CHAPTER 2

ELEMENTS OF THE SYSTEM: BUILDING PERIODICITY AND A SCIENTIFIC PETERSBURG

> At present one can consider it universally acknowledged that among the phenomena of inanimate nature there is no arbitrary will; here the unshakable connections between phenomena rule with complete authority—relations which we call laws. In the invariance of these relations we are even inclined to see the characteristic sign which differentiates the inanimate from the living.
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> —A. N. SHCHUKAREV[1]

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 has appeared before in a rather obscure St. Petersburg chemical journal, published in Russian. In fact, in only the 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 every day 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 toward 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 eventually 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 studying 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 the Great Reforms. On 16 February Mendeleev noted in his diary that he had "heard a lot about Emancipation" in the bathhouse.[2] The very air was charged.

Mendeleev, like his peers, bridled with anticipation. A young, bright newcomer, he arrived at precisely the moment when the Great Reforms provided astonishing 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, stopgap solutions to pressing personal crises. Mendeleev would take the University and elevate it as a symbolic citadel for the priests of technical expertise and develop his hasty periodic system into a "law" that would undergird his evolving 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 loyal in his intellectual affections. 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's economy and society.

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 projects. 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.[3] 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, Mendeleev 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 his career.[4] He did not even recognize his "periodic system" as a law. Why would he? He was no prophet—at least not until 1871. His confidence in that eventual prophecy is a tale of 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.[5] These were refractions of the metaphor of Karlsruhe that had propelled him along his new chemical path. 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 Petersburg educational institutions 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.

THE EDUCATION OF DMITRII MENDELEEV

Mendeleev came to St. Petersburg in 1850 as a last resort. After his graduation from the local *gymnasium* in Tobol'sk, 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 for good), shifted the school's focus from training teachers to independent research. The curriculum was built around the 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 *gymnasia*.[6] The Institute was located on the grounds of St. Petersburg University, but was "closed" (in the parlance of the time), meaning that students lived and studied on campus, and were denied access to ordinary University students or the public at large. Rather than finding this environment stifling, as did many of his peers, Mendeleev thrived here, enjoying the attention of distinguished University faculty (who also taught at the Institute): mathematician M. V. Ostrogradskii, mineralogist S. S. Kutorga, physicist Heinrich F. E. Lenz, and chemist A. A. Voskresenskii.[7]

Mendeleev was encouraged to pursue his scientific interests, in particular by Voskresenskii, who was Mendeleev's chief mentor in the Petersburg academic world. Mendeleev's early work explored organic isomorphism, the phenomenon whereby two substances with different chemical composition express the same crystalline structure. Discovered by Eilhard Mitscherlich in 1822, this finding cast into disrepute the long-standing notion that crystalline structure was a unique reflection of underlying chemical composition. Mendeleev's 1856 candidate thesis, "Isomorphism 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.[8] Mendeleev would later draw on certain aspects of this research when formulating his periodic system: a concern with the elements' *physical,* not chemical, properties, attention to classification, and a reconsideration of atomic-weight values.[9]

On 14 April 1859, after an unpleasant stint teaching secondary school in the Crimea—inadequate facilities, stifling weather, and abominable students—Mendeleev left for Heidelberg on a government-subsidized trip to further his studies in chemistry. Upon arrival, he obtained a spot in the laboratory of distinguished German chemist Robert Bunsen, 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.[10] 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 claim to co-discovery of the "critical point" of liquids.

Mendeleev was socially active among Russian students and travelers, many of whom later remarked that his powerful personality formed the center of the Russian student community. As physiologist I. M. Sechenov recalled: "Mendeleev made himself, of course, the center of the circle; all the more since, despite his young years (he is years younger than I), he was already a trained chemist, and we were [merely] students."[11] Mendeleev's closest friends while he was abroad were Sechenov, who later cut a colorful and politically charged career in Russia, and fellow chemist A. P. Borodin, who would eventually divert some of his attention from chemistry to compose music, including the renowned opera *Prince Igor.* All were repelled by what they characterized as the bourgeois pretensions of the German students.[12] Despite this obstacle, the time in Heidelberg was extremely important for the young Mendeleev, cementing bonds between fellow Russian chemistry students and bringing him to Karlsruhe.

