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Development of the periodic system and its consequences

Mary Virginia Orna, Editor
Marco Fontani, Editor

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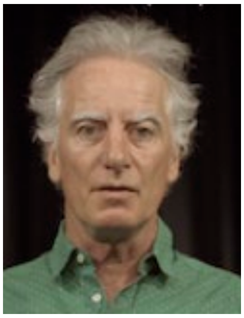

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Preface

It is a great honour for me to write these few lines of preface to the special issues of *Substantia* dedicated to the 150th anniversary of the Periodic Table by Dmitrij Mendeleev. In 2019 there are other important anniversaries besides that of the periodic table. One of these is the centenary of Primo Levi's birth. I believe these two anniversaries are strictly related, in fact *The Periodic Table* by Levi has been considered by the *Royal Institution of Great Britain* as the "best book of science ever written". It would be sufficient to recall an impressive excerpt from "Iron", a tale of the *The Periodic Table*, to acknowledge the uniqueness of this literary work:

> "*We began studying physics together, and Sandro was surprised when I tried to explain to him some of the ideas that at that time I was confusedly cultivating. That the nobility of Man, acquired in a hundred centuries of trial and error, lay in making himself the conqueror of matter, and that I had enrolled in chemistry because I wanted to remain faithful to this nobility. That conquering matter is to understand it, and understanding matter is necessary to understand the universe and ourselves: and that therefore Mendeleev's Periodic Table […] was poetry …*".

When we designed the project related to these special issues, we had in mind Levi's work and in particular his wonderful tales that belong to *The Periodic Table*. I like to recall this homage to a chemist-writer-witness to introduce the six topics that are associated to the special volumes of *Substantia*.

As President of the University of Florence which is the owner of the publisher *Firenze University Press*, I am truly grateful to the Editors – Marc Henry, Vincenzo Balzani, Seth Rasmussen, Luigi Campanella, Mary Virginia Orna with Marco Fontani, and Brigitte Van Tiggelen with Annette Lykknes and Luis Moreno-Martinez – for accepting the invitation made by the Editor-in-Chief Pierandrea Lo Nostro and for the extraordinary work for the preparation of these special issues. Of course the choice of the six subjects was not accidental: we tried to identify some features of the chemistry realm, related for several reasons to the periodic table. They are strikingly associated to the great challenges for our future: these are water, sustainability, energy, open chemistry, the history and the educational perspectives of the periodic table.

During its long path of progress and civilisation mankind has strongly modified nature to make our planet more comfortable, but at present we must be very careful with some dramatic changes that are occurring in our Earth. Science and technology, and chemistry primarily, can help mankind to solve most of the environmental and energy problems that emerge, to build a radically different approach from that that has prevailed in the last two centuries. It is a fantastic challenge, since for the first time we can consider nature not as a system to simply exploit, but a perfect ally for improving life conditions in the whole planet. Chemistry has already engaged and won a similar challenge when, understanding the pollution problems generated by a chaotic and rapid development, succeeded in setting up a new branch, green chemistry, that turned upside down several research topics. Now is the time to develop sustainable chemistry: the occurring events demand that chemists propose new routes and innovative approaches. In the last two centuries we have transformed immense amounts of matter from nature into waste without thinking that we were using non renewable energy sources. We have been acting as our natural resources were unlimited, but knowing that they are instead limited. Now we are realizing that it is not possible to continue along this road. Our planet and our atmosphere are made of finite materials and their consumption during the last two centuries has been impressive. Some elements that are crucial for current and future industrial countries are known to be present on Earth crust in very small amounts and their recycling from waste cannot be a choice anymore, but it is rather an obligation.

Climate is another big problem associated to the terrific changes occurring in some equilibria, both as a consequence of the violent industrial development and energy consumption. We need, and we will always need more and more, an immense amount of energy. The only solution to secure wellness to future generations is the conversion to renewable energy sources. In this view, food and water, due to the strong increment in the demographic indices, could become the true emergencies for billions of individuals. Looking at the picture I tried to draw in this short preface it becomes more clear why we selected those topics for our special issues.

I am optimistic, and I have the strong confidence that chemistry, that studies matter and its transformations, will give mankind the picklock to overcome those challenges.

We will definitely need insightful minds, creativity, knowledge and wisdom.

Luigi Dei
President of the University of Florence

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Editorial

Setting the Table: A Retrospective and Prospective of the Periodic Table of the Elements

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Abstract. The major theme of this special issue volume is "The History of The Periodic Table, the Discovery of the Elements, and of the Materials that Changed the Course of History: The Development of the Periodic System and Its Consequences." After a brief chronological retrospective on the development of the periodic table, each paper contributed to this volume will be summarized, with some editorial comments.

Keywords. Ordering Elements, Periodic Table, History, Understanding Chemistry, Mendeleev Sesquicentennial.

INTRODUCTION

This year we celebrate the 150th anniversary of the periodic system (1869-2019), indisputably "one of the most significant achievements in science, capturing the essence not only of chemistry, but also of physics and biology;[1] ...[the] table it gave birth to hangs in every chemistry classroom in the world and is one of the field's most recognizable symbols. But the solid squares and familiar patterns of today's table mask one of its fundamental characteristics: 'the' periodic table does not exist"[2] and when 'the' table really came into being is a matter of debate. Some would place its beginnings in 1860 at the Karlsruhe Congress, where some 140 European scientists from 11 European countries and Mexico gathered to debate the chaos surrounding fundamental definitions and measurements in chemistry.[3] This was probably the most inconsequential conference ever held in the sense that very little was actually resolved on site. On the last day of the conference, the Italian chemist, Stanislao Cannizzaro (1826-1910) of the University of Genoa, described his teaching method regarding the importance of atomic weight. Thanks to one of his colleagues, the conferees went home with a reprint of Cannizzaro's paper published two years earlier in the Italian chemical journal, *Il Nuovo Cimento*, in 1858.[4] The paper stressed the importance of Avogadro's hypothesis which, taken to its logical conclusion, was critical in determining the atomic weights of the elements.[5] By their own admissions, it was this document that inspired the creation of Dmitri Mendeleev's (1834-1907) and Julius Lothar Meyer's (1830-1895) periodic tables.[6] But realizing that we stand on the shoulders of the giants of the past, we cannot forget that it was Antoine Laurent Lavoisier (1743-1794) who, toward the end of the 18th century, published the first credible list of elements upon which all future chemical endeavor was based.[7] From there, it was a matter of intellectual stepping stones that led us to the creation of the periodic table – a perfect illustration of how science makes progress.[8]

PATHWAY TO THE PERIODIC TABLE

Departing from Lavoisier, the first such stepping stone was John Dalton's (1766-1844) revival of the Greek concept of atom in 1805, taking it a step beyond by quantifying relative atomic weights based on hydrogen with a weight of one. What follows is elucidated in much greater detail in Eric Scerri's very helpful paper, "The Discovery of the Periodic Table as a Case of Simultaneous Discovery".[9] In 1829, Johann Döbereiner (1780-1849) discerned a relationship among "triads" of elements in which the central member's atomic weight was the average of those of the other two. He also discerned similarities in their chemical and physical properties, but not all of the known elements fit into his groupings.[10]

A German chemist, Leopold Gmelin (1788-1853), chemist and son of the prominent chemist Johann Friedrich Gmelin (1748-1804), professor at the University of Heidelberg, among other things, worked on the elements' classification. In 1843 he established the basis for expanding Döbereiner's classification system.[11] In addition to those of Julius Quaglio (1833-1899) and Heinrich Adolf Baumhauer (1848-1926), his table is believed to be one of the earliest precursors to the periodic table.[12]

According to Eric Scerri,[13] among Mendeleev's competitors "there was a Danish chemist and mineralogist Gustavus Hinrichs who fled to the United States when he was a young man. He set up a very interesting and rather original periodic system which was arranged like spokes of a bicycle". Hinrichs stated his ideas as early as 1855 and published it in his book *Programme der Atommechanik* in 1867.

In 1862, shortly after the Karlsruhe Congress, geologist Alexandre-Émile Béguyer de Chancourtois (1820-1886) proposed classifying the elements on a cylindrical three-dimensional form arranged in order of Cannizzaro's atomic weights. His resulting "*vis tellurique*" clearly showed periodic trends in the elements.[14] In 1864, William Odling (1829-1921), an attendee of the Karlsruhe Congress and a strong proponent of Cannizzaro's view, published a table containing 57 elements and noted proportional numbers of the elements as seen in successive rows.[15] We can reckon that Béguyer de Chancourtois' and Odling's contributions were giant steps along the way to the development of the periodic table and the latter occurred almost simultaneously with John Alexander Reina Newlands'(1837-1898)[16,17] promulgation of his "law of octaves" in which he arranged the known elements in order of atomic weight, assigned to each an ordinal number (!), and correctly predicted the existence of the then-unknown element germanium. This was a major advance, especially the almost prescient divination of the number 8 before any hint of the existence of electrons or electronic configuration.[18] But we are not there yet.

In 1862, Julius Lothar Meyer published a table containing 27 elements. He classified the elements into six chemical families according to their valences – a first-time conceptual advance in arranging the elements according to their combining power. He published an updated table containing 50 elements two years later, and also predicted the possibility of yet undiscovered elements, but gave no details. Meyer's evolution of thought was brought to a head by his 1870 publication in Liebig's *Annalen*[19] in which he plotted the molar volumes of the elements as a function of atomic weight that clearly showed periodicity. However, since Dmitri Mendeleev had published his table in 1869, a long drawn-out priority dispute arose from which Mendeleev eventually arose the victor – some say because of his longevity: he outlived Meyer by twelve years. Both scientists were honored for their mutual "discovery of the periodic relations of the atomic weights" with the Royal Society of London's Davy Medal in 1882.

MENDELEEV'S DISCOVERY

So, who really discovered the periodic table? The question seems moot since the IYPT was promulgated for 2019, the 150th anniversary of Mendeleev's publication, not Meyer's nor anyone else's. Our own opinion would be to answer "all of the above." We all stand on each other's shoulders. Our ideas come from somewhere and someone else. Mendeleev was indebted to those who went before, most notably Cannizzaro, but also those others who stepped into the roiling sea of elemental chaos and attempted to put some order into it.

