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How Mendeleev issued his predictions: comment on Andrea Woody

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Abstract
Much has been said about the accuracy of the famous predictions of the Russian chemist Dmitrii Ivanovich Mendeleev, but far less has been written on *how* he made his predictions. Here we offer an explanation on how Mendeleev used his periodic system to predict both physical and chemical properties of little-known and entirely unknown chemical elements. We argue that there seems to be compelling evidence in favour of Mendeleev genuinely relying on his periodic system in the course of issuing his predictions—a point recently contested by Woody (in: Soler, Zwart, Lynch, Israel-Jost (eds) Science after the practice turn in the philosophy, history, and social studies of science, Routledge, Abington, 2014). In particular, by using the known properties of a number of near neighbours of the three entirely unknown elements (the so-called eka-elements), we seek to show how the very format of his table enabled it to function as a powerful tool for Mendeleev in arriving at his predicted values. We suggest that Mendeleev's use of the periodic system in making his prediction gives an illuminative example of what Woody calls "theoretical practices" in science.

Keywords Mendeleev · Periodic table · Prediction · Eka-elements · Theoretical practices

Introduction

In a recent article, Andrea Woody (2014, p. 124) argues in favour of viewing theories as practices that involve active engagement with "representational artifacts." Woody illustrates such theoretical practices with the example of chemistry's periodic law. The periodic law provides a compelling case, because several chemists issued different periodic systems and also emphasised different uses of the systems (see Gordin 2012). Exploring the various ways in which the chemists represented periodicity and then used those representations gives an insight to chemists' different theoretical practices. In particular, they tell us how their design related to the subsequent uses of the systems.

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We agree with Woody that periodic systems give an interesting case-study of chemists' theoretical practices. However, we offer a differing interpretation of how the Russian chemist Dmitrii Ivanovich Mendeleev used his periodic system of the chemical elements. In particular, we dispute Woody's suggestion that Mendeleev did *not* use his periodic system for making detailed predictions of unknown elements. After having recalled Mendeleev's (1872) predictions for eka-aluminium, eka-boron and eka-silicon, Woody (2014, p. 134) states:

> Does it seem reasonable to assume that Mendeleev relied on the table in making these predictions, or that in some meaningful way the table has the capacity to support such predictions? I do not see how; the very format of the representation rules out the possibility.

In our commentary, we seek to show that there is compelling evidence in favour of Mendeleev relying on his periodic system for making predictions. Furthermore, contrary to Woody, we see that the very format of Mendeleev's representation of the periodic law guided his predictions. As such, Mendeleev's use of the system to make predictions gives us a vivid example of how a theoretical practice can be mediated through a representational artifact—in this case, the (tabular) periodic system of elements. By showing this, we also provide an account of *how* Mendeleev made his predictions, as recently called for by Scerri (2019).

We suggest that Mendeleev's use of the table can be characterised as a two-fold process. Firstly, Mendeleev's earliest published scheme accommodated the sixty or so known elements in atomic weight order where natural families of elements with similar chemical properties are grouped together (this stage included atomic weight predictions, as his first table included atomic weights for missing elements). Secondly, the tabular format enabled Mendeleev to project his thoughts concerning the properties of little-known and previously unknown elements such as the three now famous eka-elements: eka-boron, eka-aluminium and eka-silicon.

After providing a brief outline of Woody's case (Sect. 2), we will respond to Woody's claim concerning Mendeleev's use of the system first by considering Mendeleev's predictions of the physical properties of the eka-elements (Sect. 3). After doing so, we then consider Mendeleev's use of the system to predict the chemical properties of little-known and unknown elements (Sect. 4). We will conclude that it is reasonable to claim that, by relying on his periodic table, Mendeleev was able to accurately predict a number of physical and chemical properties for the three unknown elements: eka-aluminium, eka-boron and eka-silicon.

A brief outline of Woody's case

According to Woody (2014, pp. 123–124), the "turn to practice" refers to a family of interrelated changes in the philosophical literature on science. One of such changes includes a shift in the conception of theories. No longer are theories just seen as abstract concepts with a logical structure, but viewed as different kinds of artifacts. Taking seriously the idea that theories are artifacts highlights that they can also be tools for use. As Woody notes, even though we are familiar with *experimental* practices, less has been said about theoretical practices. On these grounds, Woody proposes a "parallel conception of theoretical practice" where she invokes chemistry's periodic law as an example. In their commentary on Woody's article Régis Catinaud and Frédéric Wieber (2014, p. 152) capture her approach as:

> [C]ontributing to the development of a renewed conception of theory in science, a conception of theory *as practice*. Within such a conception, an analysis of the theo-

> retical tools and models constructed and used by scientists becomes central. (emphasis in the original)

Central to Woody's inquiry are the representations of the periodic law developed by Julius Lothar Meyer and Mendeleev. In brief, Meyer provided a number of tables for chemical elements, but his most famous representation was a graph which plotted the atomic volumes of the chemical elements against atomic weight. Mendeleev, who issued a number of tabular representations, did not favour graphic format for periodic systems (Bensaude-Vincent 2001). On his tables, Mendeleev arranged the elements in order of atomic weight such that elements with similar physio-chemical properties were collected together in groups.

The similarities and contrasts between Meyer's and Mendeleev's projects provide fruitful grounds for Woody's investigation on how possible understanding of the periodic law is affected by its representational format. However, the periodic law was not endorsed by the broader community of chemists just in virtue of its representations, but because their helpfulness at issuing predictions. Several authors have brought up the discovery of scandium, gallium, and germanium as something that brought the periodic law in the ontology of chemists—at least in some national contexts (Brush 1996; Kragh 2015, pp. 174 and 178).[1] However, when examining the representations of periodic law, Woody argues that they did not support making predictions. As to Meyer's graphic representation of periodicity, Woody (2014, p. 134) states that: "Clearly, the graphical format does not indicate the presence of missing elements in any straightforward sense. It does not reveal 'holes'". As to Mendeleev, Woody argues that "Since the table has no explicit metric, but only ordering relations, the table reliably supports only interval predictions that result from this ordering. In other words, it can provide something we might loosely call 'ballpark' predictions if any predictions at all." On these grounds, Woody (2014, p. 134) concludes that "the very format of the representation rules out the possibility [of making predictions]".