Before leaving Heidelberg, his Russian friends (and his German patron, Emil Erlenmeyer) threw the young chemist a farewell party that, according to Mendeleev's diary, touched him deeply. The contrast between the collegiality and ease of Heidelberg and the loneliness of the subsequent struggle in Petersburg could scarcely be more blatant. Poor and desperate for money in February 1861, he 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—a theoretical framework that concentrated on the classification of families of compounds and maintained an agnostic stance toward the internal structure of molecules—which was being displaced by the rise of structure theory, which broke organic molecules down into their component parts and remains the basis of organic theory today.[13]

Mendeleev submitted the manuscript to the Petersburg Academy of Sciences in hope of winning their Demidov Prize for outstanding scholarly work. The committee, composed of two of his patrons, J. Fritzsche and N. N. Zinin, awarded Mendeleev the prize in early 1862; he used the money to marry Feozva N. Lesheva. As the Demidov citation pointed out, most textbooks were either an abbreviation of existing data or a catalog of limited facts: "Mr. Mendeleev's book *Organic Chemistry* presents us with the rare occurrence of an autonomous development of a science in a brief textbook; a development, in our opinion, which is very successful and in the greatest degree appropriate to the mission of the book as a textbook."[14] Reception among students was equally enthusiastic. "I remember with what interest we, still students, greeted the appearance in 1861 of his *Organic Chemistry*," N. A. Menshutkin, later professor of analytic chemistry at St. Petersburg University, recalled. "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."[15] Mendeleev now had the reputation on which he would build a career.

That career was almost entirely bounded by St. Petersburg University.[16] Upon returning to Petersburg, Mendeleev approached his undergraduate mentor, Aleksandr Voskresenskii.[17] 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. The importance of a university education in Imperial Russia changed significantly with the restructuring of promotions in the civil service. In 1809, legislation made university-level examinations mandatory for advancement in the bureaucratic ranks system, a connection cemented by the 1835 university statute.[18] As a result, any young man who wanted advancement in Russia needed to attend university, and attending the one in the Imperial capital was the surest way to ascend rapidly. (Women's higher education would not even emerge as a contested political issue until the late 1860s, to say nothing of their service in the bureaucracy.)

The Emancipation of the serfs in 1861 considerably changed the situation. Once the serfs were legally freed of their obligations to the landowners, it became possible for poorer students to flock to the universities. Even though, in the late 1850s, the proportion of noble and civil-servant sons increased in the

university, so did the absolute number of students from other (lower) estates. In the next two decades, 40–60% of students received some sort of financial assistance, and an average of 2,000 a year received tuition exemptions.[19] These new realities were particularly apparent at St. Petersburg University, which in fall 1861 became the center of student turmoil, an event that would profoundly shape Mendeleev's vision of the role of the University in a modernizing Russia.

This unrest was the result of a misunderstanding, the consequence of a bureaucracy slow to adapt to the policies of Alexander II. During the spring and summer of 1861, new regulations substantially relaxed restrictions concerning student assembly and university policing. These changes, however, were kept secret until the very last minute. Rumors that stricter regulation was imminent sparked a walkout by students. The situation exploded into rampant street protests.[20] The professoriate was caught in the middle. Uneasy in their role as civil servants, unaccustomed to enforcing police orders, and pressed by their own liberal sympathies and the desire to gain popularity among the student body, professors walked a tightrope that put them in the bad graces of the Ministry of Popular Enlightenment and, when they wavered in their convictions, called forth the antipathy of their students.[21]

Mendeleev experienced this oscillation firsthand as a docent at the University. Amid fog-of-war rumors about the nature and extent of the protest, Mendeleev recorded in his diary a strong sympathy for the students in their desire for more openness from the regime. What most upset him, in turn, was the lack of proper procedures to guide the police. He had heard that the police had received authorization to shoot and beat students: "Horrible things. It is unbelievable that this went through the hands of the ministers and the sovereign in our times."[22] On 24 September the University was shut down until further notice. On 12 October, after some students were wounded in conflicts with police, Mendeleev was so incensed at the perceived violations of legality that he contemplated resigning.[23] The University remained closed into 1862; not until fall 1863 did it resume normal operations. Mendeleev, profoundly shocked by the semester of rebellion, became a fierce advocate for the government's eventual solution to the stalemate: the university statute of 1863.