The standard version for Mendeleev's discovery reads something like this: on a single day, February 17, 1869 (according to the Julian calendar then in use in Russia), he produced his first variant, which he called an attempt at a system of elements based on their atomic weights and chemical similarity, written on the back of a letter received from a friend. From there he proceeded to two incomplete rough drafts, arranging the elements horizontally so that those closest in atomic weight would fall under one another in the same column. His methodology was to make a card for each of the 63 then-known elements, including its symbol and chief properties, and then arrange the cards by playing a "game" of "chemical solitaire" that led to the full draft table of the elements.[20] Igor Dmitriev, Director of the Mendeleev Museum and Archives at Saint Petersburg State University, takes issue with this version. He claims that Mendeleev discovered the periodic law in the process of writing his textbook, *Principles*, by following a non-linear, complicated, and difficult pathway that occurred in stages involving an enormous amount of work and the reconciliation of often incorrect and contradictory information. In his thinking, Mendeleev denied the existence of sharp boundaries, which almost forced him to construct an initial arrangement of elements that contained three major divisions, or structural blocks, arranged from left to right:

Typical metals	Intermediate elements "with a less sharp chemical character"	Typical non-metals

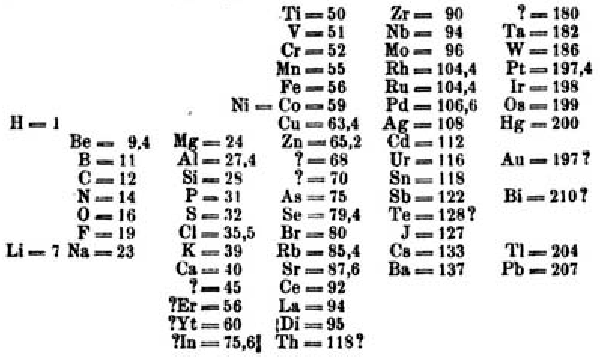
Working with at least five variants of the above structure, Mendeleev was able to confirm in his own mind his two major hypotheses: the causal dependency of the elements' properties on their atomic weights, and the periodic nature of this dependence. It was on the basis of these two fundamental concepts that he drew up the table we are familiar with today, and that he allowed room for yet-undiscovered elements whose properties he uncannily predicted[21] (Figure 1). Note the question marks for elements that would be expected to have atomic weights of 45, 68, and 70. According to Dmitriev, his table did not spring full blown "from the head of Zeus" all in one day.[22]

So, one hundred and fifty years later, we are still struggling with "the" table – or some variant of it, of which there are hundreds. Although the typical classroom-style table has become an icon, with its 18-column main body and two rows of f-block elements arranged in order of increasing atomic number, it does not satisfy the demands placed on it by the development of quantum mechanics and atomic physics. Now we know that one of Mendeleev's principles, that of the causal relationship of the elements to atomic weight, is not the logic that dictates the arrangement. There is also the challenge of reconciling an order based on chemical properties vs. an order based on electron configuration.

A TABLE FOR EVERYONE

As a result of these problems, there is no one standard periodic table. Some chemists prefer a table based strictly on adherence to atomic number as the organizing principle, leading naturally to a 32-column arrangement, favored by Eric Scerri.[23] Another 32-column table, the so-called left step table, devised by Charles Janet (1849-1932) in 1928, based strictly on atomic orbital and electron-filling order, is getting more attention these days.[24] Janet's table follows the Madelung Rule, which Janet intuited before Erwin Madelung (1881-1972) ever even published it! Some scientists think it may be a solution to the f-block-Group 3 dispute.[25,26] For futurists, the 172-element table devised by University of Helsinki theoretical chemist Pekka Pyykkö, is based strictly on calculated electron configurations, effectively bypassing the current placement questions.[27] Carnegie Mellon chemist Paul Karol takes another tack when viewing his crystal ball: he bases his predictions about future synthesis, measurement, and determination of chemical properties of new elements on qualitative, rather than theoretical, considerations.[28]

Consensus has it that there are enough periodic tables to go around for everyone. We can all have our own favorite table. As for us, what works best is best; what is comfortable, like a pair of old slippers, is the favorite.



			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	Pd = 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 1. Mendeleev's 1869 Table as published in the *Russian Journal of Chemistry*, **1869**, *1*, 60 and in the *Zeitschrift für Chemie*, **1869**, *12*, 405-406.

THIS SPECIAL ISSUE

Here is a brief glimpse of the delightful and informative essays that make up this special issue.

Initially, John Emsley takes up the theme of the volume in the title of his paper, "The Development of the Periodic System and Its Consequences." Of the many hundreds of forms of the periodic table that have been proposed, one has come to the forefront: that approved by the International Union of Pure and Applied Chemistry (IUPAC). In his lead-off paper, The Development of the Periodic Table and its Consequences, Emsley traces the 250-year old story of how chemists arrived at it in the first place.

Next, father and son team of Jürgen Heinrich and Alexander Maar discuss the periodic table from the standpoint of its universality in many different senses: geographical, historical, pedagogical and philosophical, as well as what we deem "universal" in virtually every field of human endeavor, from poetry to pop culture to science fiction.

Although the periodic table as we know it had its genesis in the latter half of the 19th century after many tentative "baby steps" along the way toward the concept of the elemental universe as an ordered one, Professor Ferdinand Abbri puts his finger on the driving force for order: the feverish discovery of elements in Scandinavia over the course of the 18th century. The figure of Jöns Jacob Berzelius dominates these efforts through his own vision and classification of substances, influencing the course of scientific thinking throughout the first half of the 19th century.

Orna and Fontani in "Mendeleev's Family," point out that Dmitri Mendeleev himself now occupies a well-deserved place within the periodic system under the title of "mendelevium," element 101, and that, by this attribution, he belongs to a special "family," the actinides. How this family was uncovered, grew, and developed is the topic of their essay.

To be credited with the discovery of an element is a singular honor awarded to only a chosen few. But "discovery" is not a simple issue in terms of priority recognition, neither in the distant past nor the recent present. Professor Helge Kragh explores some of the controversies arising over priority disputes with respect to their reasons and their scientific implications.

Carl Auer von Welsbach (1858-1929) was a world-famous entrepreneur, discoverer, inventor and experimental chemist. In this issue, his work in the field of the rare earths and related elements is described using source material from the archives of the Auer von Welsbach Museum (founded in 1998) heretofore not accessible to the general public. From 1880 to 1882, Auer von Welsbach studied with Robert Bunsen in Heidelberg, specializing in the field of spectral analysis. Using this method, he discovered praseodymium and neodymium in 1885 and ytterbium and lutetium in 1905. Gerd Löffler shows how his three great discoveries in addition – the incandescent mantle, the metal filament lamp, and pyrophoric flint – were the basis for his ongoing exploration of the chemical and physical properties of the lanthanides and actinides.

Since one of the great unifying principles of all science is embodied in the periodic table, an examination of the many extant written documents leading up to its creation and improvement is a rich and rewarding activity. Professor Gregory Girolami reviews and assesses the value of some of these works, spanning a time frame from Boyle and Lavoisier to just before Mendeleev.

The chapter by Seth Rasmussen, "A Brief History of Early Silica Glass: Impact on Science and Society," follows the evolution of silica glass from the wide variety of glass vessels developed in the Roman period to improvements in glass quality through new composition formulae and production techniques that reached their culmination in the borosilicate glasses of the 20th century. The virtually perfect glass for use as chemical glassware would not have been possible without the expansion of our knowledge of new elements via the periodic system.

In 1907, four years after Dmitri Mendeleev's death, St. Petersburg State University, where he lived and worked for forty years, set up the Mendeleev Museum and Archives. Mendeleev's own personal effects form the basis of this remarkable museum, which is well worth a visit. "Mendeleev at Home" describes the contents of the museum, embellished by personal photographs taken during a visit in 2007. This short contribution at the end of this special issue aims to convey the atmosphere in which the most iconic of scientific icons was conceived and developed.

CONCLUSION

We can conclude in no better fashion than to quote the inimitable Peter Atkins for his view of the unique character of the periodic table. "The periodic table is arguably the most important concept in chemistry, both in principle and in practice. It is the everyday support for students, it suggests new avenues of research to professionals, and it provides a succinct organization of the whole of chemistry. It is a remarkable demonstration of the fact that the chemical elements are not a random clutter of entities but instead display trends and lie together in families. An awareness of the periodic table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of chemistry, the chemical elements… for it is a part of scientific culture."[29] And no matter how many areas of chemistry the periodic table has influenced, we can never forget that it was a chemist who provided physicists with the key to unlock the structure of the atom, to perceive its essentially orderly arrangement both physically and mathematically, and to literally give birth to the field of atomic physics. Given the achievements of the past 150 years, we cannot even conceive of the developments to be made over the next 150 years using the periodic table as a tool and guide.

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The Development of the Periodic Table and its Consequences

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Abstract. Chemistry is fortunate among the sciences in having an icon that is instantly recognisable around the world: the periodic table. The United Nations has deemed 2019 to be the International Year of the Periodic Table, in commemoration of the 150th anniversary of the first paper in which it appeared. That had been written by a Russian chemist, Dmitri Mendeleev, and was published in May 1869. Since then, there have been many versions of the table, but one format has come to be the most widely used and is to be seen everywhere. The route to this preferred form of the table makes an interesting story.

Keywords. Periodic table, Mendeleev, Newlands, Deming, Seaborg.