As we will show in the following sections, we believe there is more evidence in favour of Mendeleev using the system to make predictions than for him not using it. Although here, it would be possible to argue that we are conflating the *law's* possible predictive powers with those of its *representations,* we highlight that especially in the 1860s and 1870s, and especially for Mendeleev, the law and its representations were extremely closely associated with one another. Mendeleev brought up the law of *periodicity* most forcefully in his article of 1871, but he had already discussed the possible underlying law already in 1869 (Brooks 2002, p. 131). What also speaks for their close connection is that Mendeleev's process for developing the periodic system in 1869–1871 was also a process for developing the law of periodicity. We take that Woody (2014, p. 133) too is cognizant of the close relationship between the law of nature and the means of expressing it, as she highlights that

> At the time of its introduction, the content of the periodic law was neither obvious nor settled. There were standard under-determination issues; from finite data, chemists had to project the law, and there were multiple ways to do so. It was not even clear what sort of relations grounded the periodic law, as evidenced in part by the widely varying formats. Yet because it would condition practitioners' thought and direct research efforts, *the particular representation scheme adopted would likely influence the subsequent specification of the law's content. In this regard, such representational choices are substantive and significant for the future elaboration of the content these representations aim to capture.* In this respect, representing is intervening. (emphasis added).

[1] The confirmation of Mendeleev's predictions seems not to have entered the discussion much in Norway (Lykknes 2015, pp. 191–192) or in Sweden (Lundgren 2015).

Table 1 Mendeleev's predictions for the eka-elements taken from Woody (2014, p. 124)

	Prediction	Experimental results
	Eka-aluminum (1871)	Gallium (1875)
Mendeleev's predictions of unknown elements		
Atomic weight	68	69.9
Specific gravity	6.0	5.935 (4.7)
Atomic volume	11.5	11.7
	Eka-boron (1871)	Scandium (1879)
Atomic weight	44	43.79
	Eka-silicon (1871)	Germanium (1886)
Atomic weight	72	72.3
Specific gravity	5.5	5.47
Atomic volume	13	

Our comment focusses on Woody's seeming denial that Mendeleev relied on the table in making his predictions for the eka-elements. It is worth noting that Woody (2014, p. 133) distinguishes two types of prediction: "(i) predicting the *existence* of new elements, and (ii) predicting the *physical and chemical properties* of elements, whether previously identified or not." (emphasis in the original). In what follows, we will argue that Mendeleev used the periodic system to predict the properties of unknown and little-known elements.

Mendeleev's predictions of the physical properties of the three eka-elements

Scerri (2019) recently challenged Woody's paper on practice and Mendeleev's periodic table. This contribution adopts in part Scerri's (2019) challenge to Woody that, 'a more fruitful strategy…might be to look at how Mendeleev actually made his predictions' which is lacking in Woody's analysis. As part of her account Woody (2014, p. 129) centres on Mendeleev's predictions of the physical properties of the three eka-elements (reproduced below) (Table 1).

We agree with Woody's (2014, p. 126) when she describes the periodic law as "an odd bird…[in that]…it is never explicitly cast as a logical conditional". Where a law is stated as a mathematical relationship—such as Newton's laws of motion—it is possible to determine or predict a particular outcome if all other quantities forming the expression are known. For example, $v = u + at$: a moving object's final velocity (v) can be determined if its initial velocity (u), acceleration (a) and time of travel are all known. The periodic law is not expressed as a mathematical relation and so, as Woody (2014, p. 147) states, it can "generate no precise quantitative relations".

Why then did Mendeleev use the mathematical function 'periodic' rather than favour alternative expressions (e.g.'regular')? When Mendeleev (1875, p. 144) claims that the properties of the chemical elements and the formulae and properties of their compounds are, "periodic functions of the atomic weights of the elements" he was, we would argue, alluding to an exact form of periodic motion—simple harmonic motion—a concept borrowed from physics. Writing some 14 year later Mendeleev (1889, p. 181) makes a clear link between his periodic law and the laws of physics when he states, "[t]he periodic law has shown that our chemical individuals display a *harmonic periodicity* of properties, dependent on their masses" (emphasis added). In his *Principles of Chemistry*, Mendeleev (1897 Part III, p. 21 n. 11) argues that the periodic law not an ordinary periodic function, thereby repositioning *periodic* in the context of his inquiry:

> But in ordinary periodic functions one variable varies continuously, whilst the other increases to a limit, then a period of decrease begins, and having in turn reached its limit a period of increase again begins. It is otherwise in the periodic function of the elements. Here the mass of the elements does not increase continuously, but abruptly, by steps, as from magnesium to aluminium. So also, the valency or atomicity leaps directly from 1 to 2 to 3, &c., without intermediate quantities, and in my opinion, it is these properties which are the most important, and it is their periodicity which forms the substance of the periodic law.

A few pages on Mendeleev (1897 Part III, p. 29 n. 31) states that, "Newton laid the foundation of a truly scientific theoretical mechanics of external visible motion" and that whilst "a Newton has not yet appeared in the molecular world; when he does, I think that he will find the fundamental laws of the mechanics of invisible motions of matter…in the chemical structure of matter". We would suggest that Mendeleev's use of "periodic" to describe the relations between the physical properties of the chemical elements was a direct allusion to Newtonian mechanics and perhaps the beginnings of its emergence in "the chemical structure of matter". It is Gordin's (1998, p. 110) view that Mendeleev sought "desperately" to be a successor to Newton and Lavoisier.

