandium." Cleve then produced what would later become a famous double table:

<i>Supposed characteristics of eka-boron</i>	<i>Observed characteristics of scandium</i>
Atomic weight, 44	Atomic weight, 45

Eka-boron should have only one stable oxide, Eb^2O^3 , a base more energetic than that of aluminum, with which it should have several characteristics in common. It should be less basic than magnesium.

Just as yttrium must be a more energetic base, one can predict a great resemblance between yttrium and the oxide of eka-boron. If eka-boron is found mixed with yttrium, the separation should be difficult and based on delicate differences, for example, on differences of solubility, on differences in basic energy.

The oxide of eka-boron is insoluble in alkalis; it is doubtful that it will decompose ammoniac salt.

The salts should be colorless and give, with KOH , Na^4CO^3 [sic] and HNa^2SO^4 , etc., gelatinous precipitates.

With potassium sulfate, it should form a double salt, having the composition of alum, but barely isomorphic with that salt.

Only a small number of salts of eka-boron should crystallize well.

Water should decompose the anhydrous chloride of eka-boron with the liberation of HCl .

The oxide should be infusible, and it should, after calcination, dissolve in acids with some difficulty.

The density of the oxide is around 3.5. The density of the oxide is exactly 3.9. [69]

Such double tables would soon become standard presentations of the discovery. The correspondence is all the more remarkable in that it was impossible to confirm all Mendeleev's predictions until 1937, thirty years after his death, when scandium was finally isolated in pure form [70]. Nilson himself was delighted at the coincidence of properties, and believed that Cleve's observations, when combined with the case of gallium, had truly confirmed the Periodic Law:

As has already been remarked above, it is of rather special interest that from my identification the derived atomic weight of scandium gives exactly the same number as Mendeleev has conferred on the atom of his predicted basic substance *eka-boron*, that without a doubt is identical with scandium. Since now both the atomic weight and the properties of the element *eka-*

Scandium oxide is less basic than yttrium, and their separation is based on the differing stability of their nitrates under heat.

The hydrate of scandium is insoluble in alkalis; it does not decompose ammoniac salt.

The salts of scandium are colorless and give, with KOH , Na^2CO^3 and HNa^2SO^4 , etc., gelatinous precipitates.

The double sulfate of scandium and of ammonium is anhydrous, but it has the composition of alum.

The sulfate of scandium does not give distinct crystals, nor does its nitrate, its acetate, and its formiate.

The crystallized chloride decomposes and liberates HCl when heated.

The calcinated oxide is an infusible powder which dissolves with difficulty in acids.

aluminum, also incidentally predicted by Mendeleev, coincide with those of the gallium discovered by Lecoq de Boisbaudran, so the speculations of the Russian chemist — which not only predicted the existence of the named substances but was also able to give the essential properties of them in advance — are thus confirmed in the most evident manner. [71]

Yet, Mendeleev's "most interesting" element, eka-silicon, the core of the Periodic system, remained elusive. It is ironic that this was the last of Mendeleev's three eka-elements to be discovered, since Mendeleev had believed it would be discovered first. It would eventually become the most persuasive example of the power of Mendeleev's predictions; in his most extensive obituary, the comparison of eka-silicon and germanium was the only one discussed in detail, presented again in a Cleve-style dual table [72]. The process of the discovery of germanium was very similar to that of scandium.

On 6 February 1886 (N.S.), German chemist Clemens Winkler announced his discovery of a new non-metallic element in a mineral that had been found in the summer of 1885 near his Mining Academy in Freiberg, and — in a somewhat curious pattern — named this element after his native country [73]. (None of the three chemists knew of the connection with the other two elements when they discovered their own, which makes this coincidence entirely fortuitous.) On 25 February 1886 (N.S.), V. F. Richter, who had once been the Petersburg correspondent of the German Chemical Society (and had reported on the first announcements of Mendeleev's Periodic system in 1869), wrote to Winkler of the correspondence with Mendeleev's prediction:

Germanium, which name you should preserve since you are factually its father, is the element eka-silicon, Es-73, predicted by Mendeleev, the lowest homolog of tin, standing in the first large period between Ga (69.8) and As (79.9)... Eka-silicon is the element which we have awaited with great anticipation, and in any case the immediate study of germanium will be the most definitive *experimentum crucis* for the periodic system. [74]

Winkler was immediately enthusiastic about the connection. In a telling comment that would reinforce Mendeleev's own views about the physics-like predictive powers of his law, Winkler suggested renaming the element neptunium, because like the planet Neptune it was discovered by a prediction from interpolation. Much as Newton's laws were famously confirmed by the independent ascertainment of perturbations in the orbit of Uranus to a hypothesized Neptune by John Couch Adams of England (1843) and Urbain-Jean-Joseph Le Verrier of France (1846), Mendeleev would later draw on this physical analogy and the power of prediction to defend his Periodic Law. (Today's neptunium follows a different astronomical

analogy.) Winkler retreated from the analogy and resolved instead to retain the name of his country, which — while it drew attacks as overly nationalistic from some French chemists — received only approval from Mendeleev [75].

Eka-silicon was the only eka-element that Mendeleev seriously undertook to investigate in the laboratory. Even before finishing his theoretical work on the Periodic Law, he outlined a research program directed towards finding this element [76]. In the middle of 1871, Mendeleev wrote to his Heidelberg friend, chemist Emil Erlenmeyer: "My plan is long-term, but I am not afraid of length. I want first to go through every point with the rare elements, during which I will try to find affirmation of those changes in atomic weights which I proposed first for Ce, La, Di, then for Yt, Er. Then I will turn to Ti, Zr, Nb and Ta to study them and when I am the master of these chemical rarities I will try, studying the appropriate instances, to find among them one of my predicted eka-elements." [77]. On 5 December 1870, he asked Karl F. Kessler, rector of St. Petersburg University, to obtain specific minerals from the Mining Institute (a few blocks away from the University): "Wanting to verify even a part of the conclusions I expressed with respect to this [periodic dependence], I am obliged to occupy myself with research of certain rare minerals, which I thus request you to turn to the Mining Institute and ask from them certain minerals, which they have in their reserves designated for scientific work." Mendeleev made a similar request to the Russian Technical Society, and received his supplies. He even refused a post at Moscow University on the grounds that he did not want to give up his current research on the rare earths [78]. Nevertheless, this particular effort was soon abandoned, as Mendeleev turned again to the Technical Society to begin a much more ambitious project aimed at deeper laws of nature: the gas laws, which he investigated from 1871 to 1881. He would not return again to active research on the Periodic Law.

3. RUSSIAN NEWTON: MENDELEEV THE LAWGIVER

The view of the Periodic system as the pinnacle of Mendeleev's career — eventually encouraged by the chemist himself — was a retrospective construction. Mendeleev was not concerned in 1869 with establishing a basic law of chemistry. He was concerned with writing a textbook for young chemists at St. Petersburg University. These very local concerns are exactly what become obscured when one detaches the man from his context. From 1871 on, Mendeleev himself would delineate periodicity and repeatedly reinterpret the Periodic Law as an emblem of proper science and himself as the linchpin of a modernizing Russia.

Mendeleev's Periodic system had tremendous success both at home and abroad, especially after the discoveries of the eka-elements. So much so, in fact, that Mendeleev would occasionally grumble when feted by his peers and the public: "Genius, genius, genius. I work hard, I worked hard all my life, and they say:

genius, genius." [79]. The complaint was somewhat disingenuous, since no one had done more than Mendeleev to endow him with this label. Yes, he had worked hard, but he also devoted part of that hard work to building the reputation of a genius. As he aged, Mendeleev began to adapt his image as radical maverick into an interpretation of himself as a successor to Newton. Mendeleev did not reformulate himself, notice, as a seminal figure in *chemistry*; his aims were grander.

At the basis of this transformation lay the Periodic Law. By 1871, Mendeleev was convinced that the Periodic Law was indeed a *law*; the difficulty now was to develop a sense of what laws *meant* in the natural sciences. When the stakes were raised, he turned to an obvious exemplar: Newton's three laws of motion and his law of gravitation, which had enabled physicists for a century and a half to describe the motion of heavenly bodies with astonishing accuracy. They also allowed scientists to predict (and eventually discover) new planets from aberrations in orbital motion. The Newtonian model became increasingly important over the course of Mendeleev's career. As the discovery of his eka-elements affirmed his confidence (and the confidence of other chemists) in the Periodic Law, Mendeleev began to elevate the Periodic Law from an "ordinary" law of nature — such as the gas laws — to a fundamental law like Newton's. One of the clearest ways to observe this shift is to follow the eight editions of the *Principles of Chemistry*. Mendeleev heavily revised each edition following the first (1869–1871), often by adding lengthy discursive footnotes. These notes, Mendeleev's signature feature, often elicited comments from reviewers: "The work as a whole appears as a highly idiosyncratic effort. Philosophical postulations, excursions in the areas of astronomy, physics, mineralogy, geology, technology are present in so rich a quantity that one often forgets, for example just reading the footnotes, that a textbook in *chemistry* lies before you." [80]. These revisions, akin to geologic strata, record Mendeleev's own changing understanding of the power of laws.

While each edition was indeed revised, not all revisions were equal. Mendeleev altered the second edition (1873) remarkably little. In the third edition (1877), however, he approached the Periodic system quite differently. Just the year before, Lecocq de Boisbaudran had discovered gallium. Mendeleev promptly revised his original plan for the *Principles*: "Having become convinced in the truthfulness of the basic principle, I am bringing it into this edition more strictly than it was in the two preceding." [81]. The fourth edition (1881) was little changed, and appeared when it did largely to finance Mendeleev's divorce [82]. The most substantial revision of the *Principles* came with the fifth edition (1889) — also the most widely translated — with heavy attention to Winkler's discovery of germanium (eka-silicon). Mendeleev also reduced the dimensions of the book and moved the small type intended for specialists into massive footnotes.