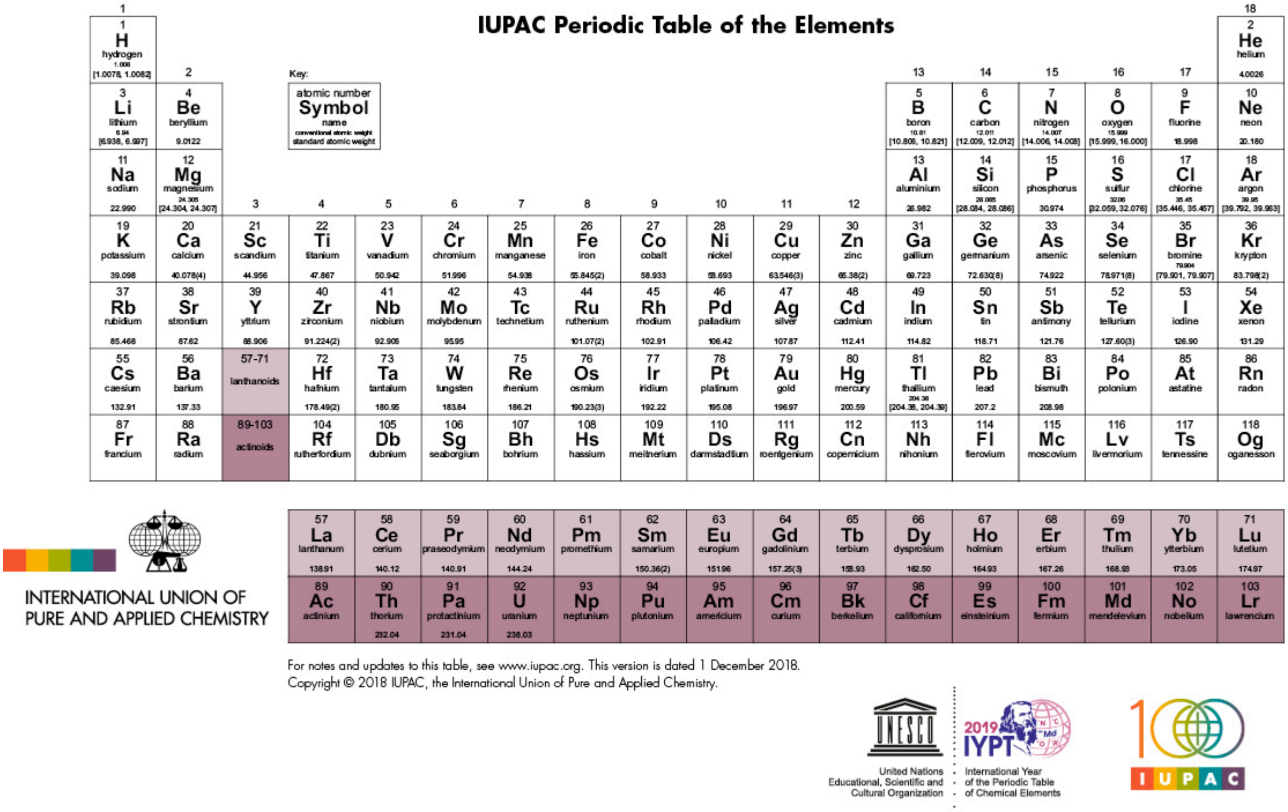
INTRODUCTION

There are hundreds of periodic tables but the one that is widely reproduced has the approval of the International Union of Pure and Applied Chemistry (IUPAC) and is shown in Fig.1. How chemists arrived at this iconic table makes an intriguing story and it can be traced back more than 250 years. However, it has become invariably linked to a man who lived in St Petersburg in the mid-ninteenth century: Dimitri Mendeleev.

EARLY ATTEMPTS TO BRING ORDER TO THE ELEMENTS

The great French chemist, Antoine Laurent de Lavoisier (1743–1794) was interested in the elements and, in 1789, he sought to bring order to them in his book *Traité Elémentaire de Chemie* (*Elements of Chemistry)*[1]. In this he listed 33 substances which he regarded as elements – see Fig. 2.

Lavoisier separated them into four categories that we could describe as *Gases,* which comprised light, heat, oxygen, nitrogen, and hydrogen; *Nonmetals,* which consisted of sulfur, phosphorus, carbon, chloride, fluoride, and borate; *Metals,* this was the largest group with antimony, arsenic, bismuth, cobalt, copper, gold, iron, lead, manganese, mercury, molybdenum, nickel, platinum, silver, tin, tungsten, and zinc; and *Earths,* which were lime, mag-



IUPAC Periodic Table of the Elements

Key:
atomic number
Symbol
name
conventional atomic weight
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H hydrogen 1.008 [1.0078, 1.0082]																	2 He helium 4.0026
3 Li lithium 6.94 [6.938, 6.997]	4 Be beryllium 9.0122											5 B boron 10.81 [10.806, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990	12 Mg magnesium 24.305 [24.304, 24.307]											13 Al aluminium 26.982	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.95 [39.792, 39.963]
19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2)
37 Rb rubidium 85.468	38 Sr strontium 87.62	39 Y yttrium 88.906	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906	42 Mo molybdenum 95.95	43 Tc technetium	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.91	46 Pd palladium 106.42	47 Ag silver 107.87	48 Cd cadmium 112.41	49 In indium 114.82	50 Sn tin 118.71	51 Sb antimony 121.76	52 Te tellurium 127.60(3)	53 I iodine 126.90	54 Xe xenon 131.29
55 Cs caesium 132.91	56 Ba barium 137.33	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.95	74 W tungsten 183.84	75 Re rhenium 186.21	76 Os osmium 190.23(3)	77 Ir iridium 192.22	78 Pt platinum 195.08	79 Au gold 196.97	80 Hg mercury 200.59	81 Tl thallium 204.38 [204.38, 204.39]	82 Pb lead 207.2	83 Bi bismuth 208.98	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson

57 La lanthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium	62 Sm samarium 150.36(2)	63 Eu europium 151.96	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 173.05	71 Lu lutetium 174.97
89 Ac actinium	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

For notes and updates to this table, see www.iupac.org. This version is dated 1 December 2018.

Figure 1. The periodic table.

nesia, barytes, alumina, and silica. Lavoisier and his colleagues suspected that the 'earths' were probably capable of being broken down further and he wrote: 'We may even pressume that the earths may soon cease to be considered as simple bodies.'

Clearly light and heat were wrongly classified as elements, and borate was boron-with-oxygen, as were the earths which were the oxides of calcium, magnesium, barium, aluminium and silicon. Technology of the time could not decompose them further. Heating a mineral with carbon in a furnace would generally remove all the oxygen as CO_2, but for some minerals this did not happen, hence Lavoisier's belief that these were fundamental elements.

In all, his list included 26 that we now know to be true elements. However, he made no attempt to organise his list into elements with similar properties, so his list cannot be regarded as a fore-runner to the periodic table, although he might have eventually listed the elements in other ways, had he not been guillotined in 1794.

Meanwhile chemistry was undergoing a major shift with the writing of John Dalton who, in 1805, not only proposed that elements must exist as single atoms but he calculated their relative weights.

The next attempt to bring order to the elements was a theory put forward in 1815 by 30-year-old William Prout (1785–1850). He submitted a paper entitled 'On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms' and he asked that it be published anonymously, although it became known he was the author.[2]

In this paper he proposed that all elements had relative weights, so-called 'equivalent weights', which were multiples of the weight of hydrogen, taken as 1. His theory would explain why so many weights were whole numbers, or nearly so. It was a far-sighted suggestion, and today we know the explanation is that 99.98% of the mass of an atom resides in its nucleus which is made up of protons and neutrons both of unit mass. Because the majority of elements have one dominant isotope, this explains why their weights are whole numbers. However, there were several important exceptions, such as chlorine (35.5), copper (63.5), and zinc (65.4) which have a variety of isotopes.

Charles Daubeny (1795-1867) was appointed Professor of Chemistry at Oxford University in 1822. He

	Noms nouveaux.	Noms anciens correſpondans.
Subſtances ſimples qui appartiennent aux trois règnes, & qu'on peut regarder comme les élémens des corps.	Lumière	Lumière.
	Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
	Oxygène	Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué. Mofète. Baſe de la mofète.
	Hydrogène	Gaz inflammable. Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobalt	Cobalt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtène.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'epſom.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

Figure 2. Lavoisier's classification of the elements.

produced a panel listing 20 elements with their relative weights, which still exists, and his listing was reproduced in the third edition of E. Turner's *Elements of Chemistry*, published in 1831. However, the list in no way corresponds to a periodic table.

Another chemist to make a contribution to classifying the elements was Johann Döbereiner (1780 – 1849). In 1829 he announced his Law of Triads.[3] He called it 'an attempt to group elementary substances according to their analogies'. He had noticed that of three chemically similar elements, the weight of the middle element was the average of the lighter and heavier members. Lithium-sodium-potassium formed such a triad, and others were chlorine-bromine-iodine and sulfur-selenium-tellurium. By 1843, ten such triads had been identified.

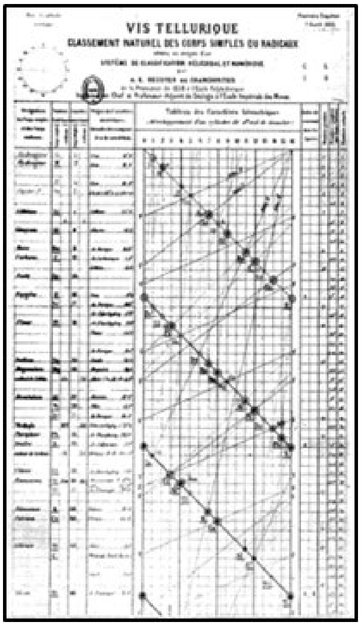


Figure 3. Chancourtois' listing of the elements [Reproduced by kind permission of the Master and Fellows of St Catherine's College, Cambridge].

The first attempt to arrange all known elements in a regular pattern was made in 1862 by a French geologist Alexandre-Émile Béguyer de Chancourtois (1820–1886). He wrote a list of them on a piece of tape, in order of weight, and then wound this spiral-like around a cylinder. The cylinder surface was divided into 16 parts, based on the atomic weight of oxygen. Chancourtois noted that certain triads came together down the cylinder, such as lithium, sodium and potassium whose atomic weights are 7, 23 (7+16), and 39 (23+16). This coincidence was also true of the tetrad oxygen-sulfur-selenium-tellurium. He called his model the *Vis Tellurique* (Telluric Screw) and published it in 1862[4] – see Fig.3. This was the first formulation which revealed the periodicity of the elements.

A boost to element discovery came with the development of atomic spectroscopy in 1859 by Bunsen and Kirchhoff in Germany. This revealed that each element had a unique pattern of lines in its visible spectrum. Because an element always gave the same pattern, no matter its source, it was realised that here was a technique for uncovering new elements. Merely submitting a mineral to atomic spectroscopy, immediately showed whether a new element was present. As a result, rubidium, caesium, and thallium were announced in the years 1860-1863.

In 1860, the Italian chemist Stanislao Cannizzaro (1826–1910) presented a paper to the First International

Chemical Congress, at Karlsruhe in which he gave the *atomic* weights of the known elements.[5] A young Russian chemist, Dimitri Mendeleev, who was doing postgraduate research in Germany, was in the audience and picked up a copy of the list and took it back to St Petersburg when he returned there in 1861. Previously, chemists had used so-called equivalent weights determined from their oxides, and which were variable.

An attempt to classify the elements was made by an Englishman, 27-year old John Alexander Reina Newlands (1837–1898). In 1863 and 1864 he had published papers dealing with relative weights and in 1864 he gave a talk entitled 'The Law of Octaves' at a meeting of the London Chemical Society. He had arranged 56 elements into groups and noted that there seemed to be a periodic repetition of similar properties at intervals of eight. The title of his talk was chosen by analogy with octaves in music. It was an inappropriate choice, and it is said that one member of his audience sarcastically asked Newlands whether he had ever thought of arranging the elements in alphabetical order instead. The society's journal refused to publish his talk as a paper. However, he wrote accounts in *Chemical News*, in 1864[6]and 1865,[7] so we know what he was proposing. Eventually, the Royal Society of London awarded him its prestigious Davy Medal in 1887 in belated recognition of his achievements, and given 'for his discovery of the periodic law of the chemical elements'.