This law was a complete revision of the standing 1835 statute. Minister of Popular Enlightenment A. V. Golovnin directed the negotiations over the new law, and succeeded not only in recruiting nineteen new professors per university (mostly in the natural sciences), but also in giving the institutions greater autonomy. The statute allowed the faculty to elect their own deans, gave them disciplinary jurisdiction over students and tenure, and provided more money to aid poor students. More than any other Imperial university statute, this came closest to meeting the demands of the professoriate. A vast majority of professors clung to this new arrangement not only as a solution to student unrest, but also as an embodiment of what it meant to be a member of the community of scholars.[24] Although it was eventually replaced in 1884, Mendeleev remained faithful until his death to the vague set of principles—autonomy, academic freedom, scholarship—of the 1863 law. His confidence in the statute was somewhat misplaced. The 1863 statute was intrinsically unstable since it was not based on a fundamental *policy* of governance, but was cobbled from a ramshackle set of regulations designed to bolster the professionalization of academics. The absence of a unified philosophy of how the universities should interact with the government meant that, ironically, the more successful the professionalization, the more suspicious the government became of the universities.[25] As Mendeleev would painfully come to realize at the end of his life, professors were civil servants just like any other bureaucrats, and had to behave accordingly.

But this would be a long time coming. Mendeleev's defense of the statute of 1863 became most pronounced after 1867, when he obtained tenure as professor of general chemistry at St. Petersburg University and could fully appreciate the benefits of professorial autonomy. For the six years between the dislocations of student unrest in 1861 and his final ensconcement at the University, he circulated among a variety of local institutions. The Technological Institute in Petersburg, administered by the Ministry of Finances, hired him as extraordinary (untenured) 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.[26] He became an ordinary (tenured) professor of chemistry there in 1864. The next year he was elected extraordinary professor of technical chemistry at St. Petersburg University, and he held both posts simultaneously, neglecting the Technological Institute even more after he was promoted to the chemistry professorship at the University in October 1867. He only resigned his post at the Institute in 1871, even though his petition to have his time-intensive laboratory teaching load eliminated or split with another professor was granted.[27] St. Petersburg University provided the framework in which he approached his classification of chemical elements.

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.[28] The 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.[29]

St. Petersburg University proved to be a fruitful setting for Mendeleev. When he took over his mentor Voskresenskii's post as professor of chemistry in October 1867, he assumed the large inorganic chemistry (or "general chemistry," as Mendeleev liked to call it) 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 being 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.[30] 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 (nonmetals) 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. A brief mental juxtaposition with the now ubiquitous short scientific article should make this plain. One could not possibly train chemists using solely a barrage of scientific articles—or at least not nearly as efficiently as with a textbook. 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 very universality. Particularly in the field of chemistry, which at both 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.[31]

So did introductory lectures, and the freshman inorganic course presented quite a challenge. This was a year-long large lecture course with integrated laboratory demonstrations. Mendeleev's responsibilities lay entirely in lecturing (laboratory duties were handled by assistants), although in the first few years this obligation was all-encompassing. The immensely successful text he wrote to guide himself and the students, *Principles of Chemistry* (*Osnovy khimii*), was divided into two volumes, each with two parts. The two parts of volume 1 were largely written in 1868, and concluded in the first month of 1869.[32]

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.[33]

Notice that Mendeleev did not introduce elements, atoms, or any theory of chemical combination. Instead, volume 1 is littered with definitions, plans for basic chemical experiments, and natural-historical information. The reader finds no direct hints of the forthcoming periodic law. Volume 1 is an empirical introduction to chemical practices and the inductive aspects of chemistry; volume 2 is a series of deductions from chemical theories, most saliently from the periodic system.