The central change in the fifth edition was not Mendeleev's views of the power of periodicity, but his conception of the properties of a *law*. Earlier, he had treated

laws as *explainable* regularities; now laws were understood as *invariant* regularities: "The laws of nature do not tolerate exceptions, and this differentiates them from rules and regularities, such as, for example, grammatical ones." [83]. He now emphasized mass as the source of periodicity, even if he had no explanation of how mass accomplished this. He reiterated this view of mass in the relatively unchanged sixth edition (1895) by analogy with Newton's law of gravity. After all, no one knew how that worked either, yet it *invariably* showed force's relation to *mass* and enabled predictions. This insistence on invariance underlay Mendeleev's continuing discomfort with the inversion of tellurium and iodine in the Periodic system: iodine weighed less than tellurium but followed it in the Periodic system. To the end of his life, Mendeleev insisted that one or the other of these atomic weights was incorrectly determined, and they appeared with question marks in every edition of the *Principles*.

It is important not to overemphasize the philosophical coherence of Mendeleev's views. For example, the American magazine *The Nation* found his notion of law particularly confusing in the third English edition (based on the seventh Russian edition):

[The book] is also valuable as expressing with unusual openness all the processes of thought of one of the greatest scientific reasoners that ever lived. It cannot, however, be called a model of judicious and calm logic. Whatever proposition Mendeleff inclines to, which must be something illuminating his most famous discovery, will be for him "a logical development"; while anything else will be a "hypothesis," regardless of its logical genesis.... On many points he is skeptical about the doctrines of the new chemistry, and sometimes his objections have no little force, but they are always exaggerated. [84]

In the seventh edition (1903), Mendeleev began not just to modify the importance of periodicity, but even to alter the history of the discovery itself. He declared that the Periodic Law had "appeared to me in its entirety exactly in 1869, when I wrote this work," a conscious falsehood [85]. The eighth edition of the *Principles* (1906) in turn stressed Mendeleev's *historical* position by emphasizing the precursors to the law and its "strengtheners" (*utvpechitel*) who had discovered the predicted elements [86].

The problem with Mendeleev's formulation of the power of laws was that periodicity did not meet it. The model for "lawlike" regularity became stronger over time, and was expressed in 1901 in strictly mathematical terms: "Now, a law always expresses a relation between variables, such as fixing their functional dependence in algebra." The real triumph would have been to deduce a mathematical representation that would replicate the core regularities of the

Periodic Law. Mendeleev spent several years on such a rendition before ruling it impossible [87]. Not meeting his own standards apparently bothered Mendeleev rather little; instead, he dwelled on the rhetoric of mathematical dependence and retreated to his general interest in invariance and generality. By 1905 he maintained that the Periodic Law was lawlike not by its invariance or generality or mathematizability or explanatory power, but by its endurance: "Apparently the Periodic Law will not be threatened with destruction in the future, but only promises refining and development.... I was lucky here, especially with the prediction of the properties of gallium and germanium." [88].

The emphasis on invariance and regularity in the power of laws elides an important transformation in the way Mendeleev understood the development of science. During his gas work of the 1870s, he explicitly opposed theory as the motive force of scientific change. The Periodic Law in its original formulation represented a generalization and explanation of available evidence about the elements; its power of prediction came later, both historically and conceptually. The collapse of the gas project and the unparalleled success of his Periodic Law, however, shifted Mendeleev's interest towards theory as *primary*.

For this, Mendeleev needed a historical model; he found him in Sir Isaac Newton. The fascination with Newton was not new. In the late 1850s, Mendeleev often taught his mentor Voskresenskii's course on the history of chemistry at St. Petersburg University. In his lecture notes on the biographies of major chemists, Newton merited eight pages, more than any chemist, including Lavoisier. He also opposed the nascent structure theory of organic molecules and its subsidiary concept, valency, on the grounds that a tetrahedral carbon tetrafluoride atom violated Newton's third law of motion [89]. Yet so far Newton had interested him not as a *personal* model, but as a man who gave science certain theories useful in accounting for data. Mendeleev would recast his relative position vis-à-vis Newton after the discovery of the eka-elements.

He would articulate his Newtonian ambitions in two lectures in England in 1889. The first, "An Attempt to Apply to Chemistry one of Newton's Laws of Natural Philosophy," delivered before the Royal Institution on 31 May 1889 (N.S.), directly attempted to connect his work with that of the former President of the Royal Society, opposing the almost universally-accepted structure theory with Newtonian dynamics [90]. Much as in his aeronautical work of the late 1870s, Mendeleev cast himself as the interpreter of Newton's intentions in the *Principia*. In fact, there was scarcely anyone better qualified than a chemist to safeguard Newton's legacy, since "it is necessary to note that Newton studied chemical experiments for a long time, and, in explaining the questions of celestial mechanics, constantly had in mind the mutual interaction of the worlds of the infinitely small which appear in chemical evolutions." [91]. If Newton based his astronomy on chemical models — and not chemistry on astronomical models — then only a chemist with access to fundamental laws (i.e., Mendeleev) would be a suitable interpreter. All theories of chemical dynamics had to be mediated not by physicists, but by a general chemist who followed the master's model:

A coming Newton will find the laws of such changes... The achievement of the laws of this harmony in chemical evolutions seems to me possible only under the banner of Newton's dynamics, which for a long time has been fluttering over the domains of mechanics, astronomy, and physics. Calling chemists to this peaceful and universal banner, I think that I am strongly serving scientific unification, by which I explain the great honor, shown to me by the much respected representatives of the Royal Institution, which gave me — a Russian — the possibility to express before Newton's countrymen an attempt at bringing into chemistry one of his immortal principles. [92]

Thus it was the British scientific community that had cast him in the Newtonian role by inviting him to speak. As to who the future Newton might be, Mendeleev feigned no hypotheses.

He treated these themes more abstractly in his Faraday lecture, "The Periodic Law of Chemical Elements," read before the same audience on 4 June 1889 (N.S.). Here Mendeleev did not lecture directly on Newton's laws, but on the nature of his own achievement. He chose to emphasize two aspects of chemistry: the communal effort of chemists to establish frameworks for knowledge, and the necessity of adhering to laws to avoid speculation. Both, he implied, were ideals Newton would support. (The historical Newton's distaste for communal work seems to have been unknown to Mendeleev.) Mendeleev's ideal of cooperation was the Karlsruhe Congress of 1860. In this fashion, Mendeleev could lionize the entire community for their contribution to his own individual success. By trusting to a morally ordered framework, Mendeleev could obtain a place in posterity akin to Newton's:

Arising from the virgin soil of newly established facts, knowledge relating to the elements, their masses, and the periodic changes of their properties, has motivated the formation of utopian hypotheses, probably because [the Periodic system] could not be foreseen by the aid of any of the various metaphysical systems, but exist[s], like the law of gravitation, as an independent outcome of natural science, requiring the acknowledgement of general laws, which have been established with the same degree of persistency as is indispensable for the acceptance of a thoroughly established fact... It is only by collecting established laws, that is by working at the acquirement of truth, that we can hope gradually to lift the veil which conceals from us the causes of the mysteries of Nature and to discover their mutual dependency. [93]

Mendeleev also admired Newton as Master of the Mint, safeguarding the integrity of English currency against counterfeiters and fraud. Mendeleev could envision his own position as Director of the Chief Bureau of Weights and Measures in a similar standardizing light. Metrology — the science of weights and measures

— also had implications for Newton's gravity. Mendeleev began a research program at the Chief Bureau to measure precisely the strength of gravity in St. Petersburg. He had already approached this problem briefly while organizing his earlier gas research, marking in his private notebook the local acceleration due to gravity (g) in Paris and St. Petersburg in order to recalibrate Victor Regnault's pressure results to his Russian lab [94]. In the late 1890s, however, Mendeleev began a full-scale program using pendulums to measure the precise local g . He also returned to his efforts to measure disparate g values, sending his associate F. I. Blunbach to Sévres, Budapest, and other European cities. Blunbach eventually calculated g in St. Petersburg at 9.8193 m/sec^2 [95]. In the publications on this topic in the journal of the Chief Bureau, Mendeleev cited Newton (and, to a lesser extent, Galileo) as a source of inspiration for placing *exact measurements of mass* at the center of the physical sciences [96].

I emphasize the importance of the physical sciences, as opposed to merely chemistry. In his later years, Mendeleev consistently turned to Newton as his own historical forerunner rather than a more chemical precursor, such as Antoine Lavoisier (1743–1794). Lavoisier actually seems almost an overdetermined choice for self-modeling. And, yet, Mendeleev made very few references to Lavoisier as a model. Instead of selecting a model that would place his Periodic Law and himself squarely in the chemical tradition, he opted for Newton, a man with interests in optics, alchemy, mechanics, mathematics, theology, historical chronology, and monetary reform — none of which were Mendeleev's strong suits. Why did Mendeleev insist on Newton? First, although Lavoisier's importance in the history of science cannot be disputed, much of that reputation was solidified in the centenary commemoration (in the 1890s) of his execution by the Jacobins, while Newton had been a representative genius since the days of Voltaire [97]. Second, much of Newton's fame stemmed from his creation of laws that could make predictions (Halley's comet, Uranus, Neptune). Lavoisier predicted only the results of specific experiments, not the structure of the universe. Mendeleev's own international reputation was heavily based on his prediction of the three ekallements, making the analogy with Newton even more appealing. I believe we should take the Newton exemplar seriously. Interpolating similarities with Lavoisier places Mendeleev at the center of the history of chemistry, a science Mendeleev considered too narrow to define him entirely.