Also, in London at the time was William Odling (1829–1921), who was at the Royal Institution. He also came near to devising the first periodic table. He published a paper in 1864 in the *Quarterly Journal of Science* entitled: 'On the proportional numbers of the elements'. He arranged the known elements in the same way as Mendeleev was to do, and he too even left gaps where there were missing elements. However, unlike Mendeleev, he didn't have the confidence to predict their existence and physical properties. Odling even left gaps that were later to be filled by helium and neon, long before the noble gases had been discovered.

Periodicity among all the elements had been noticed by the German chemist Julius Lothar Meyer (1830–1895). He drew a graph of atomic volumes of the 49 elements then known versus their atomic weights which showed a periodic rise and fall: Fig. 4. He also devised a periodic table of elements. He wrote a paper and gave it to a colleague, Professor Adolf Remelé, (1839–1915), asking for his comments. Unfortunately, these were slow in coming, and before he could submit it for publication, Mendeleev's definitive paper had appeared. Meyer's version was eventually published in 1870,[10] only a few months after Mendeleev's paper.

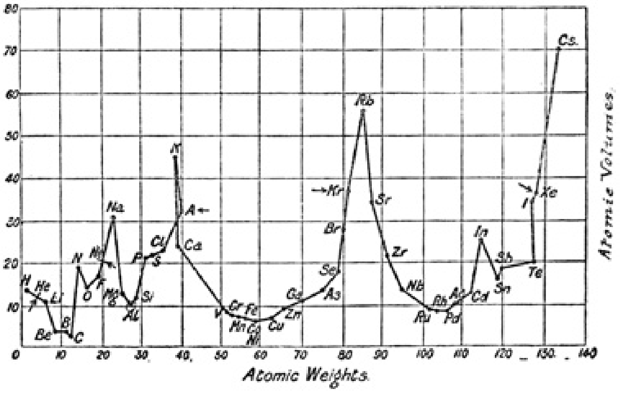


Figure 4. Lothar Meyer's graph showing periodicity.

DMITRI IVANOVICH MENDELEEV (1834–1907)
ДМИТРИЙ ИВАНОВИЧ МЕНДЕЛЕЕВ

In 1867, 35-year-old Dmitri Ivanovich Mendeleev began to write a textbook: *The Principles of Chemistry*. (This was published as a two-volume work in 1869 (vol.1) and 1871 (vol.2), and was translated into other languages.) He wondered how best to deal with the many elements with their diverse properties. He became obsessed with bringing some kind of order to the 63 elements then known, and he told his colleague A.A. Inostrantcev that he had spent sleepless nights wrestling with the problem.

Mendeleev's discovery of the periodic table is said to have occurred on February 17th. This was the date based on the ancient Julian calendar still in use in Russia. For the rest of Europe, using the Gregorian calendar, it was March 1st. On that day he had planned to visit a local cheese factory, but decided instead to work in his study.

He had written details of every element and its physical properties on pieces of card, including its atomic weight, and the formulae of any hydrides and oxides which it formed, these indicating its valency or oxidation states. He then began to arrange the cards in various ways, until one arrangement seemed to him to be the best and he wrote that down on an envelope which still exists: see Fig. 5. Its printed version is Fig. 6, from a paper he submitted to the *Russian Journal of Chemistry*, this was a new publication of the Russian Chemical Society which he had helped to set up. It appeared in May of that year.[9]

What Mendeleev had done eventually made him one of the most famous scientists of all time. He also sent copies of his table of elements to other chemists, calling it '*Essai d'une systeme des elements d'après leur poids atomiques et fonctions chemiques*' (Assessing a system of elements according to their atomic weights and chemical functions.) He wrote in French because this was the for-

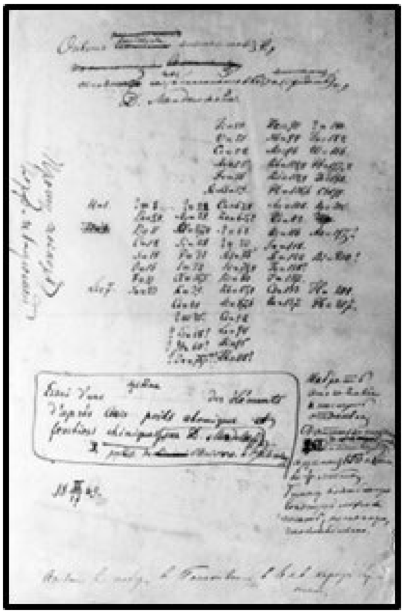


Figure 5. Mendeleev's envelope with the first periodic table.

Figure 6. The periodic table in Mendeleev's first paper.

eign language he had been taught at school and he had spent a little time in Paris when he was doing a postgraduate course in Germany under Robert Bunsen.

What Mendeleev had announced was fundamental to chemistry and science. In effect he was saying that the chemical elements conformed to a pre-determined pattern of relationships which we now call the periodic table. What followed was to transform a large part of chemistry from a disorganised jumble of facts into a disciplined science.

Mendeleev's periodic arrangement of the elements might easily have gone unnoticed, but his paper was summarised in the leading German journal, *Zeitschrift für Chemie*, and so got wide publicity. By 1872 his table had been rearranged so that the groups were vertical rather than horizontal – see Fig 7. Also, Mendeleev's first table had some elements in the wrong place because he had ranked them in order of atomic weights and these were not always reliable. These faults were soon corrected.

Mendeleev was so sure that he was right in his concept of a periodic table, that he could see there were elements missing. He predicted that these must exist and for some of them he gave their likely physical properties, such as melting point, density, and basic chemistry.

The first of these was discovered in 1875 by Paul-Émile de Boisbaudran (1838–1912) and he called it gallium. He measured its properties, including the density, which he said was 4.7 g/cm^3. He was then told that his new element was the missing one in group III of Mendeleev's table and that he had predicted its properties, for which its density would be 5.9 g/cm^3. Boisbaudran was alerted to this by Mendeleev and so checked his measurements and discovered he had made an error; the correct density was 5.956 g/cm^3 just as Mendeleev has said.

In 1879, the Swedish chemist, Lars Nilson (1840–1899), discovered scandium. It too had the properties Mendeleev predicted. It was also in column III and came below boron, and he had referred to it as eka-boron. Its atomic weight was 44 (Mendeleev predicted 44) and its density was 3.86 g/cm^3 (Mendeleev predicted 3.5 g/cm^3).

Finally, in 1886, the German chemist, Clemens Winkler (1388–1902), discovered germanium, which was almost exactly as Mendeleev had predicted for the element below silicon in group IV, right down to the density of its oxide which he said would be around 4.7 g/cm^3 and turned out to be 4.703 g/cm^3. He said that the boiling point of its chloride would be a few degrees below 100°C. It was 86°C.

Mendeleev's table had eight columns with the Roman numerals I to VIII, corresponding to the chemical valencies (oxidation states) of the elements. This property was revealed by the chemical formula of the highest oxide. Yet it brought together elements that were quite dissimilar, such as metals and non-metals. For example, in group V we find vanadium and phosphorus, which have almost no chemistry in common. Mendeleev consequently split the columns of his periodic table into two sub-groups labelled A and B. Vanadium was in VA, phosphorus in VB. The same pattern was repeated in the other columns with the exception of group VIII which

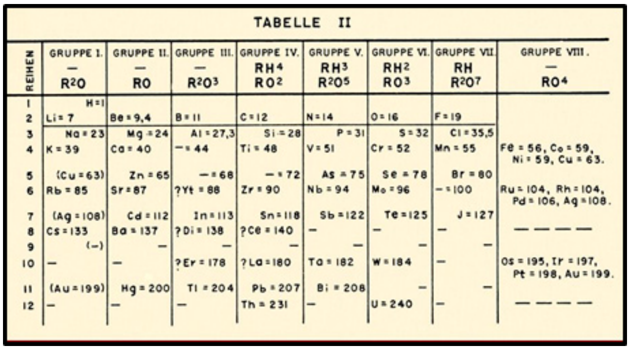


TABELLE II

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	—	— — — —

Figure 7. The first periodic table with vertical groups.

contained metals that were very similar and which occurred in sets of three. These were iron-cobalt-nickel, ruthenium-rhodium-palladium and osmium-iridium-platinum.

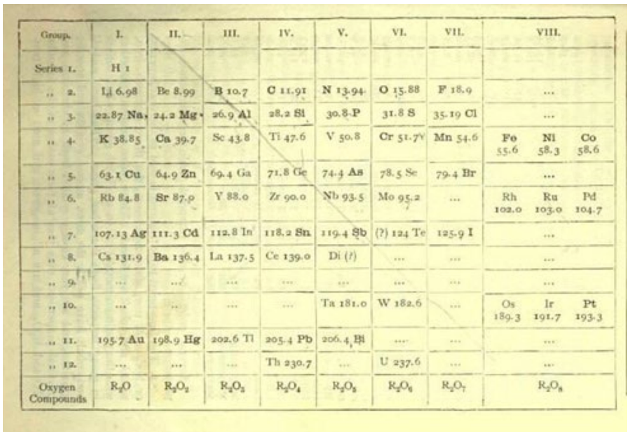
Mendeleev was to become a celebrity chemist. He visited many other countries, and won many awards such as the Copley Medal of the Royal Society of London, their highest award which had been founded in 1737. (The list of scientists given this award includes Charles Darwin, Dorothy Hodgkin, and Albert Einstein.)

For reasons that are still unclear, Mendeleev failed to gain a Nobel Prize despite being nominated three times, in 1905, 1906 and 1907, the year before he died. Had he lived another year or two it is more than likely he would eventually have been rewarded this way, but Nobel prizes can only be given to living scientists.

EARLY PERIODIC TABLES AND NEW ELEMENTS

Basically, there have been two approaches to devising a periodic table. The first lists all the elements in a continuous line, rather like the numbers on a tape measure, and this is then looped in such a way that like elements come together. The second version chops the tape into segments and stacks these in rows or columns so as to bring together elements with similar chemical properties. The former approach is what Chancourtois had used in 1862 for his telluric screw, and what many others have done since. The table versions are direct descendants of Mendeleev's table.

An example of an early periodic table – Fig.8 – can be found in the book by Henry Roscoe (1833–1915) and Carl Schorlemmer (1834-1892) called a *Treatise on Chemistry*. This was a comprehensive two volume text of 2400 pages, which first appeared in 1878 and was reprinted many times.[12] This did not sub-classify elements into A and B columns, although it placed them in alternative rows as in later editions.