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, which we now take for granted—was heavily contested in chemistry in the nineteenth century, and the periodic law eventually served as one of the strongest arguments in its favor. It does not follow, however, that Mendeleev must have been thinking in terms of physical atomism when he conceived his system.[34] In his practical work Mendeleev, of course, used the notion that substances combine in defined ratios with each other ("chemical atomism")—it was practically impossible to be a chemist without doing so—but he had long maintained a conflicted attitude to the physical interpretation of atomic theory. In his 1856 candidate 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."[35] In an 1864 lecture, Mendeleev argued that since definite compounds pointed toward 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."[36] Even as late as 1903, Mendeleev accepted atomism only as a pedagogically "superior generalization."[37]

Mendeleev's skepticism toward atomism 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.[38] 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 what 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 Antoine 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."[39]

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 at Chapter 20, which addressed 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 the central substance, sodium chloride, from sources such as seawater. A discussion of sodium and chlorine followed in the next few 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 at this point, in late January 1869. His textbook was pedagogically sound so far, and he had just sent volume 1 to the publishers, but had dealt with only 8 elements, relegating 55, fully seven-eighths of known elements, to the second volume.[40] 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. Mendeleev had traversed the material of volume 1 several times in earlier chemical lectures, but he had yet to settle on a mechanism to solve the organization of the remaining elements.[41] Now, with a contract hanging over his head, he had to devise a more consistent solution. As he recalled in April 1869:

> Having undertaken the compilation of a guidebook to chemistry, called "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 (*proizvolu*).[42]

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.[43] By Chapter 4, on the alkaline earths (the calcium family), 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.[44] In addition, these alkaline earth elements, with a valency of 2, succeeded the alkali metals, with a valency of 1. 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 the historian's 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 *Principles* in conjunction with these documents and come to some informed speculations.

There are two basic 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 in rows 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.[45] Mendeleev's only direct statement on this matter, however, shows a middle way. He wrote in April 1869 that he "gathered the bodies with the lowest atomic weights and placed them by order of their increase in atomic weight."[46] 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[47]		

I will return shortly to the "—" underneath aluminum (Al). For the moment, however, consider Mendeleev's list. These are most of what Mendeleev called the "typical elements"—the set of light elements up to chlorine that provide a neat encapsulation of the periodic system (all of the major groups are included, and the differences in the properties of each group are expressed most starkly).[48] The list also emphasizes elements treated in volume 1 and the first chapter of volume 2 of *Principles:* the "organogens" (minus hydrogen), the halogens, and the alkali metals. Here Mendeleev built "groups" and "rows" simultaneously. He took the lightest elements 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 it, precisely because the contrast between the properties of, say, beryllium (Be) and boron (B) are sharper than between two heavier members of their respective groups. These elements stood in for their groups, and Mendeleev could see 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 2.1). 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. To transform it into a recognizable form 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 counterintuitive if you organize the elements according to any physical property—atomic volume, electronegativity, electron shells, and so on. Mendeleev's "Attempt" convinced him of the importance of atomic weights as a parameter for classification and of some natural correlation embedded under the surface. 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.[49] The quality of a first draft is evident in his 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 (see frontispiece to the Preface). 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.[50]

This system, then, emerged out of need—the need for a pedagogical "classification" that answered specific necessities in presenting material to beginning chemistry students. The pedagogic utility of Mendeleev's periodic system would later be universally recognized, even by its critics. Mendeleev often 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

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	J=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

FIGURE 2.1 The first published form of Mendeleev's periodic system, dated 17 February 1869 and entitled "An Attempt at a System of Elements, Based on Their Atomic Weight and Chemical Affinity." Mendeleev had 50 of these images printed up under a French title and 150 under a Russian one, which he mailed to various chemists. In order to transform this image into a modern periodic system, it must first be rotated clockwise 90°, reflected, and then the halogens (the row beginning with F = 19) need to be placed at the opposite extreme from the alkali metals (the row beginning with Li = 7). Notice that spaces are left with question marks for elements that Mendeleev suspected existed. Source: Mendeleev, *Periodicheskii zakon. Klassiki nauki*, 9.

from the use of the periodic law, as I became convinced not only in lectures in the last two years, but also during the preparation of a course of inorganic chemistry now already finished and published by me (in Russian). At the foundation of its presentation I placed the periodic law."[51] This does not mean that the first half of the textbook was written without pedagogical goals in mind. In fact, Mendeleev found the pedagogical format of volume 1 to be so important that he never revised the fundamental structure of the book throughout its eight editions, although he later made the periodic law more prominent.[52] This old model centered on chemical *practices* derived from his *Organic Chemistry* textbook, a heritage he was loath to disown even as he confronted the lawlike status of periodicity.