Further evidence suggesting Mendeleev implied more than 'repetition' in his use of the term 'periodic' is demonstrated in this extract from his Faraday Lecture of 1889:

> The most important point to notice is, that periodic functions, used for the purpose of expressing changes which are dependent on variations of time and space, have been long known. They are familiar to the mind when we have to deal with motion in closed cycles, or with any kind of deviation from a stable position, such as occurs in pendulum-oscillations. *A like periodic function became evident in the case of the elements, depending on the mass of the atom*. (Mendeleev 1889, p. 168, emphasis added)

The periodic motion demonstrated by the simple harmonic oscillations of a pendulum is, Mendeleev argues, analogous to, or 'like', the periodic function he believes to have established between atomic weight and the properties of the chemical elements. In making this connection Mendeleev (1889, p. 168) reminds his readers that '[a]ll that was known of functions dependent on masses derived its origin from Galileo and Newton'. Mendeleev's periodic law defined atomic weight as each chemical element's essential characteristic. Later in his Faraday Lecture Mendeleev (1889, p. 168) states, '[t]he periodic law has shown that our chemical individuals display a harmonic periodicity of properties, dependent on their masses'. Hendry (2012, p. 260) picks up on the allusion to Newtonian mechanics by likening Mendeleev's claim to 'a Newtonian body interacting according to the law of gravitation, an atom's interactions with other massive bodies are determined by its mass…'. Finally, as Scerri (2019) states, 'Mendeleev is known to have modelled himself on Newton and consequently would have been pre-disposed to making predictions in the typical fashion of a physicist.'

Nevertheless, the exact form of periodicity demonstrated by the mechanical system of an oscillating spring, modelled with the aid of Hooke's and Newton's respective laws, is not demonstrated by Mendeleev's periodic law. The atomic weights of the chemical elements as arranged in the periodic table increase but not in a regular fashion. The formulae and properties of their compounds are not a mathematically exact periodic function of their atomic weights. It is for reasons such as this—reasons related to what philosophers of science usually define as a law—that Woody questions the periodic law, on which the periodic table is founded, as not being a law in this traditional sense.

Notwithstanding the points raised above about the nature of the periodic law, we will in this section, argue that by engaging with his representation of the periodic law—the periodic table—Mendeleev was able to generate predictions of the physical properties—here atomic weight and atomic volume—of the undiscovered eka-elements. Predictions which Eric Scerri (2007, p. 132) describes as being accurate to "an astonishing degree". We will shortly refer to Mendeleev's paper 'The Periodic Regularity of the Chemical Elements' (1872) published in Liebig's journal *Annalen der Chemie und Pharmacie*. Jensen (2005, p. 21) claims that this particular paper of Mendeleev's 'defined the periodic law and table for the rest of the 19th century and which served as a primary reference for western chemists.' Woody (2014, p. 134), however, was not quite so convinced that Mendeleev's predictions on atomic weight and atomic volume were supported by the table:

> For Mendeleev, any prediction of quantitative properties must rely on some calculation of ratios, something not explicitly supported by the table. Since the table has no explicit metric, but only ordering relations, the table reliably supports only interval predictions that result from this ordering. In other words, it can provide something we might loosely call "ballpark" predictions, if any predictions at all.

We agree that Mendeleev's table, whilst ordering the elements by atomic weight, has no precise metric: the intervals of atomic weight between successive elements being irregular. Nevertheless, as we shall attempt to show, Mendeleev engaged with his representation of the periodic law to proportion the difference between the properties of known elements and the neighbouring eka-elements in order to arrive at his predictions.

Mendeleev's predictions of physical properties—here atomic weight and atomic volume—depended upon two factors: the sequence of increasing atomic weights by which Mendeleev had arranged the elements within the table and the known values for near neighbour elements. The question now is, how did Mendeleev arrive at his predictions for the physical properties of the eka-elements, such as atomic weight and atomic volume? Mendeleev's method of using the periodic law to predict the physiochemical properties of the eka-elements can be glimpsed earlier in the paper, when he applies the periodic law to the systemisation of the elements. Mendeleev (1872, p. 66) argues that:

> The position of an element, R, in the system is determined by the series and the group to which R belongs, and hence by the neighbouring elements, X and Y, in the same series, as well as by the two elements in the same group with the next lowest (R′) and the next highest (R″) atomic weights. The properties of R may be determined from the known properties of X, Y, R′ and R″. Thus, we find the following series:

Series of order (n-2)	X′	R′	Y′
Series of order n	X	R	Y
Series of order (n + 2)	X″	R″	Y″

We can describe R′, X, Y and R″ as the four near neighbours of R—what Mendeleev (1872, p. 66) defines as 'atom analogs'. In part four of *The Principles of Chemistry* Mendeleev (1897, p. 25) uses this relation to demonstrate how the atomic weight of selenium can be determined

> [S]elenium occurs in the same group as sulphur, S = 23, and tellurium, Te = 125, and, in the 5th series As = 75 stands before it and Br = 80 after it. Hence the atomic weight of selenium should be ¼ (32 + 125 + 75 + 80) = 78, which is near the truth.

Mendeleev (1904, p. 16), accounts for how he arrives at such predicted values in his essay ‘A Chemical composition of the Ether’:

> I made these predictions by following what is known in mathematics as a method of interpolation, that is, by finding intermediate points by means of two extreme points whose relative position is known.

Mendeleev’s approach is described by Scerri (2019) to be ‘essentially one of interpolation between the known properties of surrounding elements on the periodic table in order to deduce the properties of any unknown element.’ Scerri (2019) supports this by citing Mendeleev’s (1891) account of how the atomic weight of selenium can be arrived at by averaging the atomic weights of it four near neighbours:

	S(32)	
AS(75)	Se?	Br(80)
	Te(127.5)	

Atomic weight Se = ¼(32 + 75 + 80 + 127.7) = 79

Scerri (2019) concludes, ‘Mendeleev calculated a value of 79, that is close to the then known experimental atomic weight of 78 for selenium, and thus helped to establish the value of this approach (Mendeleev 1891).’