4. THE DEATH OF MENDELEEV'S LAW

4.1 Chemistry under Attack: Disintegration in Fin-de-Siècle Chemistry

At the end of the nineteenth century, Mendeleev's ontological understanding of the natural world was in peril. While his views on chemical and physical laws had undergone occasional revision by the 1890s, his beliefs as to what matter was and

how it interacted were fairly set. This understanding was heavily conditioned by the Periodic Law itself. Matter, according to Mendeleev, had three essential properties: it was "atomic" (each atom was integral); it was immutable (each specific element had fixed mass and could not "become" any other element); and each element possessed a specified valency. Thus, each element in the system was placed as an *atomic individual* (in the literal sense of being "without divisions"), according to its *mass*, in a periodic relation marked by a recurrence of *valency*. Mendeleev considered these three properties of integrality, immutability, and valency to be of a piece, and I have disaggregated them here only for analytic clarity. They were simply what it meant to be a "chemical element."

Beginning in 1894, a new phenomenon had emerged to assault directly each of these qualities of matter, and these assaults threatened both the borders of chemical knowledge and the stability of the entire discipline. Mendeleev had to preserve the integrity of the chemical worldview to which his Periodic system had contributed so substantially, and he did so by endorsing the first and using it to explain away the others. The three phenomena were the discovery of noble gases, the advent of radioactivity, and the discovery of the electron and its relation to Prout's hypothesis. The integrity of Mendeleev's chemical vision was at stake in each.

Mendeleev, who had earned international fame by predicting the properties of empty spaces in his Periodic system, was taken by surprise in 1894 by William Ramsay's announcement of a new chemical element, tentatively dubbed argon — the inert one. Ramsay had been in correspondence with Mendeleev for some years concerning the latter's moribund gas expansion research. On a recent trip to England connected with his gunpowder work, Mendeleev had given Ramsay a copy of *On the Expansion of Gases*, but the latter was unable to read Russian, and he wrote Mendeleev (in French) in January 1892 to see if there were any translations or summaries of the text in Western journals, or, if not, whether the Russian could send him the chief results [98]. Mendeleev responded to Ramsay's request by sending another copy of the text and some brochures, to which Ramsay responded with gratitude and a repetition of his inability to read Russian, "but I see in the text some figures which guide me, and I will do my best to understand your beautiful work. I was quite surprised to see the immensity of your work..." [99].

Ramsay was after fundamental prey, conducting pneumatic experiments with Lord Rayleigh to review Victor Regnault's gas work. He wrote Mendeleev another sympathetic letter saying that he had met similar difficulties as Mendeleev had [100]. However, late in 1893, one of Ramsay's students discovered a problem with Mendeleev's measurement of volumes by displacement of mercury, and Ramsay tactfully pointed out that a small factor needed to be added. Afraid of angering his colleague, and perhaps aware that he had exposed a sensitive nerve, he continued: "Perhaps I am wrong, and in that case I apologize. But instead of publishing my criticisms which may very well be wrong, I turn to you in hope that you can correct

me if I have not followed your explanations due to my ignorance of your language.” [101]. Mendeleev’s error turned out to be Ramsay’s gain, for it was in the correct measurement of the volume displacement that he was able to postulate in 1894 a new constituent of the atmosphere to make up the shortfall exactly. This was to become argon.

Mendeleev’s reaction to argon was famously mixed. While he had greeted the validating discoveries of gallium, scandium, and germanium with pleasure, argon was the first announced element that he had no empty space for in the Periodic system. It had a measured atomic weight of 40, which would place it between chlorine and potassium (where there was no empty space), and it seemed to be completely unable to bond with other elements (inconceivable for an element, which by Mendeleev’s definition must display some valency). He immediately telegraphed Ramsay (in French): “Delighted at the discovery of argon. Think molecules contain three nitrogen bound together by heat.” [102]. Mendeleev here resisted novel discoveries in chemistry that could be interpreted as violating his Periodic Law. The threat was not just in Mendeleev’s head. After reviewing the properties of the inert gases discovered soon after argon, an American chemist remarked: “The appearance of so many new elements at one time will no doubt prove embarrassing with the present arrangement of the Periodic System, and attempts will probably be made to rearrange the system to conform to these new discoveries.” [103]. The strategy favored by Mendeleev was to deny argon elemental status. In Chapter 5 of the sixth edition of the *Principles of Chemistry* (1895), Mendeleev included a supplement on argon, “the new component part of air,” where he claimed that it was too soon to consider argon an element. It was more likely a compound or simple body, either of which would explain why it did not react with any other elements. Given that its “molecular” weight was roughly forty, Mendeleev suggested that, in analog to ozone (O_3), argon could be N_3 . James Dewar of England had proposed this solution even earlier, explicitly in order to save the Periodic Law [104].

Mendeleev soon changed his tune. In 1903, he considered Ramsay’s findings “some of the most brilliant experimental discoveries of the end of the 19th century,” and admitted that his early hypothesis of triatomic nitrogen was incorrect. What changed his mind? Mendeleev cited five pieces of evidence that swayed him: the finding that argon’s density was just barely greater than 19, while N_3 would have been around 21; Ramsay’s discovery of helium in 1895, which also displayed chemical inertness; the later discoveries of the other inert gases neon and krypton; the uniqueness of their spectra; and Ramsay’s proof of the constancy of chemical features when correlated with density [105]. Mendeleev now became a proud partisan of the idea that the inert gases should be considered a zero-valency 0-Group, to be placed on the far left of a Periodic system (and not the far right, as in modern representations). (See Figure 3.) This way, he argued, the system would be organized from least reactive (the inert gases) to most reactive (the halogens)

[106]. By the seventh edition of the *Principles* (1903), Mendeleev had fully endorsed the “argon Group” and considered Ramsay an affirmer (*ukrepitel’*) of the Periodic Law. He had abandoned one of his essential views of matter: valency.

Argon was something of a sideshow compared to radioactivity, which was perhaps the most controversial topic in the physical sciences at the turn of the century, eliciting claims of the disintegration of the elements, spiritual forces, revolutions in medicine, and the reemergence of the alchemists’ dream of transmuting elements. In 1896, in an effort to demonstrate that the phenomena of X-rays (discovered by Wilhelm Conrad Röntgen the year before) were related to fluorescence, French physicist Henri Becquerel undertook a series of experiments on uranium. By accident, he discovered that uranium would cloud photographic plates; a series of further experiments led him to conclude that uranium spontaneously emitted energy. In 1898, Pierre and Marie Curie, in their Paris laboratory, discovered the new elements polonium and radium, which emitted energy of extreme intensity — dubbed “radioactivity” by Marie. Radioactivity fast became one of the most vigorous fields of research in the physical sciences. Research along these lines in Russia proceeded apace [107].

Mendeleev had even begun a research program at the Chief Bureau of Weights and Measures to investigate radioactivity, part of his efforts to meld practical standardization with original scientific research. In 1903–1904, he directed one of his assistants, M. V. Ivanov, to perform experiments on the “strength” of radioactivity using what was essentially a large capacitor. A radioactive sample was placed in between two plates, and then the voltage drop caused by the radioactive emissions was measured across a wide variety of temperature and pressure conditions. Mendeleev’s commentary on the draft results indicated detailed knowledge of the Western literature on radioactivity [108]. Organizing such work was difficult, as samples of radium were hard to find in Russia. Mendeleev had to solicit a personal connection in Berlin, W. F. Giesel, for samples of radium from Braunschweig. Giesel responded promptly with a milligram of radium bromide (and apologies that he was unable to send pure radium). While Mendeleev sent the request for this radioactivity exchange under the letterhead of the Chief Bureau of Weights and Measures as an official letter, he kept Giesel’s response in his personal papers. This was not an idle mis-filing, but a characteristic slippage between the standardization work, Mendeleev’s chemical worldview, and his network of personal connections [109].

Mendeleev’s most salient exposure to radioactivity, and the genesis of most of his hostile views of the phenomenon, was his visit to the Curies’ laboratory in Paris in 1902. Mendeleev included an extended footnote on uranium’s supposed radioactivity in the seventh edition of the *Principles* (1903), arguing that one should not attribute radioactivity as a property of an element, but rather as a phenomenon that occurred to the element, like magnetism [110]. In accordance with his

conservative orientation, Mendeleev preferred innovation when it was built on long-standing tradition, such as the Periodic system. He remarked to a friend: "Tell me, please, are there are a lot of radium salts in the whole earth? A couple of grams! And on such shaky foundations they want to destroy all our usual conceptions of the nature of substance!" [111]. One of the conceptions that would be destabilized was the immutability of the elements, his conviction that elements could not "transmute" into each other — a modern alchemy.

For Mendeleev, mass was not merely a secondary characteristic of an element's properties as, say, its crystalline structure; it constituted the identity of an atom. It was how one knew an oxygen atom to be different from a cobalt atom. Mass was our most fundamental discriminator. This view stands in sharp contrast to today's understanding of matter, where each atom is composed of a definite number of protons, neutrons, and electrons, and any given proton in a cobalt atom is identical to any in an oxygen atom. In other words, Mendeleev firmly rejected any notion that atoms were *composite*, constructed out of a "primary matter." His view was not rare for nineteenth-century chemists, many of whom were united in opposition to the hypothesis of British chemist William Prout (1785–1850).

"Prout's hypothesis" was actually two different hypotheses. In 1815–1816, Prout had proposed, first, that all atomic weights were integral numbers of hydrogen's and, second, that all elements were composed of some form of primary matter — often dubbed a "protyle" — and that this primary matter was hydrogen. So, for example, the fact that a volume of oxygen weighed sixteen times that of hydrogen, carbon twelve times, and sulfur thirty-two times was explained by an atom of sulfur really being just thirty-two individual hydrogen atoms glommed together, and so on [112]. When Jean Servais Stas definitively measured several atomic weights in the early 1860s to be non-integral multiples of hydrogen, especially that of chlorine (35.5), chemists widely discarded Prout's first hypothesis. Many still saved the second by shrinking the postulated protyle, believing elements to be composed of yet smaller particles than hydrogen [113].

