

# Mendeleev's predictions: success and failure

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**Abstract** Dmitri Mendeleev's detailed prediction in 1871 of the properties of three as yet unknown elements earned him enormous prestige. Eleven other predictions, thrown off without elaboration, were less uniformly successful, thanks mainly his unbending adherence to the structure of his table and his failure to account for the lanthanides. At the end of his life he returned to his table without making the required changes, and added a theoretical discussion of elements lighter than hydrogen. The overall balance of success and failure is nevertheless in his favour. There may now be a similar failure to understand the ultra-heavy elements because of adherence to the pattern of chemical groups.

**Keywords** Periodic system · Prediction · Lanthanides

Mendeleev's ascendancy over other discoverers of the periodic system, notably John Newlands, William Odling and Lothar Meyer, resulted from his detailed predictions of future discoveries. In his major article of 1871, he devoted several pages to discussing the properties to be expected of eka-aluminium, eka-boron and eka-silicon, which were found as gallium, scandium and germanium in 1875, 1879 and 1886 respectively. He used a terminology borrowed from Sanskrit—eka, dvi, tri—for the first, second and third higher analogues. 'According to Professor Paul Kiparsky of Stanford University, Mendeleev was a friend and colleague of the Sanskritist Böhtlingk, who was preparing the second edition of

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his book on Panini, the author of a famed grammar of Sanskrit,' and who may have influenced Mendeleev.<sup>1</sup>

By 'prediction', Mendeleev meant not only that an element of the right atomic weight would be found but also that it would have properties, such as highest oxidation state, oxy-acid formation, atomic volume, metallic character and so on, corresponding to those of lighter analogues in the same group. In this sense he made only three complete predictions. His method, illustrated in detail only for these three, was to interpolate from lower analogues—and higher ones if available—and from neighbouring elements.<sup>2</sup> This was easiest with eka-aluminium and eka-silicon, which had higher analogues in indium and tin and were neighbours to each other and to zinc and arsenic. The case of eka-boron was more difficult and therefore more interesting; he thought it unreliable to argue from boron, which was in the 'typical' second row, and not enough was known of yttrium, 'didymium' and erbium, which he considered the higher analogues, so he based himself mainly on the neighbours, calcium and titanium.

The main structure of the table is based on the alternation of odd-numbered rows of 7 elements in VII groups and even-numbered rows with 11 elements in VIII groups. The groups were based on highest oxidation states, with alternating columns, later labelled A in the even rows and B in the odd ones. He picked out the 7 elements of the second row, lithium to fluorine, calling them 'типические - typical', so that the third row became 'period 1' (note the distinction between 'row' or 'series' and 'period'). The strange result was that the elements from 'eka-boron' (scandium) to manganese, and not from sodium to chlorine, are the analogues of lithium to fluorine. From then on the system worked by sheer serendipity, as  $7 + 11 = 18$ , the combined number of electrons in s plus p plus d orbitals (There was double counting, which compensated for the missing group of noble gases: copper, silver and gold were placed both in group VIII and—in brackets—in group IB).

The system broke down after barium, when f electrons became involved, and it would work again after the end of the lanthanides. On the horizon Mendeleev could see osmium to gold, which were obviously the analogues of ruthenium to silver, so he was encouraged to stick to his structure. The empty period 7 (row 9) seemed to solve the problem, creating 18 places between group II in row 8 and group III in row 10, occupied only by 'didymium' and cerium at one end and erbium and lanthanum at the other—a sort of 'dead zone' where the lanthanides should have been, but distributed over the VII + VIII groups.<sup>3</sup> His terminology—eka, dvi, tri—is disturbed by this hole in his structure.