SYSTEM INTO LAW: MAKING PERIODICITY NATURAL

It is unlikely that Mendeleev understood the generality of his system when he first developed it in February 1869. Had he been cognizant of the implications of the periodic system, he would most likely not have relegated the initial presentation of it to the Russian Chemical Society in March 1869 to his friend Nikolai Menshutkin while he went off to inspect cheese-making cooperatives for the Imperial Free Economic Society. (Mendeleev was at the time well known as a consultant on agricultural matters, and small-scale cheese production by independent artisans intrigued him as a possible model for organizing industry. His positive report on artisanal cheese was less well received than the paper he had delegated to his friend.)

By late 1871, however, in the last of Mendeleev's research articles on the periodic law, he was quite sure that he had isolated a new law of chemistry.[53] Much as the creation of the "Attempt" was rooted in one of Mendeleev's local contexts—the classrooms of St. Petersburg University—the tale of how Mendeleev came to understand the periodic *system* as a periodic *law* can only be told outside the University, as Mendeleev addressed himself to the community of chemical practitioners. Through the Russian Chemical Society's journal, Mendeleev targeted a larger audience with each elaboration of the regularities of his system, as he became increasingly bold about the possibilities of his elemental arrangement.

Mendeleev's first scientific article on his findings was published in April 1869, two months after the mailing of the "Attempt." He began this piece with an enumeration of different schemes to order the elements, most of which were based on arbitrary distinctions that could not possibly reflect the order of the world. He concluded that "at the present time there is not a single general principle which withstands criticism, is able to serve as a basis for a judgment on the relative properties of elements, and which allows one to array them in a more or less strict system."[54] But Mendeleev was interested in more than just a "system." In this same article he used the word "law" to refer to periodicity for the first time:

> All the comparisons which I made in this direction bring me to the conclusion that *the magnitude of atomic weight determines the nature of the element* as much as the weight of a molecule determines the properties and many reactions of a complex substance. If this conviction is supported by further application of the established principle for the study of elements, then we will approach an epoch of understanding the essential distinction and reason for the affinity of elementary bodies.
>
> I propose that the law (*zakon*) I have established does not go at cross-purposes with the general direction of the natural sciences, and that until now its proof has not appeared, although there were already hints of it. From now on, it seems to me, a new interest will develop in the determination of atomic weights, in the discovery of new simple substances, and in the seeking out of new analogies between them.
>
> I introduce for this one of many systems of elements, founded on their atomic weight. It serves only as an attempt (*opytom*), an endeavor (*popytkoi*) to express the result which it is possible to achieve in this matter. I myself see that this endeavor is incomplete. . . .[55]

Notice, importantly, that this "law" is not the periodic law we now know, or the one that Mendeleev would endorse within two years. Here he claimed that the weight of atoms determined their properties—which also happens to be false—not that there was a periodic dependence of properties with increasing weight. In fact, Mendeleev was rather loose with the term "law" (*zakon*), citing as laws such generalizations as Auguste Laurent's even number rule and P. L. Dulong and A. T. Petit's rule on specific heats, neither of which would pass Mendeleev's later criteria.[56]

By August of 1869 Mendeleev appeared to have 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'*).[57] This retreat was motivated by his realization of the persistence of exceptions to inflexible 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, and how it evolved from the alkali metals to the halogens.[58] 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—later codified as I to VII—based on the subscript attached to oxygen.[59]

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. By November 1870, he was utterly convinced of both the "naturalness" and the lawlike character of his periodic system. That month, he published a Russian article in which he 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 confidence 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 Mendeleev first uses "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."[60]

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. . . ."[61] 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 already moved the reader to extremely doubtful elements and showed the application of periodicity, he now moved to *completely* doubtful elements, that is, those that were unknown:

> 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 the system I propose. For me personally these propositions were finally solidified from the moment when these propositions, which were based on the periodic law (*zakonnosti*), which lies at the basis of all this research, were justified for indium.[62]

Mendeleev's landmark 1871 article supports this thinking with a great deal more detail. This article was written in July and translated into German by Felix Wreden, and eventually appeared in November.[63] 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 (like a sine or cosine wave) 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.[64] 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.