Mendeleev consistently opposed Prout's hypothesis as antithetical to both laboratory evidence and the metaphysics of chemistry. In 1886, after his three predicted elements had been discovered and several chemists proposed Prout's hypothesis as an excellent metaphysical explanation for why the Periodic Law worked, Mendeleev was careful to state that "now, as upon establishment of the Periodic Law, [I] sooner tend to see in it the induction of the recognition of an independent autonomy (individuality, heterogeneity) of elements, under the sovereignty of a general law..." [114]. Mendeleev attributed the recurrent interest in Prout's hypothesis, despite contrary experimental evidence, to chemists' desire to clarify the "munky" concept of mass with a "quantity of matter." In the seventh edition of his *Principles* (1903), he bluntly asserted that all speculations on primary matter "relate to the area of fantasy and not science, and I don't recommend to

persons beginning to study chemistry (for whom this book is written) to fall into this area." [115].

The rise of domestic advocates of Prout was only one reason why Mendeleev became yet more impassioned about immutability in the late 1890s. Comparing "chemical individuals" — modern atoms — with Democritean atoms, Mendeleev clarified the implications of his view:

Proofs of this latter [distinction] are many, but it is enough to point out that contemporary atoms have often been explained by vortex rings, that even now there is a lively effort to understand the formation of chemical atoms from each other, or from a "primary matter" and that just most recently, especially in connection with radioactive substances, some have begun to recognize the splitting of chemical atoms into smaller "electrons," and this logically wouldn't be possible if atoms were recognized as mechanically indivisible. The chemical worldview can be expressed in an exemplary fashion, comparing the atoms of the chemists with heavenly bodies: stars, the sun, planets, satellites, comets, etc. Just as from these separate entities (individuals) systems are formed like the solar system or binary star systems, or certain nebulae, etc., so one can conceive the formation of entire molecules from atoms, and of bodies and substances from molecules. [116]

Atoms were no more reducible to one primary matter than Jupiter and Venus were made of a certain number of "moon units." Mendeleev's worries about Prout's hypothesis became more acute with the discovery of the electron in 1897 by J. J. Thomson. A few even proclaimed it a new element, including Ramsay [117]. Mendeleev was not among the electron's enthusiasts; he considered it most likely an epiphenomenon of atomic interactions. He came from a chemical tradition starting from Newton, and moving through John Dalton, Jean-Baptiste Dumas, and Charles Gerhardt, all of whom emphasized integral treatments of molecules and were hostile to the electrochemical explanations of the rival tradition of Newton-Humphry Davy-Jacob Berzelius-Michael Faraday. His opposition to this supposed *element* of chemical charge is thus easier to understand.

Mendeleev could not let such transgressions against his fundamental conception of matter and, even more importantly, his Periodic Law, pass unanswered. Interpreting the situation in fin-de-siècle physical sciences as chemistry under attack by superstition and sloppy reasoning, and exasperated by people letting their irrational preferences dissuade them from proper scientific method, Mendeleev undertook a chemical interpretation of the ether that would harness the inert gases to stave off the dangers of radioactivity and Prout.

4.2 The Chemical Ether

In the seventh edition of his *Principles of Chemistry* (1903), Mendeleev reflected on the set of difficulties confronting contemporary physics and chemistry:

The root of the inadequacies of contemporary atomism, in my opinion, should be sought in the lack of clarity of the understanding of the "ether," which fills both interplanetary and interatomic space, and I propose that contemporary natural science, directed primarily to the study of the phenomena which take place in the "ether" (optical, electric, etc.), go by the natural and true path to exposing the secrets of nature. Contemporary natural science strives, but still does not know how, to come to terms with a material, but not ponderable, chemically active... ether with the necessary clarity. This is one of the tasks the 19th century dedicates to science. [118]

This was not an idiosyncratic belief. Physical scientists at the turn of the century still considered the ether an absolute necessity for the explanation of not just light undulations, but also Newton's gravity. As a result, a panoply of models continued to proliferate, even after Albert Einstein's 1905 Special Theory of Relativity had supposedly banished the ether as "superfluous." Mendeleev, for example, proposed a model of the chemical ether in 1903. Scientifically, the work reflected his almost complete obliviousness to the extensive mathematical and physical requirements of the ether developed in the West, especially in England. But mathematics was not important for Mendeleev here; he was not after equations and structure, he was after substance.

Mendeleev had long considered the ether an essential component of the physico-chemical universe, but ether began to take on new functions as he transitioned from teaching to his later bureaucratic career after 1890. The ether, "originally proposed exclusively to explain optical phenomena," could be expanded to include other forces, such as gravity [119]. Mendeleev sought a unification in the ether that was distinct from disintegration and reckless homogenization. The ether was not meant to be a substrate that *composed* everything, à la Prout; it was rather a *medium* to reconcile the interactions of nature.

In 1901, Mendeleev was approached by the editors of a new journal, the *Herald and Library of Self-Education*, to write an article on the state of contemporary science for the first issue. The publishers of this periodical were Brockhaus and Efton, who were simultaneously publishing the monumental encyclopedia for which Mendeleev edited the articles on technology and industry. This new magazine was the perfect venue to work out his ether views, since "the subject touched on many areas of the natural sciences, and seemed to me amenable

for popularization." [120]. The piece fared surprisingly well, published in four installments in the *Herald and Library* and then as an independent pamphlet. Mendeleev distributed complimentary copies widely to various scientists. It was also repeatedly translated. Mendeleev preferred the German translation over the English, which lacked his precious philosophical opening, and he fretted that "such an omission removes from the entire article the real significance which I wanted to give it in trying to introduce the ether into the system of elements." [121]. He was especially amused by the work's translation into Esperanto for the journal *Internacia Sciencia Revuo*, which his correspondent claimed would give Mendeleev a wider audience: "[W]ith the help of Esperanto, all will be clear to everyone as a clear day." [122].

The pamphlet, much like Esperanto, was intended to unify different communities. The essence of the ether project was to locate the ether in the Periodic system of elements and then use interpolation techniques to predict its necessary properties — just like the prediction of the three eka-elements in 1871. He began his quest for the ether with the issue of weight. Typical descriptions of the ether in Mendeleev's time described it as "imponderable," as having no weight. For Mendeleev the idea of a substance without weight was ridiculous. The only way we could know matter was through its set of measurable properties. So if the ether were to exist for Mendeleev, not only must it have some mass (for it must be made of something), but it had to be a definite quantity (assuming it was a pure simple substance) and could thus be located in the Periodic system. The reason the ether *seemed* to have no weight was that all substances were permeated by this ether. Just as one could not weigh air before the advent of air pumps, he argued, the ether's weight could not be determined without some kind of fictive ether pump [123].

Mendeleev conceived of the ether as a gas — specifically, a noble gas. This confounded his earlier understanding of the ether as a combination of rarefied gases. In the 1903 pamphlet, he reflected on his gas work of the 1870s:

Already then the question importunately settled upon me: what kind of thing is this ether in a chemical sense? That it is closely connected with the Periodic Table of elements occurred to me even then, but only now did I resolve to talk about it. At first I supposed that the ether is the sum of rarefied gases in a limiting state. I conducted experiments to get at an answer. But I was silent because I was not satisfied with what appeared at first glance. Now my answer is different, but it still doesn't completely satisfy me. And I would still remain guardedly silent, but I no longer have years before me for thinking and experimental trials, and thus decided to set forth the subject in its immature form, presuming that to keep silent is also not right. [124]

Such a rarefied-gas view was no longer possible because it denied the fundamental need for *homogeneity* in the ether: "Thus — and this is the most important thing — [rarefied gases], by their chemical nature and by their relations to other substances, are infinitely heterogeneous, and ether is homogeneous everywhere, as far as we know." [125]. The position here is subtle but not unstable: the ontology of the world was fundamentally heterogeneous, whether into the broad categories of matter, force, and spirit, or within matter into the non-transmutable elements; yet properties ascribed to a particular body, like the ether, had to belong to a single, homogeneous body. Heterogeneity, after all, is merely a collection of individualized homogeneities.