After his discussion of the famous three predictions, which occupy 10 out of 68 pages, he concluded this section of his 1871 paper: 'The examples that I have given are sufficient to show how, by means of the periodic law, we can predict the properties of unknown elements; consequently I will not pursue this subject for the other missing elements in the system. The discoveries which would offer the most interest would be those of the following elements: eka-caesium, Ec=175; dvi-caesium, Dc=220; eka-niobium, En=146; eka-tantalum, Et=235; and the analogues of manganese: eka-manganese Em=100 and

<sup>1</sup> Subhash Kak, 'Mendeleev and the Periodic Table of Elements' <https://arxiv.org/vc/physics/paper/s/0411/0411080v1.pdf>, accessed 16/03/2018.

<sup>2</sup> Brush, S. G., 'Prediction and theory evaluation in physics and astronomy' in A. J. Knox and Daniel M. Siegel, eds., *No Truth except in the Details*, Kluwer Academic, 1995, pp. 299–318.

<sup>3</sup> Thyssen, Pieter and Binnemans, Koen (2014) 'Mendeleev and the rare-earth crisis'. In *Philosophy of Chemistry: Growth of a New Discipline*, Boston Studies in the Philosophy and History of Science, edited by Eric Scerri and Lee McIntyre Publisher: Springer-Verlag.

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

Fig. 1 Mendeleev's 1871 table

tri-manganese, Tm=190. The absence of a whole series (the ninth) and nearly all of a large period (from Ce=140) can hardly be an accident and is probably due to the nature of the elements in question.<sup>4</sup>

A few other predictions have been found scattered through Mendeleev's works: eka-molybdenum (RAM=140), eka-cadmium (RAM=155), eka-iodine (RAM=170) and divitellurium (RAM=212).<sup>5</sup> In the absence of explanations, we must suppose that he proposed them simply because they corresponded with places in his table, marked by a blank (only eka-manganese is entered with its atomic weight in his 1871 table). For a prediction to be counted a success, it must fall on a higher analogue of the element on which it is based and have appropriate properties, but this partly depends on the structure of his table; where he provided a place that could not correspond with any future discovery, the prediction was bound to fail (Fig. 1).

<sup>4</sup> Quotations from Mendeleev are taken from W B Jensen *Mendeleev on the Periodic Law: Selected Writings, 1869-1905*. Dover Publications, 2002.

<sup>5</sup> Smith, J R, *Persistence and Periodicity*, unpublished PhD thesis, London University, 1975.

Given that the unelaborated predictions were mentioned casually without explanation, unlike the famous three, it is remarkable that Mendeleev was right with five of them: in the first rank comes eka-manganese, technetium, with an estimated RAM of 100, the only one marked in the 1871 table. Tri-manganese, rhenium, with RAM 190, is not far off the observed element with RAM 186.2. Dvi-tellurium, RAM 212, is a good estimate for polonium, RAM 209. Dvi-caesium, RAM 220, is francium, RAM 223. Eka-tantalum, RAM 235, is protactinium, RAM 231.

That leaves five predictions: eka-molybdenum, eka-niobium, eka-cadmium, eka-iodine and eka-cesium, with RAM 140, 145, 155, 170 and 175 respectively. All of these fell in the ‘dead zone’ where the lanthanides would have been; their RAM values correspond roughly to those of cerium, promethium, europium or gadolinium, thulium or ytterbium and lutecium, but they cannot be called predictions, except to the extent that Mendeleev surmised that the anomaly was ‘due to the nature of the elements in question’. In fact higher analogues were present, on the other side of the ‘dead zone’, but in his terms they would have been ‘dvi’ and not ‘eka’: those of molybdenum, niobium and cadmium were tungsten, tantalum and mercury respectively. Dvi-iodine, not eka-iodine, would have been astatine, just as dvi-caesium was francium. The problem was with rigid adherence to the VII/VIII structure. I believe we should count them not as five failed predictions but as multiple consequences of one mistake.