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."[65] He had moved from pedagogy to pure science through prediction.

CLAIRVOYANCE: 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.[66] Understandably, the discoveries of the three predicted elements have received a great deal of attention from historians and chemists, but the process by which Mendeleev made his predictions has received almost none. However, to understand how the periodic law—and prediction as a central component—formed the underlying metaphor and warrant for Mendeleev's vision of restructuring Imperial Russia, then the primary question is what convinced *him*. For him, 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."[67]

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 2.1) 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 he concluded with a list of eight advantages of his system over the competing classifications of the 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."[68] But this is a weak prediction: It is only the *sixth* point in his list, and it is remarkably vague (he did not even specify the number of elements expected). 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.[69] 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."[70]

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.[71] Once again he displayed a characteristic of his prophetic work: If an idea was promising, he would retreat from his bolder claims in favor of comprehensively studying 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. He would employ this process again in Russian tariff policy twenty years later.

[31]		Группа I	Группа II	Группа III	Группа IV	Группа V	Группа VI	Группа VII	Группа VIII. Переход к группе I
Типические элементы		H = 1 Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
Первый период	Ряд 1-й	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
	— 2-й	K = 39	Ca = 40	— = 44	Ti = 50?	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63
Второй период	— 3-й	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
	— 4-й	Rb = 85	Sr = 87	(?Yt = 88?)	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 104, Ag = 108
Третий период	— 5-й	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 128?	J = 127	
	— 6-й	Cs = 133	Ba = 137	— = 137	Ce = 138?	—	—	—	— —
Четвертый период	— 7-й	—	—	—	—	—	—	—	
	— 8-й	—	—	—	—	Ta = 182	W = 184	—	Os = 199?, Ir = 198? Pt = 197?, Au = 197
Пятый период	— 9-й	(Au = 197)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
	— 10-й	—	—	—	Th = 232	—	Ur = 240	—	
Высшая соляная окись		R^2O	R^2O^2 или RO	R^2O^3	R^2O^4 или RO^2	R^2O^5	R^2O^6 или RO^3	R^2O^7	R^2O^8 или RO^4
Высшее водородное соединение				$(RH^3?)$	RH^4	RH^3	RH^2	RH	—

FIGURE 2.2 Short-form periodic system from Mendeleev's November 1870 article. Mendeleev used this system 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 system 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. Source: Mendeleev, *Periodicheskii zakon. Klassiki nauki*, 76.

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 2.2). 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 had only 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 the next one, titanium (Ti), was close to 50, he opted for an "average" 44. [This is not an exact average of the atomic weights of K, Ca, Ti, and V (vanadium), which would be 45—Mendeleev modified the mathematics to suit his intuition.][72] 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 (such as the forms of the chloride, oxide, and hydride of the element, all of which are 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 groups, and the prefix *eka* comes from the Sanskrit word for *one*. Eb=44."[73]

After treating eka-boron in great detail, he made similar arguments for eka-aluminum (El=68). This element was immediately above indium in the short-form table, and Mendeleev had recently successfully reclassified this element, which enabled him to give an extended account of its properties.[74] He devoted less space to it, however, than to eka-boron. Finally, he 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.[75] 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 that would tie the whole system together.[76]

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.[77] He could have placed his strongest prediction, eka-silicon, first, and then moved easily from heaviest to lightest. Instead, Mendeleev followed 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 had only four elements near it (K, Ca, Ti, and V) that could serve as analogs, but those analogs were extremely well studied, and thus served as the best way to persuade a skeptic. 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.[78] He wanted to stress his predictions, but he did not want to sacrifice his credibility with the audience by moving to the most extreme case first.