We now hope to show how Mendeleev’s deployed methods such as “interpolation” to enable him to use the periodic law, as represented in his table, to determine a number of physical properties of the eka-elements. For example, we will show how Mendeleev interpolated the atomic weight of eka-boron (scandium) from its position between elements of known atomic weight.

First, it would be helpful to place a copy of Mendeleev’s (1872, p. 57) short form of the periodic table at this point (Fig. 1):

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	? Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	? Di = 138	? Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	? Er = 178	? La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

Fig. 1 Mendeleev’s short form of the periodic table from 1872

Taking first Mendeleev's (1872, p. 86) prediction for the atomic weight of eka-boron, which is placed immediately below aluminium in Group III: "[s]ince it follows that K = 39 and Ca = 40, but precedes Ti = 48 and V = 51, its atomic weight should be about Eb [eka-boron] = 44". We would argue that Mendeleev arrived at his prediction using the method of 'interpolation' and shown earlier as Mendeleev's method to demonstrate the atomic weight of selenium. Taking the atomic weights of the two elements either side of eka-boron, would lead to a predicted atomic weight of ½(Ca + Ti) = ½(40 + 48) = 44. Including the other two elements in the same row as eka-boron and mentioned by Mendeleev, titanium and vanadium, gives predicted value for eka-boron of ¼(K + Ca + Ti + V) = ¼(39 + 40 + 48 + 51) = 44.5. As Gordin (2004, p. 268 n. 72) records, "Mendeleev actually fluctuated between 44 and 45, but seemed more convinced of value 44". We might speculate that Mendeleev's reason for excluding eka-boron's two vertical near neighbours (Al and Yt) from his interpolative calculations was the uncertainty over the position of ytterbium (?Yt = 88) in his system. We argue that by using his table in this way Mendeleev was able to arrive at his remarkably accurate prediction; one which agreed exactly with the value determined on its discovery in 1879 by the Swedish chemist Lars Frederick Nilson.[2] In passing, Mendeleev's prediction falls within 2% of the currently accepted value of 44.96.

Mendeleev also predicts the atomic weight of eka-aluminium to be about 68 and that for eka-silicon to be approximately 72. No further details are given but given Mendeleev's earlier account for the atomic weight of eka-boron, it is worth exploring the relevant near neighbour atomic weights for these two eka-elements. Both sit in row (today period) 5 with eka-aluminium in Group III and eka-silicon on Group IV:

Group:	I	II	III	IV	V	VI	VII
Element:	Cu	Zn	**eka-Al**	**eka-Si**	As	Se	Br
Atomic weight:	63	65	**68**	**72**	75	78	80

But as Mendeleev (1872, p. 88) explains when setting out his predictions for the atomic volumes for eka-aluminium and eka-silicon, 'we can find atomic analogues on all sides [of the two eka-elements] and it is therefore easier to determine the properties more exactly than we could when examining Eb [eka-boron]'. The four *atomic analogues* for eka-aluminium are aluminium, zinc, indium and eka-silicon; for eka-silicon they are silicon, eka-aluminium, tin and arsenic. We can now include these elements to extend the network of near neighbour relations:

Group	I	II	III	IV	V	VI	VII
			Al	Si			
			27.3	28			
	Cu	Zn	**eka-Al**	**eka-Si**	As	Se	Br
	63	65	**68**	**72**	75	78	80
			In	Sn			
			113	118			

[2] Scerri (2006, p. 137).

Applying Mendeleev's method of averaging the atomic weights for the four near neighbour atomic analogues to the two eka-elements is complicated by each being a flanking element of the other. However, if we first take the atomic weight average of the three known near neighbours of eka-aluminium (Al, Zn and In), this gives an atomic weight for of 68.4—or as Mendeleev (1872, p. 88) states "about 68". Repeating this process for eka-silicon and averaging the atomic weights of silicon, arsenic and tin (Si, As, Sn) gives a value of 73.7. However, if the value calculated for eka-aluminum is also included, averaging the atomic weights of the four near neighbours to eka-silicon adjusts the average to 72.25—or about 72:

eka-Si   1/4(eka-Al + As + Si + Sn) = 1/4(68 + 75 + 28 + 118) = 72.25

In this textbook *Modern Theories in Chemistry*, Meyer's (1888, p. 164) statements support this approach: "[t]he properties of an element are, as a rule, the means of those of its neighbours of the groups on the one hand, and of the series on the other"—Mendeleev's four *atomic analogues*. It is Meyer's (1888, p. 165) view that this method led Mendeleev "to predict the properties of the element situated between boron and yttrium, to which he gave the name 'ekaboron', and also those of the element between aluminium and indium, which he styled 'eka-aluminium".

We agree with Woody's statement that the periodic law is not cast as a precise mathematical expression and so is unable to generate predictions in the manner of one of the laws of physics. Mendeleev (1905, p. 280) makes similar point in stating that "the periodic dependence of the elements cannot be expressed by any algebraical continuous function". Nevertheless, we would argue that Mendeleev's representational practice—his manner of setting out the relations between the chemical elements and then using this to guide his thoughts—enabled him to predict the atomic weights of the eka-elements.

Turning now to atomic volumes, we can see how Mendeleev (1872, p. 88) used near neighbour relations to determine predicted values for of eka-aluminium and eka-silicon which he claimed would be about,

> 11.5 for Ea [eka-aluminium], and 13 for Es [eka-silicon], as the volume of Zn = 9, of As = 14, and of Se = 18. We obtain the same numbers when comparing the volumes of Al, In and Tl for Ea [eka-aluminium], and the volumes of Si, Sn and Pb for Es [eka-silicon], because the first-mentioned elements are the atomic analogues of Ea [eka-aluminium], and the last those of Es [eka-silicon]. The volume of Si = 11, that of Sn = 16, thus that of Es = 13.