Mendeleev became discontented with his chemical work, perhaps because he could not find a mathematical formulation for his ‘periodic law’. December 1871 marked what Gordin calls ‘the death of *all* research by Mendeleev on the periodic system’.<sup>6</sup> He wanted to make more fundamental discoveries to rival those of Newton, so from 1872 he threw himself into research into the gas laws, under a new Commission for Research in the Elasticity of Gases. His ambition was to establish the nature of the ‘luminiferous æther’, the significance of which for 19th century physicists was comparable with that of the Higgs field for those of the 21st. It is ironic to think that if he had paid more attention to ordinary air he might have discovered argon and added the missing group to his periodic table.

The gas work absorbed Mendeleev with diminishing intensity until he resigned in January 1881. For a few years he followed the chemical literature, and in 1875 he quickly seized on the discovery of gallium as vindicating his method, but in 1879 he had to be alerted by Per Cleve to the discovery of scandium.<sup>7</sup> In 1885 when germanium was discovered and there was speculation that it was eka-stibium, Mendeleev suggested eka-cadmium, and it was Viktor von Richter and Lothar Meyer who proposed that it was eka-silicon.<sup>8</sup>

Mendeleev’s interest in the nature of the æther led naturally into concern with spiritualism—the belief that the spirits of the dead existed in the æther and could communicate through mediums in séances. This became highly fashionable in St Petersburg and attracted aristocrats, who had a preponderant role in government. In May 1875, at Mendeleev’s instigation, the Russian Physical Society set up the Commission for the Investigation of Mediumistic Phenomena, with the object of re-establishing science as the source of truth on such matters. For a year he battled heroically for the scientific view, until it became clear that the Commission was being influenced by scientists who were themselves spiritualists.<sup>9</sup>

<sup>6</sup> Gordin, M. D. *A well-ordered Thing: Dmitrii Mendeleev and the Shadow of the Periodic Table*. Basic Books, 2004, p. 50.

<sup>7</sup> Gordin, op. cit., p. 40.

<sup>8</sup> Weeks, M E. *Discovery of the Elements*, Journal of Chemical Education, 1935, p. 226.

<sup>9</sup> Gordin, op. cit., pp. 81–111.

Series	Zero Group	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII			
0	<i>x</i>											
1		Hydrogen H=1.008										
2	Helium He=4.0	Lithium Li=7.03	Beryllium Be=9.1	Boron B=11.0	Carbon C=12.0	Nitrogen N=14.04	Oxygen O=16.00	Fluorine F=19.0				
3	Neon Ne=19.9	Sodium Na=23.06	Magnesium Mg=24.1	Aluminium Al=27.0	Silicon Si=28.4	Phosphorus P=31.0	Sulphur S=32.06	Chlorine Cl=35.45				
4	Argon Ar=36	Potassium K=39.1	Calcium Ca=40.1	Sodium Sc=44.1	Titanium Ti=48.1	Vanadium V=51.4	Chromium Cr=52.1	Manganese Mn=55.0	Iron Fe=55.9	Cobalt Co=59	Nickel Ni=59	(Cu)
5		Copper Cu=63.6	Zinc Zn=65.4	Gallium Ga=70.0	Germanium Ge=72.3	Arsenic As=75.0	Selenium Se=79	Bromine Br=79.96				
6	Krypton Kr=81.6	Rubidium Rb=85.4	Strontium Sr=87.6	Yttrium Y=89.0	Zirconium Zr=90.6	Niobium Nb=94.0	Molybdenum Mo=96.0		Ruthenium Ru=101.7	Rhodium Rh=108.0	Palladium Pd=106.9	(Ag)
7		Silver Ag=107.9	Cadmium Cd=112.4	Indium In=114.0	Tin Sn=118.0	Antimony Sb=120.0	Tellurium Te=127	Iodine I=127				
8	Xenon Xe=136	Cesium Cs=132.9	Barium Ba=137.4	Lanthanum La=139	Cerium Ce=140				(-)			
9												
10				Ytterbium Yb=173		Tantalum Ta=183	Tungsten W=184		Osmium Os=191	Iridium Ir=193	Platinum Pt=194.9	(Au)
11		Gold Au=197.9	Mercury Hg=200.0	Thallium Tl=204.1	Lead Pb=206.9	Bismuth Bi=208						
12			Radium Ra=224		Thorium Th=232		Uranium U=239					