Group.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
Series 1.	H 1									
,, 2.	Li 6.98	Be 8.99	B 10.7	C 11.91	N 13.94	O 15.88	F 18.9	...		
,, 3.	22.87 Na	24.2 Mg	26.9 Al	28.2 Si	30.8 P	31.8 S	35.19 Cl	...		
,, 4.	K 38.85	Ca 39.7	Sc 43.8	Ti 47.6	V 50.8	Cr 51.7	Mn 54.6	Fe 55.6	Ni 58.3	Co 58.6
,, 5.	63.1 Cu	64.9 Zn	69.4 Ga	71.8 Ge	74.4 As	78.5 Se	79.4 Br	...		
,, 6.	Rb 84.8	Sr 87.0	Y 88.0	Zr 90.0	Nb 93.5	Mo 95.2	...	Rh 102.0	Ru 103.0	Pd 104.7
,, 7.	107.13 Ag	111.3 Cd	112.8 In	118.2 Sn	119.4 Sb	(?) 124 Te	125.9 I	...		
,, 8.	Cs 131.9	Ba 136.4	La 137.5	Ce 139.0	Di (?)	...	...	...		
,, 9.	...	...	...	...	...	...	...	...		
,, 10.	...	..	...	...	Ta 181.0	W 182.6	...	Os 189.3	Ir 191.7	Pt 193.3
,, 11.	195.7 Au	198.9 Hg	202.6 Tl	205.4 Pb	206.4 Bi	...	...	...		
,, 12.	...	...	...	Th 230.7	...	U 237.6	...	...		
Oxygen Compounds	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8		

Figure 8. Textbook version of the periodic table – 1913.

Although Mendeleev did not realise it, there was a group of elements missing from his table. These were the noble gases, and when they were discovered 30 years later, they were to exert an influence on the way the table was perceived. Roscoe and Schorlemmer's later editions contained these elements.

The lightest noble gas, helium, had in fact been reported the year before Mendeleev produced his table. It had been detected by the French astronomer, Pierre J. C. Janssen (1824–1907), on Tuesday 18th August 1868. He had travelled to India to study the total eclipse that would be observed there. Thankfully the sky was not overcast with clouds, and he was able to record the corona spectrum, which clearly showed an unknown element was present. Later that same week, two British astronomers, Norman Lockyer (1836–1920) and Edward Frankland (1825–1899), viewed the sun through a London fog and observed the same spectrum. Lockyer expected the new element to be a metal and so he called it helium, deriving the name from Helios, the ancient Greek sun god. Some chemists thought he was being presumptuous in finding a new element on the Sun and having the effrontery to name it. However, they were wrong – and so was he. It was a new element, but it was not a metal; it was a gas.

Helium is also present in the Earth's atmosphere but only in infinitesimally small amounts – 5 p.p.m. – as it is continually being lost to space. It is also present in uranium minerals that emit alpha particles which are the nuclei of helium atoms. In 1888, the US geologist William Hillebrand (1853-1925) noted that the mineral uraninite (UO_2) gave off bubbles of gas when dissolved in acid, but he could not identify it. Per Teodor Cleve

(1840–1905) at Uppsala, Sweden, in 1895, confirmed that the gas was helium.

Another unreactive gas was discovered in 1894, by Lord Rayleigh (1842–1919) and William Ramsay (1852–1916). They were intrigued by the discrepancy in the density of nitrogen gas that was extracted from air, compared to that which was formed by the decomposition of ammonia. The difference was a mere 0.05% but Rayleigh did not believe his density measurements were wrong and deduced that the nitrogen produced from air must be contaminated with another gas. He went on to isolate this and it was essentially argon which constitutes around 1% of the air and it is formed when the potassium isotope ^{40}K undergoes radioactive decay.

Ramsay now realised that helium was not a unique element, but was head of a group that was missing from the periodic table. He began the search for them and discovered three gases: neon (atomic weight 20), krypton (84) and xenon (131), which he extracted from liquid air. The element at the bottom of the group is radioactive radon, whose longest-lived isotope is ^{222}Rn with a half-life of only 3.8 days. This element was discovered by Friedrich Ernst Dorn (1848–1916) in 1900, and he discovered it as the gas which collected in sealed ampules containing radium.

Although the first inclination of chemists was to place the noble gases at the left-hand side of the periodic table because their valency was 0, they are now on the right-hand side and this is the logical location when we regard the rows of elements as additions to the various electron shells surrounding the nucleus, each being completed with a noble gas.

Moseley's system of numbering the elements – see below – revealed that those of atomic number 43, 61, 72, 75, 85, 87 and 91 were as yet unknown. These are all radioactive elements with short half-lives. Technetium (43) was first obtained in 1937 when Emilio Segrè (1905–1989) and Carlo Perrier (1886–1948) at the University of Palermo in Sicily separated it from a sample of molybdenum which had been bombarded with deuterons in the cyclotron at the University of California, Berkeley. (Segrè was to be dismissed from his academic post in 1938 because he was opposed to Mussolini's fascist regime, so he emigrated to the USA.)

Promethium (61) was claimed in 1938, by a group at Ohio State University but they lacked chemical proof that it was the missing element and, at that time, such proof was deemed as essential to support a claim for a new element. Then, in 1945, a group at Oak Ridge, Tennessee, USA, were able to separate isotope-147 of element-61 and so were able to confirm it as required. Element 61 was also made using a cyclotron to bombard neodymium with atoms of deuterium.

Element 78 (francium) was extracted from actinium in 1939 by Marguerite Perey (1909–1975) at the Curie Institute, Paris, France.

Element 85 (actinium) had been discovered by Andre Debierne (1874–1949) in 1899 and he extracted it from the uranium ore pitchblende. It was later made by bombarding bismuth (element 83) with alpha particles in a cyclotron, and this was achieved by a group at Berkeley which now included refugee Segrè. The isotope produced had a half-life of 8.3 hours which they named astatine from the Greek word *astatos* (unstable).

A dilemma of the periodic table in its earliest form was that some elements did not fit the strict sequence of ordering by atomic weight. Why did some elements have higher atomic weights than others which came after them in the table? The best example of this was the tellurium/iodine conundrum, with the former having atomic weight 127.6 while the latter's atomic weight is 126.9. Mendeleev was sure that the atomic weight of tellurium had to be wrong; it had to be less than that of iodine, so he used a value of 125, that had been determined by a Czech chemist Bohuslav Brauner.

In 1911, the English radiochemist Frederick Soddy (1877–1956) proved that elements had isotopes, which finally resolved the issue of pair reversal, thereby allowing an element of larger atomic weight legitimately to occupy a position in the table before its neighbour.

Transuranium element 93 had been wrongly claimed but never confirmed before it was finally produced in 1939 by Edwin McMillan (1907-1991) and Philip Abelson (1913-2004) at Berkeley in 1940. It had a half-life of 2.3 days. The named it neptunium based on the planet which comes beyond Uranus after which uranium (element 92) had been named. This element occurs naturally in uranium ores as a result of radioactive decay processes. Its longest-lived isotope is Np-237, with a half-life 2.14 million years.

Elements beyond uranium were produced in various ways using nuclear processes in the 1950s, 1960s… and in the current century. Eventually a group of Russian and American scientists, working at the Joint Institute for Nuclear Research in Dubna, near Moscow, were able in 2002 to produce atoms of the element at the end of the bottom row (7p) of the periodic table which is oganesson.

THE LONG FORM OF THE PERIODIC TABLE

From the time of Mendeleev's first periodic table in 1869, it has undergone several changes, although we can still recognise some of Mendeleev's original groups such as the halogens (now group 17). Despite advances in atomic theory, Mendeleev's 8-column periodic table remained in use for almost a hundred years. Eventually, the so-called long-form gradually displaced it as man-made elements were announced and interest focussed on the final row.

Today the standard version is the long-form: Fig.1. This was first advocated by the Swiss inorganic chemist Alfred Werner (1866-1919) in 1905, and had 18 columns, with two rows for the lanthanoids and actinoids. (These were previously referred to as lanthanides and actinides.)

So why did the long-form periodic table become the preferred one, compared to the hundreds of others which have been suggested? The answer is that it is logical, easy to understand, and to extract information from.

When designing a periodic table of elements, the primary data which determines their arrangement is atomic number. Clearly such a linear sequence of elements has to be organised in some way, and the most obvious guideline is the one which Mendeleev used, i.e. to place elements with similar properties in table format, with lightest elements at the top and with increasing atomic weight as you descend the group.

Although Mendeleev was not aware of it, he had based his table on the two basic properties of an element: the number of protons in its nucleus and the occupancy of its electron shells.

Understanding the periodic table came only with the discovery of the electron in 1896 by J.J. Thompson (1856-1940), the proton in 1911 by Ernest Rutherford (1871-1937), and the neutron in 1932 by James Chadwick (1891-1974). In 1904 a Japanese scientist, Hantaro Nagaoka (1865-1950), put forward the theory that atoms consisted of a central nucleus around which electrons circulated. In 1909 Ernest Rutherford proved that the nucleus was tiny and positively charged, which he did by bombarding a piece of very thin gold foil with alpha particles, and observed almost all of these passed through and that very few encountered an atom. It appeared that atoms consisted of a tiny, positively-charged nuclei in which almost all the mass was concentrated.

In 1913, the physicist Henry G.J. Moseley (1887–1915) formulated the property of atomic number in his paper[8] entitled 'The high-frequency spectra of the elements.' This we now know to be the number of protons of positive charge in the nucleus. He showed that the sequence of elements in the periodic table was really in the order of their atomic numbers. Sadly, he was shot by a sniper in World War I. That same year, Niels Bohr (1885–1962) linked the form of the periodic table to the atomic structure of atoms.

The electronic composition of the elements explains today's arrangement of the periodic table with its s, d, p, and f blocks. These reflect the occupancy of electron orbitals around the atomic nucleus, these being 2 (s), 6 (p), 10 (d), and 14 (f). The order in which these are filled, results in the extended long-form of the periodic table with rows of 2, 8, 8, 18, 18, 32, and 32 elements. Combinations of these numbers give rise to 8 (= 2+6), 18 (= 2+6+10) and 32 (= 2+6+10+14) which are the lengths of the various rows of the table.

The orbital nearest the nucleus is just a single orbital and labelled 1s, the next is a pair of orbitals labelled 2s and 2p, the next is a trio of orbitals, 3s, 3p and 3d, and so on. However, these begin to overlap, so that the next one, 4s, is actually occupied before the 3d sub-orbital..

The sub-orbitals can hold increasing numbers of electrons and these are the basis of the various blocks of the periodic table. The s-block consist of two groups (numbered 1, the alkali metals, and 2, the alkaline earths), the p-block elements consist of six groups (numbered 12 to 18), some of which have also got names such as the chalcogens (group 16) and the halogens (group 17). The d-block elements have ten groups (numbered 3 to 11), and the f-block elements consist of two rows 4f and 5f which are not given group numbers.