Arranging these atomic volumes in accord with Mendeleev's table gives the following:

Group	II	III	IV	V	VI	VII
		Al	Si			
		(10.3)[3]	11			
	Zn	**eka-Al**	**eka-Si**	As	Se	Br
	9	**11.5**	**13**	14	18	

[3] Mendeleev did not always set out the details of his calculations in full (see Scerri and Worrell (2001, p. 438). In this instance he did not include the values for the four elements in parentheses (Al, In, Pb, Tl). The atomic volumes in parentheses are values that Mendeleev is likely to have used to calculate the predicted atomic volume values for the eka-elements. The values used are taken from a Mendeleev source of the same period (c1870) as given in John Russel Smith (1976, p. 232).

In	Sn
(15.5)	16
Tl	Pb
(17.2)	(18.2)

Mendeleev does not set out his calculations or method in detail. However, he appears to be using interpolative methods, basing his estimates on the atomic weight values of neighbouring elements.

Thus, Mendeleev estimates a value for the atomic volume of eka-aluminium based on the row five elements, Zn, As, Se as well as the three group III elements Al, In and Tl. This pattern is followed for the prediction for the atomic volume for eka-silicon where Mendeleev's estimate is again based on the row five elements, Zn, As and Se as well as the group IV atom analogues, Si, Sn and Pb. It is our view that, by using the atomic volumes for the both the vertical and horizontal near elements, Mendeleev was able to arrive at the predicted values for the two eka-elements. If we first average the values for each eka-element's three nearest atomic analogues, the following estimates are derived:

eka-Al   1/3(Al + Zn + In) = 1/3(10.3 + 9 + 15.5) = 11.6
eka-Si   1/3(Si + Sn + As) = 1/3(11 + 16 + 14) = 13.6

These values for eka-aluminium and eka-aluminium whilst approximating to, are not exactly the same as Mendeleev's published values of 11.5 and 13 respectively; we have not replicated what Scerri (2007, p. 135) describes as Mendeleev's "complicated averaging method". It would appear that Mendeleev applied additional criteria to adjust the values derived from the averaging methods described earlier. But, as Scerri and Worrell (2001, p. 438) state, Mendeleev "never divulged these extra assumptions—he seems, in other words, not to have found it necessary to specify how and why he departed from the simple method of interpolation." Nevertheless, we believe that Mendeleev's predictions for the physical properties of the eka-elements, such as atomic weight and atomic volume, were founded upon calculations made using the pattern of distribution of the elements within his table and the known values of the physical properties concerned. Through his engagement with the periodic table, Mendeleev was able to both direct his thoughts on how the elements might be arranged, as well as projecting the existence of novel elements and their physical properties.

On these grounds, it is reasonable to claim, *pace* Woody, that Mendeleev did rely upon his periodic table in order to predict the atomic weights and atomic volumes of the three eka-elements. Whilst the periodic law is not cast as a mathematical relation and the table does not have an explicit metric, Mendeleev was able to use the values for elements neighbouring the eka-elements—atomic analogues—in order to arrive at his predicted values. Woody argues that the way the table is organised—its very format—rules out the possibility of it having a predictive capacity. This, we believe, is too strong a statement. To the contrary, it seems very plausible that Mendeleev used the table to successfully predict a number of atomic weights of the three eka-elements.

[151]

ТАБЛИЦА 2

Ряды	Группа I. $\overline{R^2O}$	Группа II. $\overline{RO}$	Группа III. $\overline{R^2O^3}$	Группа IV. RH^4 RO^2	Группа V. RH^3 R^2O^5	Группа VI. RH^2 RO^3	Группа VII. RH R^2O^7	Группа VIII. $\overline{RO^4}$
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	? Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	⊙Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

Fig. 2 Mendeleev's system of 1871 reprinted in Kedrov (1958, p. 116)

Mendeleev's prediction of the chemical properties

In the previous section, we argued that Mendeleev used the periodic system to predict physical properties of unknown elements. In this section, we argue that Mendeleev applied the system also to predict their *chemical* properties. We will especially highlight how Mendeleev's inclusion of the schematic row of oxides to the system guided his predictions of the chemical properties of elements that he deemed "little-known" and "unknown".

The Row of Oxides and Hydrides

When comparing Mendeleev's first systems of 1870 with those of 1871, it becomes evident that Mendeleev added two entirely new rows to the system (see Figs. 1 and 2). Unlike the other rows, the two new ones did not house the individual chemical elements. Instead, they depicted compounds. By doing so, the two new rows directed attention to how each element on the vertical column formed compounds with oxygen and hydrogen.

The two schematic rows show a gradual change in the amount of oxygen and hydrogen that the compounds could hold. As can be seen on Fig. 2, with oxides, the amount of oxygen increased when moving from left to right on the system. With hydrides, there was a converse trend. Mendeleev argued that such gradualness signalled that he had discovered a *natural* systematisation of the elements (Mendeleev 1870, p. 52, 53; 1871a, p. 75). The terminology of a "natural system" highlighted that the system took into account many properties and resemblances between the elements, where such systems were often contrasted with artificial ones that only picked one property (e.g. being metallic) and classified the elements according to whether they exhibited that property (see Foster 1863, p. 1007; Bensaude-Vincent 2009, pp. 165–186 for more details on the distinction).

According to Mendeleev, he first realised the gradual transitioning on the horizontal rows of the system, when he lined up the following chemical elements (Mendeleev 1871b, p. 107; see also Mendeleev 1869, p. 18)

Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5

These two rows would then correspond to the horizontal rows on the periodic system. It appeared that elements on each column (e.g. Li and Na) provided compounds of similar form (Mendeleev 1871b, p. 108). In particular, the elements on the rows Li–F and Na–Cl formed hydrides in the following manner:

–	–	–	RH^4	RH^3	RH^2	RH

Thus, for example, Li, Na, Be, Mg, B, Al, did not provide hydrides, but C, Si, N, P, O, S, F, and Cl did. More specifically, Mendeleev stated that the "simplicity or the decomposability" of the elements, their acidic properties, and the ability of hydrogen to replace metals "change consistently and regularly" on the row (Mendeleev 1871b, p. 108). For example, HCl was a clear acid and very simple, whereas H^2S was a weaker acid, and decomposed in high heat. With H^3P, acidic properties were almost absent and it decomposed more easily. Such properties were even more evident with H^4Si (Mendeleev 1871b, p. 108).