Order	Group	Element	Symbol	Atomic Weight
0	Zero Group			
1	Group I	Hydrogen	H	1.008
2	Group I	Lithium	Li	7.08
3	Group I	Potassium	K	39.1
4	Group I	Caesium	Cs	132.9
5	Group I	Rubidium	Rb	85.4
6	Group I	Silver	Ag	107.9
7	Group I	Gold	Au	197.9
8	Group II	Beryllium	Be	9.01
9	Group II	Magnesium	Mg	24.3
10	Group II	Zinc	Zn	65.4
11	Group II	Cadmium	Cd	112.4
12	Group II	Mercury	Hg	200.0
13	Group II	Barium	Ba	137.4
14	Group III	Boron	B	11.0
15	Group III	Aluminum	Al	27.0
16	Group III	Gallium	Ga	69.4
17	Group III	Indium	In	114.0
18	Group III	Thallium	Tl	204.0
19	Group III	Lead	Pb	207.2
20	Group III	Thoron	Th	232.0
21	Group IV	Carbon	C	12.0
22	Group IV	Silicon	Si	28.1
23	Group IV	Germanium	Ge	72.6
24	Group IV	Stannum	Sn	118.7
25	Group IV	Plumbum	Pb	207.2
26	Group V	Nitrogen	N	14.0
27	Group V	Phosphorus	P	31.0
28	Group V	Vanadium	V	51.4
29	Group V	Antimony	Sb	121.8
30	Group V	Bismuth	Bi	208.0
31	Group VI	Oxygen	O	16.0
32	Group VI	Sulfur	S	32.1
33	Group VI	Chromium	Cr	52.0
34	Group VI	Manganese	Mn	54.9
35	Group VI	Rhodium	Rh	103.7
36	Group VI	Palladium	Pd	106.4
37	Group VII	Iron	Fe	55.8
38	Group VII	Cobalt	Co	58.9
39	Group VII	Nickel	Ni	58.7
40	Group VII	Rosetta	R	—
41	Group VII	Platinum	Pt	195.0
42	Group VII	Iridium	Ir	192.2
43	Group VII	Osmium	Os	190.4
44	Group VII	Ruthenium	Ru	101.1
45	Group VII	Rhodium	Rh	103.7
46	Group VII	Palladium	Pd	106.4
47	Group VII	Mercury	Hg	200.0
48	Group VII	Gold	Au	197.9
49	Group VII	Silver	Ag	107.9
50	Group VII	Copper	Cu	63.5
51	Group VII	Zinc	Zn	65.4
52	Group VII	Cadmium	Cd	112.4
53	Group VII	Mercury	Hg	200.0
54	Group VII	Barium	Ba	137.4
55	Group VII	Strontium	Sr	87.6
56	Group VII	Calcium	Ca	40.1
57	Group VII	Strontium	Sr	87.6
58	Group VII	Barium	Ba	137.4
59	Group VII	Strontium	Sr	87.6
60	Group VII	Barium	Ba	137.4
61	Group VII	Strontium	Sr	87.6
62	Group VII	Barium	Ba	137.4
63	Group VII	Strontium	Sr	87.6
64	Group VII	Barium	Ba	137.4
65	Group VII	Strontium	Sr	87.6
66	Group VII	Barium	Ba	137.4
67	Group VII	Strontium	Sr	87.6
68	Group VII	Barium	Ba	137.4
69	Group VII	Strontium	Sr	87.6
70	Group VII	Barium	Ba	137.4
71	Group VII	Strontium	Sr	87.6
72	Group VII	Barium	Ba	137.4
73	Group VII	Strontium	Sr	87.6
74	Group VII	Barium	Ba	137.4
75	Group VII	Strontium	Sr	87.6
76	Group VII	Barium	Ba	137.4
77	Group VII	Strontium	Sr	87.6
78	Group VII	Barium	Ba	137.4
79	Group VII	Strontium	Sr	87.6
80	Group VII	Barium	Ba	137.4
81	Group VII	Strontium	Sr	87.6
82	Group VII	Barium	Ba	137.4
83	Group VII	Strontium	Sr	87.6
84	Group VII	Barium	Ba	137.4
85	Group VII	Strontium	Sr	87.6
86	Group VII	Barium	Ba	137.4
87	Group VII	Strontium	Sr	87.6
88	Group VII	Barium	Ba	137.4
89	Group VII	Strontium	Sr	87.6
90	Group VII	Barium	Ba	137.4
91	Group VII	Strontium	Sr	87.6
92	Group VII	Barium	Ba	137.4
93	Group VII	Strontium	Sr	87.6
94	Group VII	Barium	Ba	137.4
95	Group VII	Strontium	Sr	87.6
96	Group VII	Barium	Ba	137.4
97	Group VII	Strontium	Sr	87.6
98	Group VII	Barium	Ba	137.4
99	Group VII	Strontium	Sr	87.6
100	Group VII	Barium	Ba	137.4

Figure 3. Mendeleev's Periodic system with the chemical ether. The ether is the box at the upper left labeled *x*, and the element below it, *y*, is coronium. [126]

The core of this new principle of organization was the group of inert gases, elevating what was once the albatross of chemical inactivity to a virtue. Ether was the lightest element, and at the top of the 0-Group (above another postulated element, coronium) [127]. (See Figure 3.) Note that the 0-Group of inert gases is not on the right but on the left, the standard placement before today's electronic interpretation of the Periodic Law. This position left two blank spaces above helium, and led Mendeleev to some of its properties:

Thus the world ether can be conceived, like helium and argon, as incapable of chemical combination.... When we recognize the ether as a gas this means, above all, that we strive to relate its concept with the ordinary, real concept of the states of matter: gas, liquid, and solid... If ether is a gas, this means that it is ponderable, it has its own weight. We must ascribe to this if we are not to discard on its behalf the entire conception of the natural sciences which takes its origin from Galileo, Newton, and Lavoisier. But if ether has such a highly developed power of penetration that it goes through all envelopes, then it is impossible to think about experimentally finding its mass in a given quantity of other bodies, or the weight of its specific volume under given conditions, and thus one should speak not of the imponderable ether, but of the impossibility of weighing it. [128]

While the ether could not be weighed, its weight could be determined — just not experimentally. The properties of the ether had to be deduced through the Periodic Law, where the ether was a noble gas. The Periodic Law only gave an upper cap for what element *x*, in row 0 and Group 0, should weigh ($x \leq 0.17$, with $H = 1$). To find a more exact prediction, one invoked physics, specifically the kinetic theory of gases, computing what the average weight must be for the gas to escape planetary atmospheres. Upon a simple calculation using Newton's law of gravitation, Mendeleev argued that *x* had to be less than 0.038 to escape Earth's atmosphere, and 0.000013 to escape the sun's atmosphere. He then scaled up to a larger star, γ Virginis, which had 32.7 times the sun's mass. His final result was $0.00000096 > x > 0.00000000053$. Interestingly, even though mass can be canceled out of all the escape velocity equations, he did not do so in order to make the calculation more "visualizable." This stemmed from Mendeleev's fixation on Newton's concept of mass as the centerpiece of the physical sciences. He finally calculated that the ether must weigh nearly one-millionth of an atom of hydrogen, and must move at about 2,250 kilometers per second. This ether penetrated everything and produced observable effects when it interacted slightly with elements [129].

Mendeleev assimilated this project for a chemical ether seamlessly with his new self-presentation as a disciple of Sir Isaac Newton. In the chemical ether pamphlet, he added as a brief footnote: "I would like preliminarily to call it 'newtonium' — in honor of the immortal Newton." In an early draft, scrawled illegibly on both sides of a flimsy scrap of paper, he emphasized this Newtonian aspect even more, concluding: "[The ether is] the lightest elementary gas which penetrates everything (row 0, Group 0), which I would like to preliminarily call newtonium, since the thoughts of Newton penetrate all parts of mechanics, physics, and chemistry." [130].

Mendeleev considered his central contribution not the prediction of the weight of element x , but rather the ether's ascription to the family of inert gases. The ether as noble gas had two central properties: first, it was "the lightest — in this sense the limiting — gas, which has a great degree of penetrating power," taking up the mantle of the most "typical" element from hydrogen; and, second, it could dissolve in other substances without combining with them, just as argon could dissolve in air or water [131]. This enabled Mendeleev to save his system:

And secondly, recently people have begun to speak often and a great deal about the smashing of atoms into tinier electrons, and it seems to me that these should not be considered so much metaphysical as metachemical representations, which stem from the absence of any kind of definite notions related to the chemism of the ether, and I wanted in the place of these kinds of confused ideas to set up a more real representation of the chemical nature of the ether, thus, at least until something shows either the transmutation of an ordinary substance into the ether and back or the transmutation of one element into another, any representation of the breaking of atoms should be considered, in my opinion, contrary to contemporary scientific discipline, and those phenomena in which one recognizes the breaking up of atoms could be understood as the emission of atoms of the ether, which penetrates everywhere and is recognized by everyone. [132]

Mendeleev noted that the chiefly radioactive elements (uranium, thorium, radium, etc.) were the heaviest ones, and thus they must attract a large proportion of lighter matter, just as the sun attracted planets and cosmic dust. Naturally, uranium would be surrounded by a great cloud of attracted ether which dissolved and intercalated with the uranium mass itself. At some critical point, too much ether penetrated the uranium and certain chemical processes, of whose exact nature we were ignorant, caused quantities of ether to be ejected from the sample. Radioactive energy was just the reaction energy produced by the minute and highly diffusive ether. Ether atoms, and not a "decayed" part of the primary atom, were ejected. There was no transmutation, no primary matter from which all elements were constructed, and the Periodic Law was preserved in its epistemological integrity [133].

The ether also disarmed the other threat: Prout. In a draft of the ether pamphlet Mendeleev wrote: "Considering possible the existence of even one of the 'pre-hydrogen' elements... predicted by the Periodic Law, I think that the confirmation of this would serve greatly for a new unification and strengthening of such fundamental real knowledge as mechanics, physics, and chemistry — instead of the doctrine of 'primary matter.'" [134]. In the final analysis, for Mendeleev all of the various threats to his vision of the unity of the physical sciences (except for noble gases, which were domesticated and appropriated to that worldview)

stemmed from Prout. Clearly, he argued, there was little to no evidence for Prout's view that matter was composed out of bits of homogeneous primary matter; what made so many chemists adhere to this view was the *unity* it promised. The ether, on the other hand, not only dealt with radioactivity, but satisfied this yearning for unification without caving to what Mendeleev considered "metaphysics". Mendeleev was not opposed to adding elements to the ontology of the natural world; he objected to the proyle as a *reduction* of matter that would imply transmutation. Mendeleev was even willing to admit the possible existence of elements with atomic weights between hydrogen and helium, such as a very light halogen [135].