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 all, there was no reason to expect that every gap in the system had to be filled, and it was perhaps easiest to disregard Mendeleev's predictions as just so much wishful thinking. After such a bold departure, Mendeleev 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.[79] The image of a sage utterly confident in his predictions, experiment and community consensus be damned, is belied by the text.[80] 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 the atomological relations of elements will be able to be attributed to exact laws (*zakonam*), then we will approach even more the comprehension of the very essence of the distinction 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.[81]

Even though Mendeleev's article appeared in German, his periodic system received little attention aside from brief priority disputes with John Newlands in England and Lothar Meyer in Germany. But the confirmations of both gallium (eka-aluminum) and scandium (eka-boron) would make Mendeleev a household name in scientific Europe.[82]

THE VINDICATION OF PROPHECY: 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.[83] 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 (heating a substance, observing its emitted light through a diffraction grating, and noting its characteristic spectral lines). 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.[84]

Lecoq de Boisbaudran made his discovery on the afternoon of Friday, 27 August 1875 (N.S.), 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 that explicated the various properties of this new element.[85] It is clear that he had no prior knowledge of Mendeleev's predictions of eka-aluminum, but that does not imply that he was simply 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).[86] Clearly, Mendeleev was far from the only chemist interested in prediction.

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 publicly 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.[87] 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 El=68; its oxide will have the formula El^2O^3; its salts will display the formula ElX^3. Thus, for example, the (unique?) chloride of eka-aluminum will be $ElCl^3$; 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 El^2S^3, or oxysulfide $El^2(S,O)^3$, 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 El^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 $El^2(OH,X)^6$, but not acidic salts; the alum $ElK(SO^4)^2 12H^2O$ will be more soluble than the corresponding aluminum salt and less crystallizable. The basic properties of El^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.[88]

Many of the properties he lists are derivatives of the others, as simple cases of valency.

Lecoq 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 (Mendeleev questioned the density findings) until he did more work.[89] Interestingly, the simple substance of gallium was a liquid at room temperature, which was unpredictable from the periodic system. After further research, Lecoq 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.[90]

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 in both 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.[91] 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.[92] 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. . . ."[93] 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, as shown on page 41.

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.[94] 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.[95]

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.[96] The process of the discovery of germanium was very similar to that of scandium.

Supposed characteristics of eka-boron	*Observed characteristics of scandium*
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.	Scandium only gives the oxide Sc^2O^3, a base more energetic than aluminum, but weaker 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.	Scandium oxide is less basic than yttrium, and their separation is based on the differing stability of their nitrates under heat.
The oxide of eka-boron is insoluble in alkalis; it is doubtful that it will decompose ammoniac salt.	The hydrate of scandium is insoluble in alkalis; it does not decompose ammoniac salt.
The salts should be colorless and give, with KOH, Na^4CO^3 [*sic*] and HNa^2SO^4, etc., gelatinous precipitates.	The salts of scandium are colorless and give, with KOH, Na^2CO^3 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.	The double sulfate of scandium and of ammonium is anhydrous, but it has the composition of alum.
Only a small number of salts of eka-boron should crystallize well.	The sulfate of scandium does not give distinct crystals, nor does its nitrate, its acetate, and its formiate.
Water should decompose the anhydrous chloride of eka-boron with the liberation of HCl.	The crystallized chloride decomposes and liberates HCl when heated.
The oxide should be infusible, and it should, after calcination, dissolve in acids with some difficulty.	The calcinated oxide is an infusible powder which dissolves with difficulty in acids.
The density of the oxide is around 3.5.	The density of the oxide is exactly 3.9.[97]

On 6 February 1886 (N.S.), German chemist Clemens Winkler announced his discovery of a new nonmetallic 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.[98] (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.[99]

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. Newton's laws were famously confirmed by the independent ascription 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), and Mendeleev would later draw on this physical analogy and the power of prediction to defend his periodic law. (There is an element neptunium today, but it occupies the space between uranium and plutonium, following an alternative 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 approval from Mendeleev.[100]

Eka-silicon was the only eka-element that Mendeleev seriously undertook to isolate in the laboratory. Even before finishing his theoretical work on the periodic law, he outlined a research program directed toward finding this element.[101] 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.[102] Nevertheless, this particular effort was soon abandoned, and Mendeleev's attention would drift. He would not return again to active research on the periodic law.[103]