Not all of the elements on the above two rows combined with hydrogen, so hydrides were not quite so effective demonstrating the gradual change across the rows. Thankfully, elements in all groups combined with oxygen, so oxides allowed Mendeleev to highlight the gradual change across the horizontal row. To illustrate, Mendeleev included the following row of oxides to the system:

$$R^2O,\ R^2O^2,\ R^2O^3,\ R^2O^4,\ R^2O^5,\ R^2O^6,\ R^2O^7$$
$$RO \qquad RO^2 \qquad RO^3$$

From this schematic row, each form of compound corresponded to one of the eight groups on the periodic table. However, the schematic formulae were not intended to designate all the oxides formed by the elements. Rather, Mendeleev specified that the form only expressed how the elements provided *higher saline oxides*.[4] In Mendeleev's (1870, p. 51) words, "we could not choose a better sign for determining the comparative steps of the strength of the oxides than their ability to provide saline compounds". From the two rows of elements, the second row Na–Cl provided the following oxides:

Na^2O	Mg^2O^2 or MgO	Al^2O^3	Si^2O^4 or SiO^2	P^2O^5	S^2O^6 or SO^3	Cl^2O^7

[4] Oxides that form salts when reacting with an acid or a base are termed saline or salt-forming oxides. Mendeleev chose saline oxides in order to distinguish these from peroxides (such as H_2O_2 and Na_2O_2) which do not form salts in this way. The highest saline oxide depicts an element at its maximum valency—or in today's terms highest oxidation state.

where the order of these oxides corresponded to the step-wise change in the acidity and basicity of the elements. Thus, when moving from left to right on the horizontal row, the oxides appeared less basic and acidic characters start to emerge (Mendeleev 1871b, pp. 108–109).[5] In other words, the row then drew attention to the gradual transitioning from greater basicity towards greater acidity on the horizontal rows of the periodic system.

The fact that elements in all eight groups provided higher saline compounds allowed Mendeleev to draw analogies between the oxides of known elements, and those that had not been discovered. As we noted in a Sect. 3 of this article, Mendeleev utilised the row of oxides especially for predicting the atomic weights of elements. In Mendeleev's seminal paper of 1871, he stated that

> Knowing the equivalent and some properties of the element and its compounds, we can determine its atomic weight when we recognise the law of periodicity. If the given equivalent E is of the *higher* oxide provided by the element (e.g. the composition of oxide is E^2O, chloric compound ECl), then, if we multiply it with 1–7, we gain the values of its possible atomic weights (Mendeleev 1871b, p. 133, emphasis original).

Apart from the gradual transitioning from the greater basicity to acidity across the horizontal lines, Mendeleev also noted that within a group of analogous elements (i.e. the vertical columns on the system), elements with heavier atomic weights would either have more basic properties or provide weak acids (Mendeleev 1871b, p. 122). For example, he noted that the basic properties of BaO in Group II were more developed than with CaO above it. In a similar vein, the basic properties of ThO^2 in Group IV would be greater than with ZrO^2 or TiO^2 which have lighter atomic weights. In Group V, Bi^2O^3 appeared a more reactive base than Sb^2O^3 or As^2O^3, and with P^2O^3 there were hardly any basic properties. With respect to the diminishing acidity in a group of analogous elements, Mendeleev noted that Ta in Group V provided a less reactive acid than the lighter Nb and V of the same group, just as Te would in comparison with Se and S in Group VI (Mendeleev 1871b, p. 122). Thus, apart from the transition from greater basicity towards greater acidity on the horizonal rows of the system, there was a transition towards greater basicity and lessening acidity *within* the analogous groups on the vertical lines.

As we will see, the information on the gradualness in oxidisation guided Mendeleev's predictions on the chemical properties of missing elements. Although Mendeleev only included such schematic rows on the horizontal lines of the system, he also noted that there were trends towards greater basicity and lessening acidity within the groups of analogous elements, and this observation too guided his predictions on the chemical properties of elements.

[5] In an earlier publication, Mendeleev elaborated the elements that give oxides of the form R^2O (first column of the periodic system). He stated that potassium, sodium and silver do not "have saline character and compile the section of oxides that are rightly called peroxides" (Mendeleev 1870, p. 53). In the second column we can encounter "alkaline metals and metals similar to them, for which saline oxides are of the composition RO" (Mendeleev 1870 p. 53). In contrast with the previous two groups, the members on the third column "already show weak basic characteristics, emergence of acidic character is already visible" (Mendeleev 1870 p. 53). The gradual change towards acidity is visible in fourth column, where C, Si and Sn "provide acidic oxides of the form RO^2 or R^2O^4" albeit the acidic character are not very sharp yet. In sum, when transitioning across the row from one group to another, we may observe "oxides that are more and more rich in oxygen and have more visible acidic character" (Mendeleev 1870, pp. 53–54).

The row of oxides and hydrides in making predictions

In what follows, we will argue that the row of oxides guided Mendeleev's predictions on the chemical properties of little-known elements and unknown elements. Understanding how the row guided Mendeleev's predictions will also illustrate how Mendeleev used the system to make predictions of the properties didymium and yttrium, and the undiscovered elements he named eka-boron and eka-silicon.

Little-known element Didymium

Didymium is often remembered as an example of Mendeleev's unsuccessful predictions, as it turned out to be a mixture of praseodymium and neodymium (Karpenko 1980, p. 77). However, as Mendeleev's discussion of didymium illustrates effectively how he used the system to suggest the atomic weight and properties for an element that he deemed as "little-known," didymium should not be excluded when considering Mendeleev's predictions.