The reactions to Mendeleev's pamphlet at home and abroad were, in general, rather positive, as the overwhelming translation efforts would indicate. Foreign reviewers were enthusiastic about the potential of Mendeleev's theory as a unifying hypothesis, although they were somewhat more skeptical about how much Mendeleev ignored physical theory. While one reviewer of the English translation felt that "[a]ll chemists and physicists will find this pamphlet interesting and suggestive," the reviewer from *Nature* pointed out that Maxwell had proven that if a particulate ether existed, then all energy in the universe would already have been transferred to it [136]. An American review of the English translation of the seventh edition of Mendeleev's *Principles of Chemistry* (1905) considered the ether prediction as "[p]erhaps the most remarkable thing in the book" but cautioned that "[i]nasmuch as this conception is largely the result of extrapolation over a long range, the conclusions are correspondingly hazardous." [137]. The French review — from a prominent journal on radioactivity studies — was supportive. Likewise, Mendeleev was informed by a friend at the German standards bureau in Charlottenburg that the German translation in the journal *Promethens* was making quite a splash [138]. The enthusiasm was short-lived, and soon his theory faded from the international scene. Mendeleev bemoaned to Clemens Winkler, the discoverer of germanium, who was likewise skeptical of the dissociation of radium into daughter elements, that cataract surgery prevented him from attending the World's Fair in St. Louis, "although precisely there I intended to put forth my opinion about the semi-spiritualist state, into which they [radioactivity researchers] are now trying to enmesh our science. It behooves us to stop it while we can still act." [139].

5. CONCLUSION

Mendeleev's attempt to preserve his chemical worldview soon vanished amid the rising nuclear model of the atom and the general acceptance of the electron. In an interview with a Petersburg paper in January 1904, Mendeleev stated that his current scientific projects "are directed exclusively towards the confirmation of the theory, or rather, attempt, of a chemical understanding of the world ether which I

established last year." [140]. His assistant A. Ivanov attempted, under Mendeleev's instructions, to perform observations of the sun's corona to evaluate the density of coronium (and, by extension, the ether), but these efforts were soon discontinued [141]. Mendeleev's attempt to let theory guide experimental investigation into the core concepts of matter and energy, however, illustrates the transition in his views on the power of theory that is intimately tied to his reinterpretation both of the Periodic system as a law of nature, and of himself as a disciple of Newton.

Nevertheless, the theory of the Periodic Law had been hijacked from Mendeleev's hands. The very techniques that he had relied upon to assist in his successful predictions — the very predictions that had led to the beginning of the "life" of Mendeleev's law — had now foundered on the shoals of phenomena too robust to be shoehorned into his conception of his system. The life of the Periodic system had been happy, but in Mendeleev's eyes it had been all too short. He died in January 1907, convinced that chemistry was headed down the dangerous paths of metaphysics. He would never have guessed that the Periodic Law would become crucial evidence for the very suppositions he abhorred.

6. ACKNOWLEDGMENTS

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7. NOTES AND REFERENCES

Abbreviations: ADIM — Arkhiv-Muzei D. I. Mendeleeva (D. I. Mendeleev Archive-Museum); MS — D. I. Mendeleev, *Sochineniia*, 25 v. (Leningrad: Izd. AN SSSR, 1934–1954); RGIA — Rossiiskii Gosudarstvennyi Istoricheskii Arkhiv (Russian State Historical Archive); ZhRFKHO — *Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva*.

All dates are given in the old style Julian calendar, which lagged 12 days behind the new-style Gregorian calendar in the nineteenth century, 13 days in the twentieth. Exceptions will be indicated by (N.S.). Transliterations follow a modification of the standard Library of Congress format. All unattributed translations are mine.

1. N. A. Figurovskii, *Dmitrii Ivanovich Mendeleev, 1834–1907* (Moscow: Izd. AN SSSR, 1961), 56; Nathan Marc Brooks, "The Formation of a Community of

Chemists in Russia: 1700–1870" (Ph.D. Dissertation, Columbia University, 1989), 402.

2. Throughout this article, I shall use either "Periodic system of chemical elements" or "Periodic Law," with "system" referring to the visual representation in tabular form. I avoid the phrasing "Periodic Table" for several reasons: Mendeleev never considered the table the final formulation of the law; there were many different competing tables; and one never finds this appellation in the Russian originals. For a useful catalog of the various graphical forms of the Periodic system, see Edward G. Mazurs, *Graphic Representations of the Periodic System during One Hundred Years* (University: University of Alabama Press, 1974 [1957]).

3. *Kratkoe istoricheskoe obozrenie deistviiia Glavnago pedagogicheskogo instituta, 1828–1859 gg.* (St. Petersburg: Tip. Akademii nauk, 1859), 2–5.

4. MS, I, 7–137. On isomorphism in general, see E. M. Melhado, "Mitscherlich's Discovery of Isomorphism," *Historical Studies in the Physical Sciences* 11 (1980): 87–123. This concern for internal-external connections is also evident in the materials for Mendeleev's dissertation on specific volumes (1856), ADIM II-A-17-3-3; and more generally in MS, I, 139–311. On the importance of Gerhardt as an intellectual resource for Mendeleev, see M. D. Gordin, "The Organic Roots of Mendeleev's Periodic Law," *Historical Studies in the Physical and Biological Sciences* 32 (2002): 263–290.

5. R. B. Dobroin, "Rannii period nauchnoi deiatel'nosti D. I. Mendeleeva kak etap na puti k otkryitiu periodicheskogo zakona" (Candidate Dissertation, Leningrad State University, 1953).

6. M. D. Mendeleeva, "Novye materialy o zhizni i tvorchestve D. I. Mendeleeva v nachale 60-kh godov," *Nauchnoe Nasledstvo* 2 (1951): 85–94.

7. I. M. Sechenov, *Avtobiograficheskie zapiski* (Moscow: Izd. AN SSSR, 1945), 96–97.

8. Quoted in B. N. Menshutkin, *Zhizni' i deiatel'nost' Nikolaiia Aleksandrovichia Menshutkina* (St. Petersburg: M. Frolova, 1908), 7.

9. V. E. Tishchenko and M. N. Madentsev, *Dmitrii Ivanovich Mendeleev, ego zhizni' i deiatel'nost': Universitetski period, 1861–1890 gg.* (Moscow: Nauka, 1993), published as *Nauchnoe Nasledstvo*, v. 21, 75.

10. On the dearth of adequate textbooks in Russia, see M. D. Gordin, "The Organic Roots of Mendeleev's Periodic Law", and K. Ia. Parnenov, *Khimia kak uchebnyi predmet v dorevolutsionnoi i soverskoi shkole* (Moscow: Akademiia pedagogicheskikh nauk RSFSR, 1963).

11. A. Lundren and B. Bensaude-Vincent, eds., *Communicating Chemistry: Textbooks and Their Audiences, 1789–1939* (Canton, Massachusetts: Science History Publications, 2000).

12. Due to the language barrier, most histories of the Periodic Law in English are based on the translated (into French, English, and German) fifth edition of the *Principles*, which was heavily revised after the discovery of Mendeleev's predicted

- elements. The first periodic system was formulated in the middle of writing the *first* edition, which has never been translated into a Western European language. Failure to take this into account has severely distorted Western interpretations.
13. *MS*, XIII, 60–61. Ellipses added.
 14. A. J. Rooke, *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro* (Columbus: Ohio State University Press, 1984).
 15. *MS*, I, 15.
 16. From a published typescript (1864), ADIM II-A-17-9-5, reprinted in D. I. Mendeleev, *Izbrannye lektsii po khimii* (Moscow: Vysshaya shkola, 1968), 25.
 17. Quotation from the 7th volume of *Osnovy khimii* (1903), *MS*, II, 448.
 18. On the crucial distinction between simple substances and elements, see Mendeleev, "Periodicheskaya zakonost' khimicheskikh elementov (1871)," in D. I. Mendeleev, *Periodicheskii zakon. Klassiki nauki*, ed. B. M. Kedrov (Moscow: Izd. AN SSSR, 1958), 102. For further development of this distinction, see Bernadette Bensaudé-Vincent, "Mendeleev's Periodic System of Chemical Elements," *British Journal for the History of Science* 19 (1986): 3–17; and I. S. Dmitriev, "Nauchnoe otkrytie in statu nascendi: Periodicheski zakon D. I. Mendeleeva," *Voprosy Istorii Estestvoznaniia i Tekhniki*, no. 1 (2001): 31–82.
 19. B. M. Kedrov, *Den' odnogo velikogo otkrytiia* (Moscow: Izd. sotsial'no-ekonomicheskoi literatury, 1958), 21.
 20. D. I. Mendeleev, "Sootnoshenie svoistv s atomnym vesom elementov (1869)," reprinted in Mendeleev, *Periodicheski Zakon. Klassiki nauki*, 16.
 21. B. M. Kedrov, *Den' odnogo velikogo otkrytiia*, 24–26.
 22. *MS*, XIV, 122.
 23. D. I. Mendeleev, "Sootnoshenie svoistv s atomnym vesom elementov (1869)," 18.
 24. *Ibid.*, 18.
 25. M. D. Gordin, "The Organic Roots of Mendeleev's Periodic Law."
 26. I. S. Dmitriev, "Nauchnoe otkrytie in statu nascendi," 61–63.
 27. "Essai d'une système des éléments d'après leurs poids atomiques et fonctions chimiques." D. I. Mendeleev, *Nauchnyi arkhiv, t. I. Periodicheski Zakon*, ed. B. M. Kedrov (Moscow: Izd. AN SSSR, 1953), 19 and 30.
 28. D. I. Mendeleev, "Periodicheskaya zakonost' khimicheskikh elementov (1871)," 131.
 29. D. I. Mendeleev, *Periodicheski zakon. Klassiki nauki*, 9.
 30. D. I. Mendeleev, "Sootnoshenie svoistv s atomnym vesom elementov (1869)," 14.
 31. *Ibid.*, 21–22. Emphasis in original. The two words for "attemp't" (*opyt* and *popytka*) give the sense of a first try, a general outline.
 32. *Ibid.*, 14.
 33. D. I. Mendeleev, "Ob atomnom ob"eme prostykh tel (1869)," in Mendeleev, *Periodicheski zakon. Klassiki nauki*, 44 and 48.