Fig. 2 Mendeleev's 1904 table

Failure to be elected to the Academy of Sciences in 1880 was followed by the scandal of his marriage with a young painter, Anna Popova, in January 1882, even before his divorce from his first wife had been finalised—a weakness overlooked by the Czar, who remarked 'We admit that Mendeleev has two wives, but we have only one Mendeleev.' Undeterred, he started campaigning and writing on public education in Russia, the low quality of which he blamed for ignorance and superstition. He widened his concern with public affairs and began to write about reform of the economy and the organisation of the Empire. He also became quite a showman, and in 1887, in front of a large audience, he ascended in a balloon to observe an eclipse.<sup>10</sup> He even tried his hand as an art critic.

In spite of his polymathic career, Mendeleev did not completely forget chemistry. When the awarding of Nobel prizes began in 1901, it seemed he had a chance of one, but the rules said the prizes were for work done in the past year. He published a final version of his periodic table in 1904,<sup>11</sup> but it had hardly changed in 35 years. The noble gases had been added, making good the 18-element width, and copper and silver had been definitively moved to group IB (gold was missing),. Eka-manganese (technetium, the one blank that had been marked with an atomic weight in 1871) had become a plain blank. The dead zone was still empty except for lanthanum, now in the right place, cerium and ytterbium. Otherwise he had not added any of the 'rare earth elements', although by then 13 had been identified. It was a bit early to be sure of polonium, but he should at least have added actinium (Fig. 2).

<sup>10</sup> Gordin, M. D. *A well-ordered Thing: Dmitrii Mendeleev and the Shadow of the Periodic Table*. Basic Books, 2004, pp. 196–7.

<sup>11</sup> Mendeleev, D. I., translated Kamensky, *An Attempt towards a Chemical Conception of the Ether*, Longmans Green, 1904.

...																	...											
H																	... He											
Li											Be	B	C	N	O	F	Ne											
Na											Mg	Al	Si	P	S	Cl	A											
K	Ca											Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr											Y	Zr	Nb	Mo	...	Ru	Rh	Pd	Ag	Cd	Jn	Sn	Sb	Te	J	Xn	
Cs	Ba	La	Ce	Nd	Pr	...	Sa	Eu	Gd	Tb	Ho	Er	Tu	Y	...	Ta	W	...	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	...	...
...	Ra	La $\alpha$	Th	...	...	...	...	U	...	...	...	...	Ac	...	...	...	...	...	...	...	...	...	...	Pba	Bia	Tea	...	

FIGURE 8.—WERNER'S PERIODIC TABLE

Fig. 3 Werner's table, 1905

Mendeleev's main modification was to add the æther in a new 'row zero'. He also added coronium as a noble gas lighter than hydrogen, and he marked blanks for six more elements between hydrogen and helium. In the text he presented purely theoretical calculations of the atomic weights of æther and coronium, which was thought to explain a green emission line seen in the solar corona during the eclipse of 1869, eventually identified as due to a highly ionised form of iron and named 'coronium' by Gruenwald.<sup>12</sup> This was not the stuff of which Nobel prizes are made.

The information and ideas that Mendeleev needed for re-thinking his table were fully available, as proved by Alfred Werner (1866–1919). In his 1905 table he 'snipped out' Mendeleev's dead zone', put it to the side and filled it with lanthanides, virtually producing the modern long form. He even placed the then known actinides underneath them.<sup>13</sup> He also included spaces for two elements lighter than hydrogen and two elements between hydrogen and helium, but this just shows that such ideas were around at the time and were not an innovation of Mendeleev's. Werner deservedly won the 1913 Nobel Prize in Chemistry for his work on the coordination compounds of transition metals. Mendeleev was nominated for the 1906 prize but, by 5 votes to 4, it was awarded to Henri Moissan for his invention of the electric furnace (1892) and his isolation of fluorine (1886). It was the end of both men's careers; the following February, by the Gregorian calendar, both men died (Fig. 3).