Mendeleev reflected on didymium's atomic weight and chemical properties in the course of discussing cerite metals more broadly. As the cerite metals had very close equivalent weights and many similar properties, determining their exact atomic weights was difficult (Mendeleev 1871b, p. 141). After denying that they should be placed in the iron group, Mendeleev saw that there were three options for the placing didymium and lanthanum (at this stage, Mendeleev considered them both in conjunction, as their equivalent weights were so close). The first option was to fit either didymium or lanthanum to group III, between Ba = 137 and Ce = 140? on the 8th row (1871b, p. 145). If opting for this solution, their equivalent weights would have to be 138/3 = 46. When considering the analogies (Cs, Ba, Ce), the available position on the eight row of group III should be best suited for an element that gave a clearly basic and not very volatile chloride salt (Mendeleev 1871b, pp. 145–146).[6]

The second option was to assign their oxides the formula RO^2, which rendered the atomic weights of didymium/lanthanum close to 138. In this case, they would be situated in Group IV, before Ta = 182 on the 10th row, so that the analogues would be Ce = 140? and Th = 231. Thus, the atomic weight of the element fitted to this spot should be close to 180, and it should have an oxide of the form RO^2 with an equivalent weight of 43. These properties were close to those of lanthanum and didymium (Mendeleev 1871b, p. 146). The final option was to place the elements in group V on the 12th row, so that their oxide would be of the form R^2O^5. In this case, the element fitted to the position would have an atomic weight close to 235 and an equivalent close to 49.

We get a sense of Mendeleev's use of the system from his assessment for the suitable position for didymium and lanthanum. In particular, Mendeleev saw the third option as problematic. This was because the expected equivalent of the element fitted to this position was much higher than what didymium and lanthanum indicated. Furthermore, the oxide of the element placed here should have a weaker base, or a less energetic base than ThO^2. As the oxides of lanthanum and didymium appeared to Mendeleev to be a clearly basic, they did not seem to fit the properties expected for group V. For this reason, Mendeleev (1871b, p. 146) suggested placing didymium in the group III vacancy and lanthanum in group IV.

[6] Chloride salt formed by reacting an oxide with hydrochloric acid (e.g. NaCl, $CuCl_2$. A 'chloric salt' is the result of reacting with chloric acid ($HClO_3$).

Little-known element Yttrium

With didymium/lanthanum, we sensed of how the row of oxides guided both Mendeleev's atomic weight determination and the identification of a place on the system that would correspond to the chemical properties. With yttrium, Mendeleev relied more on the trend on the vertical columns as he predicted its basicity with the help of the surrounding elements that were similar to it.

Mendeleev placed yttrium on the 6th row in Group III. As strontium oxide and zirconium oxide (on the same horizontal row with yttrium) were stronger bases than calcium oxide and titanium oxide above them, the oxide of yttrium should provide a "base quite energetic, just as the oxide of zirconium is already a base quite distinct" (Mendeleev 1871a, p. 93). As we saw in Sect. 4.1, within a group of analogous elements (i.e. the vertical columns on the system), elements with heavier atomic weights would either have more basic properties or provide weak acids. As strontium oxide and titanium oxide were heavier than calcium oxide and titanium oxide, and more basic, Mendeleev saw it safe to assume that yttrium (or an unknown element fitted to this position instead) would also be more basic.

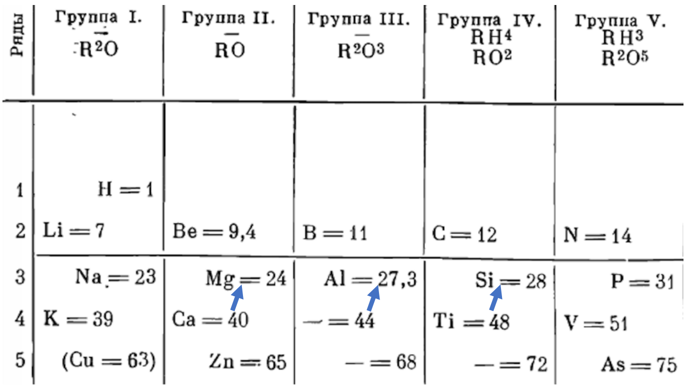
This concludes our discussion of Mendeleev's predictions of the chemical properties of little-known elements. With the unknown elements, Mendeleev mostly used the periodic system to visually demonstrate the analogical relations between elements which guided his descriptions of their properties. In what follows, we will show how Mendeleev used the periodic system, and especially the row of oxides in predicting the chemical properties of two undiscovered elements: eka-boron and eka-silicon.

Unknown element Ekaboron/Scandium

Eka-boron can be found from the fourth row, where it is preceded by potassium (K = 39), calcium (Ca = 40) and followed by titanium (Ti = 48) and vanadium (V = 51). As a group III element, Mendeleev expected that it would provide a higher saline oxides of form R^2O^3 (i.e. Eb^2O^3). More specifically, in all its relations with other elements, Eb^2O^3 should have intermediate properties of calcium oxide (CaO) and titania (TiO^2) (Mendeleev 1871b, p. 151). Thus, eka-boron would form a transition from Ca to Ti. This corresponds to eka-boron's positioning on the table.

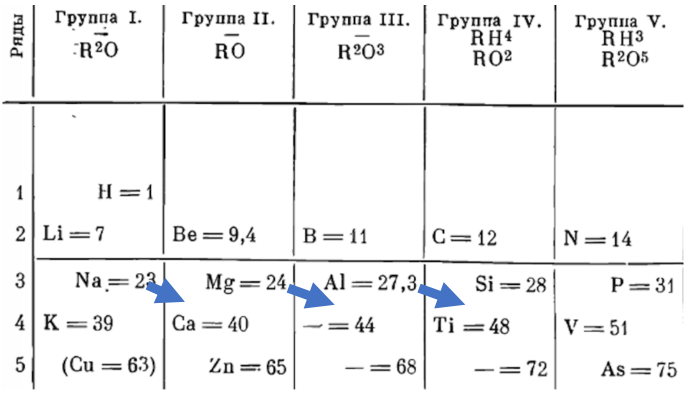
Mendeleev (1871b, p. 151) then suggested that Eb^2O^3 would enjoy a similar relationship towards its upstairs neighbour alumina as observed between eka-boron's left-hand neighbour calcium oxide (CaO) and magnesium oxide (MgO), and between eka-boron's right-hand neighbour titania (TiO^2) and silica (SiO^2) As aluminium is directly above eka-boron (and magnesium is directly above calcium and silicon is above titanium) the visual position of the elements in the system coheres with the prediction that Eb^2O^3 behaves to alumina in the same way as calcium oxide behaves to magnesia, as can be seen from Fig. 3.