34. D. I. Mendeleev, "O kolichestve kisloroda v solianykh oksidakh (1869)," in Mendeleev, *Periodicheski zakon. Klassiki nauki*, 57. On the importance of this "oxygen limit," see Dmitriev, "Nauchnoe otkrytie in statu nascendi," 76–77.
35. D. I. Mendeleev, "Estestvennaya sistema elementov i primenenie ee k ukazaniu svoistv neotkrytykh elementov (1870)," in Mendeleev, *Periodicheski zakon. Klassiki nauki*, 74.
36. *Ibid.*, 75. Emphasis in original.
37. *Ibid.*, 89–90.
38. D. Mendeleev, "Die periodische Gesetzmässigkeit der chemischen Elemente," *Liebigs Annalen der Chemie und Pharmacie*, Supp. VIII (1872): 133–229. I quote from the Russian original from which Wreden made his German translation, as there are some discrepancies between the two.
39. D. I. Mendeleev, "Periodicheskaya zakonost' khimicheskikh elementov (1871)," 107. Emphasis in original.
40. *Ibid.*, 123.
41. *Ibid.*, 124–125.
42. S. G. Brush, "The Reception of Mendeleev's Periodic Law in America and Britain," *Isis* 87 (1996): 595–628. For an opposing view, see E. R. Scerri and J. Worrall, "Prediction and the Periodic Table," *Studies in History and Philosophy of Science* 32 (2001): 407–452.
43. D. I. Mendeleev, *Nauchnyi arkhiv, t. 1*, 623.
44. D. I. Mendeleev, "Sootnoshenie svoistv s atomnym vesom elementov (1869)," 31. Emphasis in original.
45. B. M. Kedrov commentary in Mendeleev, *Nauchnyi arkhiv, t. 1*, 54.
46. D. I. Mendeleev, "Ob atomnom ob"eme prostykh tel (1869)," 42.
47. D. N. Trifonov, *Redkoizmen'nye elementy i ikh mesto v periodicheskoi sisteme* (Moscow: Nauka, 1966).
48. Mendeleev actually fluctuated between 44 and 45, but seemed more convinced of the value of 44. See the editor's comments in Mendeleev, *Periodicheski Zakon. Klassiki nauki*, 696.
49. D. I. Mendeleev, "Estestvennaya sistema elementov i primenenie ee k ukazaniu svoistv neotkrytykh elementov (1870)," 90–92. Mendeleev's 1871 predictions are slightly more detailed but the same in essence: Mendeleev, "Periodicheskaya zakonost' khimicheskikh elementov (1871)," 150–152.
50. D. I. Mendeleev, *Periodicheski zakon. Klassiki nauki*, 76.
51. D. I. Mendeleev, "Estestvennaya sistema elementov i primenenie ee k ukazaniu svoistv neotkrytykh elementov (1870)," 92–95.
52. *Ibid.*, 95–98, quotation on 95.
53. R. B. Dobrovin, "K istorii otkrytiia germaniia (ekasilitsiia)," *Vestnik Leningraskogo universiteta*, no. 10 (1956): 55–59; B. M. Kedrov, "Die Vorhersage des Ekasiliziums und die Entdeckung des Germaniums," *VTM* 3, no. 8 (1966): 11–37; and R. B. Dobrovin and A. A. Makarova, "Prognozirovaniye svoistv

- skandīa i germanīa v rabotakh D. I. Mendeleeva," in B. M. Kedrov and D. N. Trifonov, eds., *Prognozirovanie v uchenii o periodichnosti* (Moscow: Nauka, 1976): 53–70.
54. S. F. Savchenkov, "Omosheniia mezhdū atomnymi vesami elementov," *Gornyi zhurnal*, 1871, reproduced in Mendeleev, *Nauchnyi arkhiv*, t. 1, 759–760.
55. D. I. Mendeleev, "Periodicheskaia zakonnost' khimicheskikh elementov (1871)," 153–156.
56. D. I. Mendeleev, "Estestvennaia sistema elementov i primeneniie ee k ukazaniiu svoisty neokrytykh elementov (1870)," 98.
57. *Ibid.*, 101. Ellipses added.
58. J. W. van Spronsen, *The Periodic System of Chemical Elements: A History of the First Hundred Years* (Amsterdam: Elsevier, 1969).
59. G. Urbain, "L'œuvre de Lecoq de Boisbaudran," *Revue générale des sciences pures et appliquées* 23, no. 17 (1912): 657–664; and A. de Gramont, "Lecoq de Boisbaudran: Son œuvre et ses idées," *Revue Scientifique* 51, no. 4 (1913): 97–109.
60. P. Lecoq de Boisbaudran, "Caractères cliniques et spectroscopiques d'un nouveau métal, le Gallium, découvert dans une blende de la mine de Pierrefite, vallée d'Argelès (Pyrénées)," *Comptes Rendus* 81 (1875): 493–495; and *idem*, "Sur quelques propriétés du gallium," *Comptes Rendus* 81 (1875): 1100–1105.
61. I. S. Dmitriev, "Teoreticheskie issledovaniia P. E. Lekoqa de Buabodrana po klassifitsatsii khimicheskikh elementov i sistematike spektrov," in D. N. Trifonov, ed., *Ucheniie o periodichnosti: Istoriia i sovremennost' (Moscow: Nauka, 1981)*: 19–36. On the correct atomic weight of gallium, see P. Lecoq de Boisbaudran, "Sur l'équivalent du gallium," *Comptes Rendus* 86 (1878): 941–943.
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64. P. Lecoq de Boisbaudran, "Sur quelques propriétés du gallium," 1105.
65. P. Lecoq de Boisbaudran, "Nouvelles recherches sur le gallium," *Comptes Rendus* 82 (1876): 1036–1039. For the density experiments, see *idem*, "Sur les propriétés physiques du gallium," *Comptes Rendus* 82 (1876): 611–613.
66. R. B. Dobrotrūn and A. A. Makarenia, "Prognozirovanie svoisty skandīa i germanīa v rabotakh D. I. Mendeleeva," 56–60.
67. L. F. Nilson, "Om Scandium, en ny jordmetall," *Oftersigt af Kongl. Vetenskaps-Akademiens Föreläsningar*, no. 3 (1879): 47–51.
68. Quoted in Dobrotrūn and Makarenia, "Prognozirovanie svoisty skandīa i germanīa v rabotakh D. I. Mendeleeva," 57.
69. P. Clève, "Sur le scandium," *Comptes Rendus* 89 (1879): 419–422, on 421–422.

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72. P. Walden, "Dmitri Ivanowitsch Mendeleeff," *Berichte der Deutschen Chemischen Gesellschaft* 41 (1908): 4719–4800, on 4751.
73. C. Winkler, "Germanium, Ge, ein neues, nichtmetallisches Element," *Berichte der Deutschen Chemischen Gesellschaft* 19 (1886): 210–211.
74. Quoted in A. Lissner, "Svazi D. I. Mendeleeva s gomoi akademiei vo Freiberge," *Voprosy Istori Estestvoznaniia i Tekhniki*, no. 5 (1957): 50–55, on 51.
75. C. Winkler, "Ueber die Entdeckung neuer Elemente im Verlaufe der letzten fünfundzwanzig Jahre und damit zusammenhängende Fragen," *Berichte der Deutschen Chemischen Gesellschaft* 30 (1897): 6–21, on 15.
76. See the account by B. M. Kedrov, "Predvideniie i poiski D. I. Mendeleevym ekasilitsia (budushchego germanīa)," *Khimiia rezhikh metallov*, no. 1 (1954): 7–17.
77. Reproduced in D. I. Mendeleev, *Nauchnyi arkhiv*, t. 1, 707.
78. See the reproductions in D. I. Mendeleev, *Nauchnyi arkhiv*, t. 1, 186–187. On the Moscow job, see D. I. Mendeleev to A. Iu. Davydov, 28 September 1871, quoted in B. M. Kedrov, "Predvideniie i poiski D. I. Mendeleevym ekasilitsia," 17.
79. Recollection by M. N. Mladentsev, published in Fishchenko and Mladentsev, *Dmitrii Ivanovich Mendeleev, ego zhizn' i deiatel'nost'*, 382.
80. C. A. Bischoff, Review of Mendeleeff's *Grundlagen der Chemie*, *Rigische Industrie-Zeitung* 17, no. 22 (1891): 264. Emphasis in original.
81. *MS*, II, 258. Mendeleev admitted in the preface to the third edition (*MS*, XXIV, 4) that he had not realized in 1869 how widely applied his principle could be.
82. *MS*, XXIV, 13. By the terms of the divorce, Mendeleev's first wife received his University salary, so he had to support his new family with consulting and royalties from the *Principles*.
83. *MS*, II, 328n13.
84. Review of D. I. Mendeleeff's *Principles of Chemistry*, 3d. English edition, *The Nation* 80, no. 2083 (1905): 438.
85. *MS*, XXIV, 41.
86. This historical approach first appeared in the fifth edition, and was highlighted in the eighth. *MS*, XXIV, 27.
87. D. Mendeleev, "Comment j'ai trouvé le système périodique des éléments," *Revue générale de chimie pure & appliquée* 1 (1899): 211–214, 510–512; 4 (1901): 533–546, on 533. On efforts to articulate quantitative periodicity, see D. N. Trifonov, *O kolichestvennoi interpretatsii periodichnosti* (Moscow: Nauka, 1971).
88. Diary entry of 19 July 1905, in S. A. Shchukarev and S. N. Valk, eds., *Arkhiv D. I. Mendeleeva*, t. 1: *Avtobiograficheskie materialy, sbornik dokumentov*