In a 'score-card' of Mendeleev's predictions, Eric Scerri includes the eight successes discussed above, the five that failed because of the VII/VIII structure and also æther and coronium. He remarks 'A success rate of half is clearly not outstanding by any stretch of the imagination. The fact that Mendeleev made as many failed predictions as successful ones seems to belie the notion that what counted most in the acceptance of the periodic system were Mendeleev's successful predictions.'<sup>14</sup>

I believe a different weight should be attached to the various predictions. The 'big three'—gallium, scandium and germanium—were triumphs with great scientific and

<sup>12</sup> A. Gruenwald, 'On Remarkable Relations Between the Spectrum of Watery Vapour and the Line Spectra of Hydrogen and Oxygen', *Chemical News*, vol. LVI, No. 1462, 2 December 1887, p. 232.

<sup>13</sup> Werner, A., Beitrag zum Aufbau des periodischen Systems. *Berichtungen der deutschen chemischen Gesellschaft*. 38, 914–921. 1905.

<sup>14</sup> Scerri, E. R. *The Periodic Table*, Oxford University Press, 2007, pp. 142–3.

psychological impact. The five lesser successes also deserve recognition, especially the analogues of manganese, though a certain amount of luck attached to the 'post-lanthanide' predictions of francium and protactinium. The five predictions that fell foul of the lanthanides do not deserve equal weight, being repetitions of a single mistake, which was unavoidable in 1869, but should have been corrected by 1904. As for the æther and coronium, his reasoning did not connect them to any properties of any known element; they were as completely detached as ectoplasm from chemistry and the rest of the periodic table.<sup>15</sup> With eight successful predictions, one multiple error and two irrelevancies, Mendeleev comes off with a great deal of credit. If he had maintained his interest in chemistry he might have accomplished even greater things. With supreme irony, his 1904 article now figures on esoteric websites.<sup>16</sup>

Chemists may now be repeating Mendeleev's mistake, being so committed to the sequence of groups that they fail to see that a new pattern develops in the ultra-heavy elements. A recent theoretical study of oganesson ( $Z=118$ ) suggests that the shell structure breaks down for both electrons and nucleons.<sup>17</sup> Studies of copernicium ( $Z=112$ ) found that it appears to behave as noble gas, which is not altogether surprising in an analogue of monatomic mercury. However, the same has been found for flerovium ( $Z=114$ ), which is unexpected in an analogue of lead.<sup>18</sup> One wonders whether the same anomaly may not be involved in all three elements, in which case how far back may it reach? Almost everything that is said about elements from  $Z=100$  onwards is based on their supposed group membership, but it is conceivable that some or all of the 6d elements and the whole of the 7p series are subject to a new phenomenon. We must not fall into a new version of Mendeleev's 'dead zone'.

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<sup>15</sup> Bensaude-Vincent, B. 'L'ether, element chimique: un essai malheureux de Mendéléev (1902)?' *British Journal for the History of Science*, 15 (1982), pp. 183–188.

<sup>16</sup> For example <http://www.rexresearch.com/index.htm> (accessed 1/03/2018).

<sup>17</sup> Jerabek, Paul, et al. 'Electron and Nucleon Localization Functions of Oganesson: Approaching the Thomas–Fermi Limit' *Phys. Rev. Lett.* 120, 053001 (31 Jan. 2018).

<sup>18</sup> Kratz, J. V. 'The Impact of Superheavy Elements on the Chemical and Physical Sciences' *4th International Conference on the Chemistry and Physics of the Transactinide Elements*. (5 September 2011).