Mendeleev (1871b, p. 151) then suggested that Eb^2O^3 should be more basic than alumina. Although he did not here elaborate why, he had earlier noted that eka-boron formed transition from Ca to Ti. As the row of oxides suggested that on the on the left to eka-boron CaO was more basic than MgO, and on the right of eka-boron titania (TiO^2) appeared more basic than silica (SiO^2), and eka-boron's oxide formed a transition from Ca to Ti, then ought to Eb^2O^3 appear more basic than alumina above it. This prediction corresponded to the positioning of these elements on the periodic system.



Ряды	Группа I. R^2O	Группа II. RO	Группа III. R^2O^3	Группа IV. RH^4 RO^2	Группа V. RH^3 R^2O^5
1	H = 1				
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75

Fig. 3 Ekaboron (=44) and its analogies. Extract from the periodic system. For a full table, see Fig. 2



Ряды	Группа I. R^2O	Группа II. RO	Группа III. R^2O^3	Группа IV. RH^4 RO^2	Группа V. RH^3 R^2O^5
1	H = 1				
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75

Fig. 4 Ekaboron (=44) and its analogies. See Fig. 2

Finally, Mendeleev predicted that magnesia ought to be more basic than Eb^2O^3 because calcium oxide is less basic than sodium oxide and as titania TiO^2 is less basic than alumina (Al^2O^3). As Mendeleev (1871b, p. 151) saw that eka-boron was the transition between the two in all its relations, then its eka-boron's oxide had to be less basic than MgO. This demonstrates a diagonal relation between the oxides of the elements in the periodic system (see Fig. 4).

After concluding his predictions concerning eka-boron, Mendeleev proceeded to predict the properties of two other unknown elements (=68 and=72). As both elements were to be situated between Zn and As, and formed analogies with silicon and aluminium, Mendeleev proposed to call them eka-silicon and eka-aluminium, where Mendeleev (1871b, p. 153) expected both to have more acidic properties than their analogues Eb and Ti on the fourth row. In what follows, we will especially discuss Mendeleev's predictions to eka-silicon, as Mendeleev's predictions on its chemical properties are more numerous than with eka-aluminium.

Unknown element Ekasilicon/Germanium

Earlier, we saw that Mendeleev's predictions on the properties of little-known yttrium were guided by trends within the same group. Similarly, trends within group IV played a central role in Mendeleev's process of discerning the chemical properties of eka-silicon (= 72). Mendeleev (1871b, p. 153) argued that ekasilicon (= 72) would occupy the middle position between eka-aluminium (= 68) and arsenic (As) on the same horizontal row, and between silicon (Si) and tin (Sn) in group IV (as can be seen from Figs. 2 and 3). More specifically to chemical properties, Mendeleev (1871b, p. 154) expected eka-silicon's oxide EsO^2 to appear more "clearly acidic" than TiO^2 above it in the system. Furthermore, Mendeleev (1871b, p. 154) suggested that "the basic properties of oxide of eka-silicon ought to be even weaker than with TiO^2 and SnO^2, but clearer than with SiO^2." The reference to SnO^2 (below eka-silicon) was omitted from the German version of the article published on the same year (Jensen 2005, p. 85).

To sum, there is more evidence in favour of Mendeleev's use of the system for making predictions than for him not using it. The system supported predicting the properties of little-known and undiscovered elements by visualising analogies (e.g. the schematic row of oxides and hydrides) and encoding the analogies (e.g. the trends on the vertical lines). In this light, we maintain that Mendeleev used the system in the course of predicting the chemical properties of little-known and unknown elements.

However, we note that it is an entirely different question whether Mendeleev was justified in using the system in making such predictions. Some of Mendeleev's contemporaries criticised Mendeleev's reliance on the higher saline oxides. In his extensive doctorate thesis on Mendeleev's periodic system, John Russell Smith brings attention to Wilhelm Ostwald, who criticised Mendeleev's suggestion that the oxides on the row were typical or even the highest form of oxidisation. For Ostwald, they were not the only typical oxides provided by the elements, and in many cases they were "often unknown and incapable of existence (Smith 1976, p. 310; see also Venable 1896, pp. 115–117). In a similar vein, in 1896 Grégoire Wyrouboff found Mendeleev's characterisation of the groups of the system in terms of higher saline oxides arbitrary. Despite this criticism, some of Mendeleev's contemporaries found his discussion on oxides valuable, such as Meyer (1872, pp. 330–332), who even included a section discussing the gradualness of oxidisation in the second edition of his textbook.

Conclusion

According to Woody, the so-called "turn to practice" in philosophy of science was accompanied with a new conception of theories as artifacts (2014, p. 123). We agree with Woody that the early periodic systems give a vivid example of theories as artifacts–artifacts which were "constructed," "manipulated" and "shaped by practical concerns and contingent, contextually determined goals" (2014, 124). In particular, we demonstrated that there is compelling evidence for Mendeleev using his representation of the periodic law to direct his reasoning about atomic weights, atomic volumes, and chemical properties of little-known and unknown elements. In order to highlight *how* Mendeleev used his system in this way, our findings may be stated in more abstract terms as follows:

- The system supported interpolating the atomic weights of undiscovered elements by placing analogical elements together.
- The system supported predicting the properties of little-known and undiscovered elements by visualising and encoding the analogies between the elements.

This suggests, *pace* Woody, that is reasonable to assume that Mendeleev relied on his table in making his various predictions and that this was made possible by the very format of the table.

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