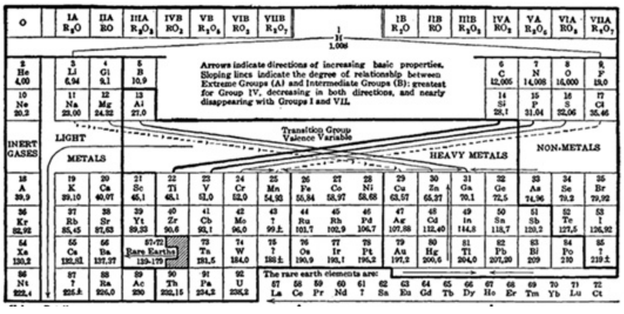
At first approximation, the order of occupancy of orbitals is as follows: 1s / 2s, 2p / 3s, 3p / 4s, 3d, 4p / 5s, 4d, 5p / 6s, 4f, 5d, 6p / 7s, 5f, 6d, 7p. It still remains to be satisfactorily explained by quantum mechanics.

If the elements are arranged in rows of increasing atomic number, and in columns having the same electron outer shell, then we arrive at the long form of the periodic table. Across a row of the periodic table we are adding electrons to a particular shell until that shell is full when we arrive at one of the noble gases. Consequently, these represent a natural break in the table.

However, the long-form of the periodic table predates our knowledge about electron configuration, and it first appeared in 1923 when the American chemist Horace G. Deming (1885–1970) created it for his textbook *General Chemistry* – see Fig. 9.

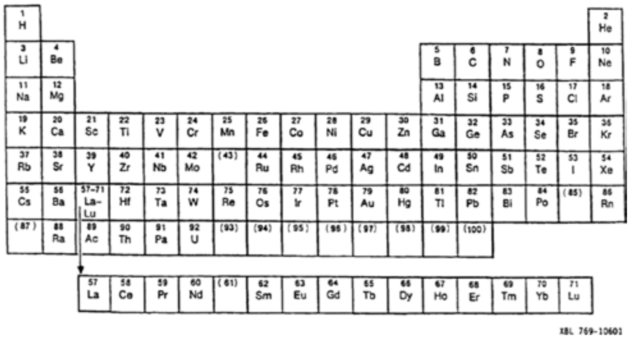
He placed the lanthanoids at the bottom of the table. He referred to them as 'rare earths' although some are relatively abundant. The value of Deming's table was soon appreciated, and within a few years it was widely used. The pharmaceutical company Merck employed it in its advertising. It was also distributed to American schools as a teaching aid.

In an internal document of the Lawrence Berkeley Laboratory of the late 1930s there is a periodic table closely resembling the modern form (Figure 10). However, it places thorium below hafnium, protactinium below tantalum, and uranium below tungsten.



0	IA R_2O	IIA RO	IIIA R_2O_3	IVB RO_2	VB R_2O_5	VIB RO_3	VIIB R_2O_7				IB R_2O	IIB RO	IIIB R_2O_3	IVA RO_2	VA R_2O_5	VIA RO_3	VIIA R_2O_7
									1 H 1,008								
2 He 4,00	3 Li 6,94	4 Gl 9,1	5 B 10,9											6 C 12,005	7 N 14,008	8 O 16,000	9 F 19,0
10 Ne 20,2	11 Na 23,00	12 Mg 24,32	13 Al 27,0											14 Si 28,1	15 P 31,04	16 S 32,06	17 Cl 35,46
18 A 39,9	19 K 39,10	20 Ca 40,07	21 Sc 45,1	22 Ti 48,1	23 V 51,0	24 Cr 52,0	25 Mn 54,93	26 Fe 55,84	27 Co 58,97	28 Ni 58,68	29 Cu 63,57	30 Zn 65,37	31 Ga 70,1	32 Ge 72,5	33 As 74,96	34 Se 79,2	35 Br 79,92
36 Kr 82,92	37 Rb 85,45	38 Sr 87,63	39 Yt 89,33	40 Zr 90,6	41 Cb 93,1	42 Mo 96,0	43 ? 99±	44 Ru 101,7	45 Rh 102,9	46 Pd 106,7	47 Ag 107,88	48 Cd 112,40	49 In 114,8	50 Sn 118,7	51 Sb 120,2	52 Te 127,5	53 I 126,92
54 Xe 130,2	55 Cs 132,81	56 Ba 137,37	57-72 Rare Earths 139-175		73 Ta 181,5	74 W 184,0	75 ? 188±	76 Os 190,9	77 Ir 193,1	78 Pt 195,2	79 Au 197,2	80 Hg 200,6	81 Tl 204,0	82 Pb 207,20	83 Bi 209	84 Po 210	85 ? 219±
86 Nt 222,4	87 ? 225±	88 Ra 226,0	89 Ac 230	90 Th 232,15	91 Pa 234,2	92 U 238,2	The rare earth elements are:										
							57 La 58 Ce 59 Pr	60 Nd 61 ?	62 Sa 63 Eu	64 Gd 65 Tb	66 Dy 67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Ct	

Figure 9. The Deming periodic table of 1923.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	(43)	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57–71 La–Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	(85)	86 Rn
(87)	88 Ra	89 Ac	90 Th	91 Pa	92 U	(93)	(94)	(95)	(96)	(97)	(98)	(99)	(100)				
		57 La	58 Ce	59 Pr	60 Nd	(61)	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	

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Figure 10. The Lawrence Berkeley periodic table of the 1930s.

In 1929, the amateur French chemist Charles Janet (1849–1932) came up with an extended long form of the table – see Fig. 11.

Mendeleev knew of thorium and uranium, and their chemistry made them suitable to place in his groups IV and VI respectively. And so, things remained, until synthetic elements started to be produced in the 1940s. Then, in 1942, the American chemist Glenn T. Seaborg (1912–1999) drew the table in the form we know today with the f-block elements shown as a separate group below the d-block. Seaborg's colleagues at the University of California advised him not to publish his table as it was mere speculation, but he went ahead anyway and today we have names for all 15 of these elements. Eventually the number of artificially produced elements has extended the periodic table to element 118 (organesson); atoms of this lasted all a fraction of a millisecond. (Its half-life is 0.89 milliseconds.) Whether physicists can extend the table further remains to be seen.

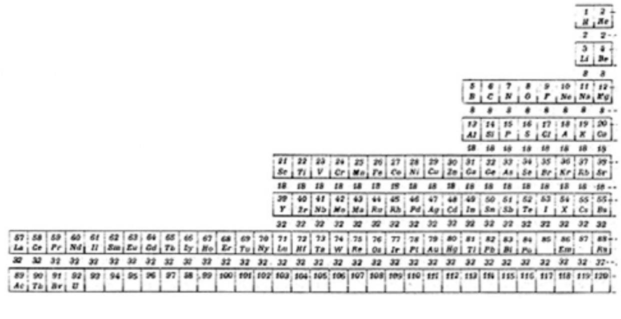

Figure 11. Charles Janet's table of 1929.

Seaborg avoided the controversy of which elements should go below scandium and yttrium in group 3 – lanthanum and actinium, or lutetium and lawrencium. He put all of them in the f-block, giving it 15 elements instead of the 14 which theory demands, and this is the table that the International Union of Pure and Applied Chemistry (IUPAC) has on its website – see Fig 1. Seaborg was eventually to be honoured by having element 106 named after him: seaborgium.

NUMBERING OF THE GROUPS

The normal periodic table has 18 columns numbered 1 to 18, but it was not always so. Before IUPAC judged this to be the preferred configuration, there were other conventions, including Roman numerals and letters.

The change-over from the 8-column periodic table to the modern form was not without its difficulties. When Mendeleev's periodic table of 8 groups was turned into the long form of 18 groups, the Europeans numbered the groups on the left-hand side IA to VIII, and on the right-hand side they were numbered IB to VIIB, thus:

IA, IIA, IIIA, IVA, VA, VIA, VIIA, VIII, IB, IIB, IIIB, IVB, VB, VIB, VIIB, VIIIB

However, the American journals favoured a different classification:

IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA, VIIIA

which was more in keeping with Mendeleev's notation. Both systems numbered the alkali metals groups IA, and the alkaline earth metals IIA but after that they diverged.

The Scandinavians preferred a system based on letters rather than Roman numerals:

M1, M2, T1, T2, T3, T4, T5, T6, T7, T9, M2', M3, M4, M5, M6, M7, M8

With M standing for main groups and T for transition metals. When the American Chemical Society also decided to drop Roman numerals, they use a simple numbering system but differentiated the transition metals groups with a 'd' thus:

1, 2, 3d, 4d, 5d, 6d, 7d, 8d, 9d, 10d, 11d, 12d, 13, 14, 15, 16, 17, 18.

The numbering of groups was tackled in *New Scientist* in January 1984 when readers were asked to comment on the various systems and to suggest alternatives. The response was overwhelming and came from all over the world. Hundreds of letters were received and the consensus was that simply numbering the columns 1 to 18 was best. The International Union of Pure and Applied Chemists (IUPAC) preferred the groups simply be numbered this way and, after much heart searching, the American Chemical Society (ACS) agreed. The f block does not fit into the numbering system but this poses no problem since the 4f and 5f periods of elements are best dealt with as separate rows below the table.

PROBLEMATIC ELEMENTS

We may think that the arrangement of the periodic table has finally been determined, but there are five elements whose position in the table is still debated. They are hydrogen (element atomic number 1), helium (2), lanthanum (57), lutetium (71), and actinium (89).

Hydrogen and **helium.** Because hydrogen has a single s-electron, logic says that it should be in group 1 of the s block, but the other elements in that group are the alkali metals and clearly that is not what hydrogen is. Helium has two s-electrons and so should be in group 2 but it's not a metal either. Helium is a noble gas and so placed at the top of group 18 while hydrogen sits incongruously at the head of group 1. However, helium is not a p-block element so it is out of place in that part of the periodic table. It has been possible for helium to form stable chemical bonds, so maybe Janet was right to put it above beryllium and this is where it is to be found in some tables.

There are tables which place hydrogen by itself, or with helium, in the very centre of the table, floating free above the other elements. Others place hydrogen above fluorine, although it shares little in common with the halogen gases. Some tables give it double billing and place it above both lithium and fluorine. There are other ways of deciding how to place these elements based on their atomic radii or 1st ionisation potentials.

Lanthanum and lutetium. The lanthanoids, elements of atomic numbers 57-71, posed a problem for the early periodic table since only a few of these had been discovered, and yet all seemed to prefer the oxidation state 3 so should come in group III of the periodic table.