CONCLUSION: GATHERING THE ELEMENTS OF THE SYSTEM

The view of the periodic system as the pinnacle of Mendeleev's career—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 repeatedly abstract periodicity from its context at St. Petersburg University under the university statute of 1863 and the pressures of writing an introductory textbook, making it seem an emblem of pure science. This is the process that accounts for the surprise of our imagined historian at the beginning of this chapter upon encountering Mendeleev's very early efforts. Those early papers *are* the origin of the periodic law; it is how those sketches turned into an immutable law that requires explaining. The vision that Mendeleev would develop over his life was consciously built, just like the periodic system, out of diverse elements that were harmonized for the sake of internal consistency. Mendeleev's predictions themselves had naturalized periodicity by demonstrating the predictive power of his system. He then used this success to naturalize the other components of his Great Reforms model. They had all been created together, and they were all naturalized together.

This success of periodicity was bolstered by the paucity of critics. Rarely has a foundational scientific development been introduced with so little debate. That is not to say that the system was immediately accepted by practicing chemists, but it was not dismissed either. The early attention it received was not about its utility for pedagogy or its potential for chemistry, but mostly concerned priority disputes among the major competing systems.[104] Among the few criticisms, two are especially revealing for the way they resisted periodicity's redefinition of what it meant to do chemistry. The first came from one of Mendeleev's Petersburg mentors, Nikolai Zinin, who in 1871 told Mendeleev to "get back to work" and stop engaging in speculations. He wanted Mendeleev to return to empirical organic chemical research. Irritated, Mendeleev wrote to Zinin in 1871:

> I write you directly: what do you want, that I leave my area [of study], that I busy myself with the discovery of new bodies, that I worry about how often people are citing me? . . . I consider the elaboration of the facts of organic chemistry in our time as not leading to a goal as quickly as it did 15 years ago, and so I'm not going to busy myself with the petty facts of this sprig of chemistry. . . . I ask either don't censure and don't judge me, or say already what the errors are in my works, and not that I am not working. . . . I would look at who would have done as much as I have in my position, and I attribute your words to a lack of attention to my works, which suffer precisely from the fact that they do not comprise only the one-sided interest found in studies *today*. . . . [105]

He never sent this letter, more from a diplomatic calculation than a reconsideration of his position. From the moment Mendeleev came to believe that he could predict using periodicity, he was no longer interested in empirical fumbling. A law of nature demanded no less.

The other criticism came from G. N. Wyrouboff, a Russian émigré chemist working in France, at the very late date of 1896. This was long after the three eka-elements had been established and Mendeleev's position as the prophet of chemistry was quite secure. Wyrouboff, however, critiqued precisely the vulnerable core of Mendeleev's worldview, the notion of *law:*

> But M. Mendeleeff has aimed at producing something more and better than a mere *catalogue raisonné* of the elements. He converted his classification into the periodic system. It was a philosophic view, borrowing arguments from the kindred sciences, and imposing itself on us by its universality. He formulated, as the fundamental law of the physico-chemical sciences, the dictum that "all the properties of bodies are periodic functions of their atomic weights". . . .
>
> On reaching this point of its development, the conception of Prof. Mendeleeff becomes essentially injurious. Under the pretext of a law which has still to be demonstrated, it forbids us to throw light upon pure matters of observation, and forces us to remain in a vicious circle from which there is no escape. I think that it is time to show clearly that there is nothing which merits the name of *law* or *system.*[106]

The example Wyrouboff cited was the inversion of tellurium and iodine in the periodic system. Up to the present day, heavier tellurium has preceded the lighter iodine, breaking the order of monotonically increasing atomic weights

in favor of chemical analogy. (Rethinking periodicity in terms of atomic number instead of weight removes the conceptual difficulties this raises.) The fault of Mendeleev's program was that periodicity was not *enough* of a law, not that it was too much of one. But Wyrouboff's criticism was too little, too late—and increasingly beside the point. Mendeleev's reformulation of chemistry and the notion of law had long ago saturated the field—and, just as importantly, the culture of late Imperial Russia.