- (Leningrad: Izd. Leningradskogo gosudarstvennogo universiteta, 1951), 34–35. Ellipses added.
89. For his lecture notes, see "Biografi N'iutona, Zherara i Gei-Liussaka, Louvuz'e i dr.," ADIM II-A-17-1-5. On Newton's third law and valency, see Mendeleev, "Periodicheskaia zakonnost' khimicheskikh elementov (1871)," 74.
90. D. I. Mendeleev, "Popytka prilozheniia k khimii odnogo iz nachal estestvennoi filosofii N'iutona (1889)," in Mendeleev, *Periodicheski Zakon. Klassiki nauki*, 537.
91. *Ibid.*, 532.
92. *Ibid.*, 554. Ellipses added.
93. D. Mendeleev, "The Periodic Law of Chemical Elements," *Journal of the Chemical Society* 55 (1889): 634–656, on 649–650. Ellipses added.
94. Zapismaia knizhka, 1874–1876, #20, ADIM II-A-1-1-9, ll. 8–9 [undated but probably Spring 1874].
95. Blumbach telegram to Mendeleev, 26 May 1897, ADIM Alb. 1/458; F. Blumbach, "Geograficheskoe polozenie Glavnoi Palaty mer i vesov," *Vremennik Glavnoi Palaty Mer i Vesov* 3 (1896): 108–117.
96. D. I. Mendeleev, "K izucheniiu napravleniia tiazhesi po pomoshchi nesvobodnogo padeniia tel (1905)," *MS*, XXII, 387; and Mendeleev, "Podgotovka k opredeleniiu absolutnogo napravleniia tiazhesi v Glavnoi Palate mer i vesov pri pomoshchi dlinnago maiatnika s zolotym sharom." *Vremennik Glavnoi Palaty Mer i Vesov* 8 (1907): 1–41.
97. B. Bensaude-Vincent, "Between History and Memory: Centennial and Bicentennial Images of Lavoisier," *Isis* 87 (1996): 481–499.
98. Ramsay to Mendeleev, 6 January 1892 [N.S.], ADIM Alb. 3/500, ll. 1–2.
99. Ramsay to Mendeleev, 20 January 1892 [N.S.], ADIM Alb. 3/501, l. 1.
100. Ramsay to Mendeleev, 7 July 1892 [N.S.], ADIM Alb. 3/502, l. 4.
101. Ramsay to Mendeleev, 26 December 1893 [N.S.], ADIM Alb. 3/505.
102. Mendeleev to Ramsay, 12 February 1895, ADIM I-A-41-1-17.
103. J. E. Gilpin, "Krypton, Neon, Metargon, and Coronium — Recently Discovered Constituents of the Atmosphere," *American Chemical Journal* 20 (1898): 696–699, on 699.
104. *MS*, II, 401–403. Other chemists disputed kinetic theory, which was the basis for establishing argon's atomic weight as 40. On these disputes, see R. F. Hirsh, "A Conflict of Principles: The Discovery of Argon and the Debate over Its Existence," *Ambix* 28 (1981): 121–130.
105. D. I. Mendeleev, "Popytka khimicheskogo ponimaniia mirovogo eifra," *Vestnik i Biblioteka Samoobrazovaniia*, nos. 1–4 (1903): 25–32, 83–92, 113–122, 161–176, on 115–116, quotation on 89.
106. *Ibid.*, 118; *MS*, II, 451–452. Belgian physical chemist L. Ertera proposed the zero-group formulation in 1900 while investigating the periodicity of magnetic

- properties. L. Ertera, "Magnétisme et poids atomiques," *Académie Royale de Belgique. Bulletin de la Classe des Sciences* (1900): 152–161.
107. L. L. Zaitseva and N. A. Figurovskii, *Istledovaniia iavlenii radioaktivnosti v dorevolutsionnoi Rossii* (Moscow: Izd. AN SSSR, 1961), 16–64.
108. See D. I. Mendeleev's commentary on M. V. Ivanov, "Nabludeniia nad razriadnoi sposobnost'iu radiia," ADIM II-A-17-2-1, ll. 1–2.
109. Mendeleev to Geisel [sic], 7 (20) November 1902, RGIA f. 28, op. 1, d. 294, ll. 2-2ob.; Geisel to Mendeleev, 24 November 1902, ADIM Alb. 3/536.
110. *MS*, II, 461n.
111. Quoted in N. Morozov, *D. I. Mendeleev i znachenie ego periodicheskoi sistemy dlia khimii budushchego* (Moscow: I. D. Sytin, 1908), 89.
112. W. H. Brock, *From Protyle to Proton: William Prout and the Nature of Matter, 1785–1985* (Bristol: Adam Hilger Ltd., 1985).
113. R. Siegfried, "The Chemical Basis for Prout's Hypothesis," *Journal of Chemical Education* 33 (1956): 263–266; and H. Kragh, "The First Subatomic Explanations of the Periodic System," *Foundations of Chemistry* 3 (2001): 129–143.
114. Protocol of the Russian Chemical Society, 9 January 1886, *MS*, II, 311. Ellipses added.
115. *MS*, II, 454n. See also Mendeleev, "Popytka khimicheskogo ponimaniia mirovogo eifra," 164; and the second edition of the *Principles* (1873), *MS*, II, 227.
116. D. I. Mendeleev, "Popytka khimicheskogo ponimaniia mirovogo eifra," 30.
117. W. Ramsay, "The Electron as an Element," *Journal of the Chemical Society* 93 (1908): 774–788.
118. *MS*, II, 449. Ellipses added.
119. D. I. Mendeleev, "Elementy (Khimicheskii) (1904)," *MS*, XV, 638.
120. From the preface to the offprint of the ether pamphlet, published in 1905 by M. P. Frolova, reproduced in *MS*, II, 463.
121. D. I. Mendeleev, "Elementy (Khimicheskii) (1904)," *MS*, XV, 638n1.
122. I. Chetverikov to Mendeleev, 30 November 1904, ADIM II-V-25-Ch. The translation was published as *Pravo de Kemia kompreno de l'monda etero de P. Mendelejev* (Paris: 1904).
123. D. I. Mendeleev, "Popytka khimicheskogo ponimaniia mirovogo eifra," 28.
124. *Ibid.*, 29n.
125. *Ibid.*, 30.
126. D. Mendeleef, *An Attempt towards a Chemical Conception of the Ether*, transl. G. Kamensky (London: Longmans, Green, and Co., 1904), 26.
127. I do not address the particularities of coronium here since it did not play a large role in Mendeleev's treatise. It had already been predicted from irregularities in the sun's spectrum. Its chief function for Mendeleev was to round out the first period of the table so that the ether could be in both the 0-group and the 0-period. He calculated that coronium should have a density of 0.2, a weight of 0.4, and

- should move 2.24 times faster than hydrogen. This was too heavy to be the ether.
- D. I. Mendeleev, "Popytka khimicheskogo ponimania mirovogo eifra," 120-122. Coronium was eventually identified with excited states of helium and hydrogen. See H. Kragh, "The Aether in Late Nineteenth Century Chemistry," *Ambix* 36 (1989): 49-65; and V. Karpenko, "The Discovery of Supposed New Elements: Two Centuries of Errors," *Ambix* 27 (1980): 77-102.
128. D. I. Mendeleev, "Popytka khimicheskogo ponimania mirovogo eifra," 89-90. Emphasis in original.
129. *Ibid.*, 165-167.
130. *Ibid.*, 163n; and ADIM II-A-25-2-4, 1. 10b. I would like to thank N. G. Karpilo for her assistance in transcribing this text.
131. D. I. Mendeleev, "Popytka khimicheskogo ponimania mirovogo eifra," 92.
132. *Ibid.*, 115.
133. *Ibid.*, 171-172.
134. Quoted in A. A. Makarena, *D. I. Mendeleev o radioaktivnosti i slozhnosti elementov* (Moscow: Atomizdat, 1965), 28.
135. Motivated by the existence of only four halogens but five alkali metals, he felt hydrogen should have a halogen complement, possibly with an atomic weight of 3. Mendeleev, "Popytka khimicheskogo ponimania mirovogo eifra," 119n. For others' similar predictions, see Karpenko, "The Discovery of Supposed New Elements."
136. I. Remsen, Review of Mendeleev's *An Attempt towards a Chemical Conception of the Ether*, *American Chemical Journal* 33 (1905): 517-519, on 519; and J. L., Review of D. I. Mendeleev's *An Attempt towards a Chemical Conception of the Ether*, *Nature* 69 (1904): 558.
137. E. T. Allen, Review of D. Mendeleëff's *The Principles of Chemistry*, 3d. English edition, *Journal of the American Chemical Society* 27 (1905): 789-790.
138. L. Marout, "L'éther considéré comme élément chimique," *Le Radium* 1 (1904): 116-117; G. Eldman to Mendeleev, 22 January 1904, ADIM II-B-24-2-E, reproduced in R. B. Dobrothin, M. G. Ter-Avakova, and T. V. Volkova, "Perepiska D. I. Mendeleeva s zarubezhnymi uchenymi," *Voprosy Istorii Estestvoznaniia i Tekhniki*, no. 3 (1957): 176-189.
139. Mendeleev to Winkler, 10 (23) May 1904, ADIM I-A-4-2-10, 1. 2.
140. Quoted in R. B. Dobrothin, et al., *Letopis' zhizni i deiatel'nosti D. I. Mendeleeva* (Leningrad: Nauka, 1984), 453.
141. Ivanov article draft, October 1902, ADIM II-A-17-2-1, II. 3-5.