The story of rare-earth discoveries began with yttrium in 1794. This metal was contaminated with traces of other rare-earths. First erbium and terbium we extracted from it in 1843, and then erbium yielded holmium in 1878, thulium in 1879, and so on, until finally lutetium was identified in 1907. This came as a result of painstaking work by the French chemist, Georges Urbain (1872-1938) at the Sorbonne in Paris. He called the element lutecium, later changed it to lutetium.

For these elements to be incorporated into the periodic table, they had either to be placed as in the unwieldy extra-long form of the table, or be located in rows beneath the table. The question then arose as to which element should occupy group 3, below scandium and yttrium, with lanthanum (element 57) being the most obvious on as it follows immediately from element 56 (barium), with actinium (element 69) below it.

In 1982, William B. Jensen (1948–) of the University of Wisconsin-Madison took issue with this arrangement. He gave chemical reasons why the element in group 3 of the main table should be lutetium,[11] and many agreed with his point of view. This being so, then the lanthanoids were lanthanum to ytterbium.

Some periodic tables fudge the issue and have both lanthanum and lutetium as part of a 15-member list at the bottom of the table, indicating this with La-Lu in group 3. However, this jars somewhat as there cannot be 15 f-electrons, but this is the arrangement in the IUPAC table of Fig. 1.

In 1902 the Czech chemist Bohuslav Brauner (1855–1935) had said that there should be an element 61, coming between neodymium and samarium. This was confirmed by Moseley in 1914. Attempts were made to discover it and, in the 1920s, chemists in Italy and in America, claimed to have found it. The difficulty with promethium is that the isotope with the longest half-life is Pm-145, and that is only 17.7 years. There was no way that this element could be successfully extracted from terrestrial sources. Tiny amounts do occur in uranium ores as a result of fission, but the calculated amount is around a picogram (10^{-12} g) per tonne of ore.

A more realistic claim to have obtained element 61 was made in 1938 by a group at Ohio State University. They bombarded praseodymium and neodymium with neutrons, deuterons and α-particles in a cyclotron and detected element 61 in the debris. They proposed the name cyclonium for the new element, but their detection of element 61 was not accepted as a discovery because *chemical* proof for the missing element was lacking.

Finally, such proof was forthcoming in 1945 from the work of J.A. Marinsky, L.E. Glendenin, and Charles D. Coryell at Oak Ridge, Tennessee, USA. They had the new technique of ion-exchange chromatography at their disposal and with it they were able to separate isotope-147 of the missing element and analyse it. They wanted to call the element clintonium after the Clinton

Laboratories in which the work was done, until Coryell's wife suggested promethium basing it on the Prometheus of Greek mythology who stole fire from the gods and gave it to humans, and this became its name.

Element 103: Both American and Russian physicists claimed to have been the first to make atoms of atomic number 103, and so complete the actinoid series, giving them the right to name it. In 1958 physicists at the Lawrence Berkeley National Laboratory bombarded curium-244 with nitrogen-14, and californium-252 with boron, and said they had identified it. They named it lawrencium.

Then, in 1965, physicists at the Soviet Union's nuclear research centre bombarded americium-243 with oxygen-18 and obtained atoms of it. They also repeated the Lawrence Berkeley experiment and failed to confirm what the Americans had claimed. The Russians proposed that element 103 be named rutherfordium. This dispute over names was part of a larger issue regarding the claims and names of various new elements in this part of the periodic table. The disputes were only resolved in 1992 when an international committee called the Transfermium Working Group (TWG) met to decide the issue of names. As regards element 103, they decided that the discovery of 103 had been made by both Russian and American laboratories and that the name should be lawrencium; rutherfordium was then to be the name of element 104.

Completing the bottom row of the periodic table became the province of atomic scientists and the strict chemical proof, that had previously to be met to confirm a new element, no longer applied.

CIRCULAR PERIODIC TABLES

Soon after Mendeleev published his table, other chemists suggested other ways of arranging the elements. Among the alternative types of table, a circular arrangement was common and indeed one such table appeared soon after Mendeleev's publication – see Fig. 12. This was proposed by a German mineralogist and chemist, Heinrich Baumhauer (1848–1926), in 1870. He continued to promote this version and produced a cobweb-like table in 1902 – see Fig. 13. Neither version became popular.

In 1957, the Latvian chemist Edward Mazurs compiled a complete list of all 700 known periodic tables and published them in his book: *Types of Graphic Representation of the Periodic System of Chemical Elements.* Today there are more than a thousand, although many are very similar, and logging on to Google images reveals many of them.

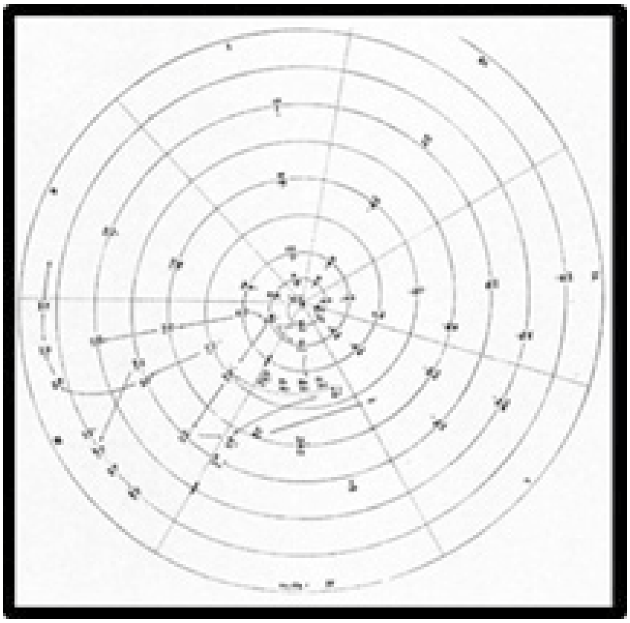

Figure 12. The first circular table.

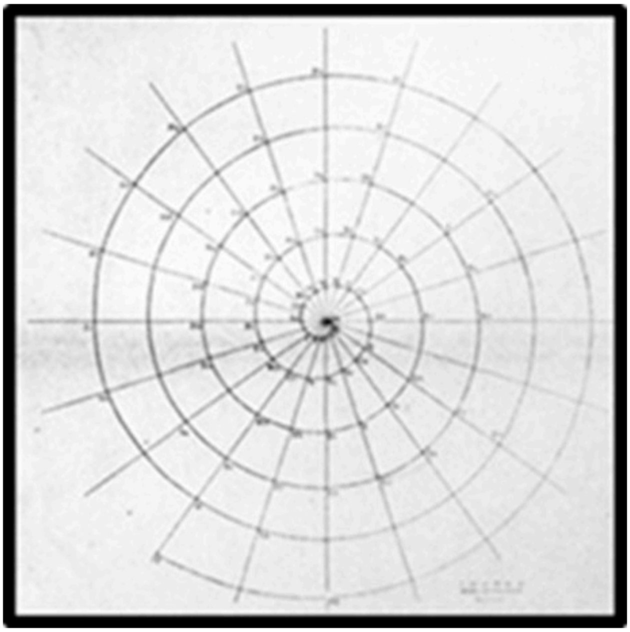

Figure 13. The 1902 table.

Most tables are two-dimensional, but there are several three-dimensional versions and these come in the shapes of cylinders, pyramids, spirals and even trees. These artistic versions can be very attractive and make ideal displays for science exhibitions, but they are not very practical when it comes to teaching chemistry and extracting information about the elements and their relationships.

One circular table which was well publicised was that drawn by Otto Theodor Benfey (1925-). He was born in Berlin but was educated in England, and eventually moved to the USA in 1947. In 1963 he became editor of the ACS magazine *Chemistry,* and in 1964 he published his own circular version of the periodic table in that journal. He justified it by saying that he wanted to highlight the continuity of the elements, and he referred to it as the periodic snail – Fig. 14. Part of his aim was to emphasise the lanthanoids and actinoids and also to include a section for the elements beyond the actinoids.

Circular versions of the periodic table continue to be proposed, but despite their elegance and the tantalising analogy with electrons in shells around a nucleus they all suffer the drawback of being difficult to read and to abstract the information from. Moreover, they tend to crowd together the more important elements at their centre while giving the less important elements more room at the periphery.

Some circular periodic tables verge on being works of art and one such is that devised by Philip J. Stewart of Oxford University which he published in 2007 and which he describes as a galaxy of elements;[12] Fig. 15.

If you want to examine all known tables consult Mark Leach of Manchester, England, who has a complete collection of periodic tables on his website meta-synthesis.com. There is also the website *Internet database* of periodic tables (address : https://www.meta-synthesis.com/webbook/35_pt/pt_database.php?PT_id=943) where there are hundreds of them of bewildering diversity.

A FINAL WORD

It is probably impossible to say definitely that the periodic table which today appears everywhere, in books and lecture theaters, on T-shirts and ties, on TV programmes and in films, is the ultimate version. It will of course change slightly if new elements are produced. Since atoms of these will last for less than a second, then it may appear pointless to extend the table. In which case it is more than likely that the IUPAC table (Fig. 1) will still be the preferred version so long as there is chemistry. And Mendeleev's achievement has been acknowledged by naming an element in his honour: element 101 is Mendeleevium (Md). This was first made in 1955. It is highly radioactive with a half-life of 52 days.

Even if someday we communicate with another part of the universe, we can be sure that one thing both cultures will have in common is an ordered system of the elements that will be instantly recognisable. Perhaps the most artistic periodic table is that by the Glasgow artist, Murray Robertson, which is entitled 'Visual Elements' and for which he had created a stunning computer graphic for each element. This can be accessed, via the Internet, on the Royal Society of Chemistry's web site.

If you wish to access a more dramatic version online, there is the Periodic Table of Videos produced by Nottingham University (www.periodicvideos.com) with presenters Martyn Poliakoff and Pete Licence. Also accessible as an app is the periodic table of Theodore Gray which is also available in book format. Finally, if you want a real hands-on periodic table this is available from RGB Research and produced by Max Whitby and

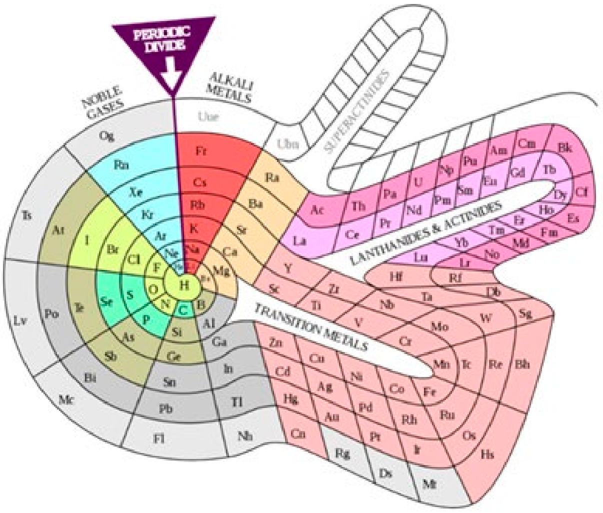

Figure 14. The 'snail' periodic table.

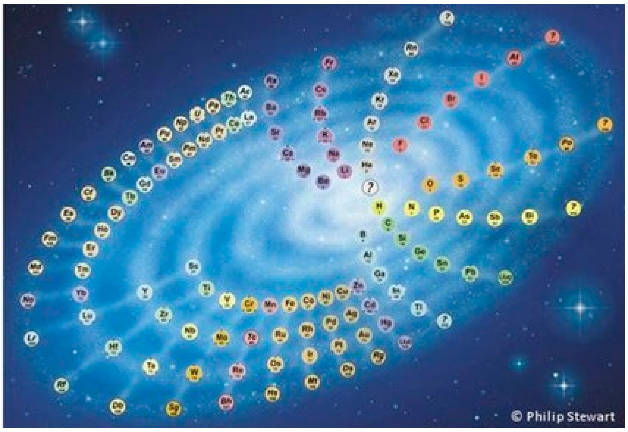

Figure 15. The Galaxy periodic table.

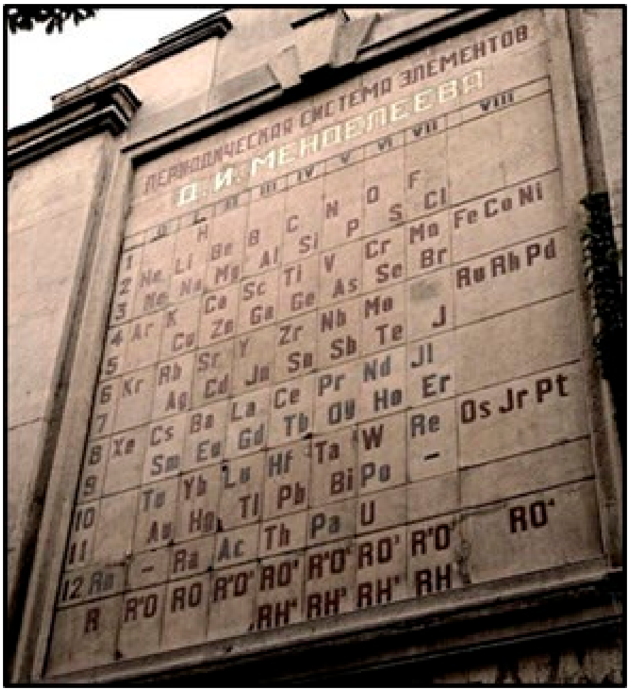

Figure 16. Periodic Table on a Wall. Saint Petersburg, Russia.

Fiona Barclay (https://periodictable.com/). It comes complete with a sample of each element that it is legally available. The larger versions of this kind of table of so-called 'Element Collections' can be seen at several institutions, such as the Science History Institute in Philadelphia, Pennsylvania, and at company sites such as the Dow Chemical headquarters in Michigan. Theo Gray is the author/web-master of the remarkable website https://periodictable.com/ and he has written a book: *The Elements*.

Today there is a permanent tribute to Mendeleev's discovery of the periodic table in the form of an impressive sculpture on the wall of the building where Mendeleev worked: Fig. 16.

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The Periodic Table and its Iconicity: an Essay

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Abstract. In this essay, we aim to provide an overview of the periodic table's origins and history, and of the elements which conspired to make it chemistry's most recognisable icon. We pay attention to Mendeleev's role in the development of a system for organising the elements and chemical knowledge while facilitating the teaching of chemistry. We look at how the reception of the table in different chemical communities was dependent on the local scientific, cultural and political context, but argue that its eventual universal acceptance is due to its unique ability to accommodate possessed knowledge while enabling novel predictions. Furthermore, we argue that its capacity to unify apparently disconnected phenomena under a simple framework facilitates our understanding of periodicity, making the table an icon of aesthetic value, and an object of philosophical inquiry. Finally, we briefly explore the table's iconicity throughout its representations in pop art and science fiction.

Keywords. Dmitri Mendeleev, the periodic table of elements, philosophy of chemistry, science and pop art, science fiction.

> *The Periodic Table was incredibly beautiful, the most beautiful thing I had ever seen.*
> *(Oliver Sacks)*
>
> *An exposition of all that matters in matter.*
> *(Bruce Greenhalgh)*

INTRODUCTION

The periodic table of elements is chemistry's most universal 'tool', used both as a teaching method and research instrument. But it is also a sign and icon that unites all chemical knowledge. In philosophy of language, 'iconicity' is the name given to a certain similarity relation between the form and the meaning of a sign. The lack of similarity is arbitrariness, which means that there is nothing in the form of the sign that resembles its meaning, and simple convention associates the two. We borrow such terminology to claim that the periodic table is truly an icon, not just convention. Each of the little 'squares' in any of the table's representations encloses the totality of chemical and physical knowledge about a given element. In this sense the table is truly iconic: it is perceived as being so closely similar to that which it represents (the totality of chemical knowledge), that form and meaning become intrinsically bounded.

Since its first formulation, the table has become a universally accepted icon which transits in many places of knowledge. It transits in classrooms and books as a didactic tool, it transits through research laboratories as a reference source, and it transits in annals and records of chemistry as a repository of scientific information and interpretations collected over time. Considering its widespread presence, we believe the table parades a dual nature: it *is* the consolidation of current chemical knowledge, but also a heuristic tool used by chemists in their attempts to expand and consolidate such knowledge. Surprisingly perhaps, the 'tool' has not changed much since its conception.

In the words of Scerri:

> *The periodic table of elements is one of the most powerful icons of science: a single document that consolidates much of our knowledge of chemistry [and] despite the dramatic changes that have taken place in science in the last hundred years [relativity and quantum mechanics] there has been no revolution in the basic nature of the periodic system.*[1]

Let us next say a few things about how the table came about, from early attempts to find analogies among chemical elements, to more refined views on periodicity.

ANALOGIES

The practice of classifying is an important task in any science. It is a task that involves obtaining the particulars (objects) to be classified, finding non-spurious similarity relations – analogies – between the object and other entities thought to be of the same kind, and drawing empirical and logical conclusions from the way entities are organised. Scientific disciplines often make great efforts to divide particulars into kinds and theorise about the nature of these kinds. If one has realist inclinations regarding scientific knowledge, one will often think of a kind as being 'natural', i.e. a grouping of particulars that is made possible by how nature *is* (and not by one's interests or actions). If this is the case, then scientific taxonomies correspond to real natural kinds. And, as Bird and Tobin put it, "the existence of these real and independent kinds of things is held to justify our scientific inferences and practices."[2]

A classic example is Carl von Linné's (1707-1778) botanical and zoological classification in his *Systema Naturae* (1735), which became a 'model' of classification for other sciences as well. It inspired, for instance, Johann Beckmann (1739-1811) to classify technological activities in his *Entwurf einer allgemeinen Technologie* (1806).

Chemists too felt the need to classify elements and substances. Lavoisier himself, in presenting his table of elements in 1789, classified them. Each of the four groups of 'simple substances' presents similar or even identical qualities. If we look more closely at a Table of Affinities, such as that of Torbern Bergman (1735-1784) from 1775, we will find a classification: each group of substances presents qualitatively equal and quantitatively decreasing properties.

After Lavoisier, the concern of chemists in classifying became more evident, and we can cite classificatory attempts of Richter (1792), Döbereiner (1817, 1829), Meinecke (1819), Thenard (1813), Ampère (1816), Gmelin (1842), Gibbs (1845), among many others. All these attempts are analogical in form, i.e., elements are grouped together based on how the author 'perceives' similarities and differences among the elements' properties. There is an obvious challenge for objectivity here, as similarity relations of one kind will often take priority over other similarity relations, depending on the authors' theoretical preferences. None of these attempts was a periodic classification, however.

The concept of analogy was important to the prevailing *Naturphilosophie* at the time, especially in Germany. Associated with Romanticism, such classificatory attempts were motivated by a desire to formulate a system of thought capable of encompassing both empirical knowledge and *a priori*, deductive reasoning. Natural philosophy has been gradually eliminated from scientific thought; thanks to the rise of empiricism. John Locke, for example, argued that the prior formulation of hypotheses and the use of analogical reasoning played a minor role in science – a view consistent with that of experimental philosophy.[3] With the decline of speculative philosophy, early classificatory attempts – except maybe Döbereiner's and Gmelin's – became of little philosophical relevance. Furthermore, there is an element of subjectivity motivating the formulation of such classificatory systems. An author's philosophical preferences will often play a decisive role in what counts as relevant in analogical arguments, and therefore on how the elements are classified. Let us see how.

For Jeremias Benjamin Richter (1762-1807), once a student of Kant, some mathematical relations are *a priori* hypotheses – a view he formulated based on his studies of ponderal and stoichiometric relations. For him, any chemical classification had to consider the laws (such as the law of definite proportions, which says that the ratio by weight of the compounds consumed in a chemical reaction stays always the same) according to which substances unite to form compounds. Eduard Farber[4] and Georg Lockemann[5] consider Richter to be the first chemist to consider mathematical aspects in his theories.

Johann Ludwig Meinecke (1781-1823) reasoned from analogy by giving priority to the notion of chemical affinity, i.e., the tendency exhibited by atoms or compounds to combine (chemically react) with certain atoms or compounds (of unlike composition) in preference to others. This is, of course, a well-established theory today, but during his time 'affinity' referred only to bodies who reacted intensively, perhaps 'unavoidably', one with the other. It was this older conception of affinity that inspired Goethe to write his metaphorical novel *Elective Affinities*, in which human passions appear to be governed by the laws of chemical affinities, with the potential to undermine social institutions such as marriage.

André-Marie Ampère (1775-1836), criticising what he saw as an exaggerated importance given to oxygen, attempted a natural classification or order, or even in the words of Jean-Baptiste Dumas (1800-1884), "a classification of bodies into groups based on primary properties capable of determining all secondary properties." Ampere used an experimental criterion for the classification of the elements, as he focused on "associations and products to which elements are known to be committed."[6]

Johann Wolfgang Döbereiner (1780-1849), in his "An Attempt to Group Elementary Substances according to Their Analogies" (1829), ascribed great importance to numbers representing the atomic weights of the elements forming the four "Döbereiner Triads". Döbereiner identified a pattern with the elements of the triads: if you order them according to their atomic masses, the average of the molar mass of the first and third element of the triad equals the molar mass of the second element (sulphur, selenium and tellurium, for example). On a modern periodic table, these elements are stacked vertically. His work started on the same insight that would later result in the formulation of the periodic law and classification of the elements.

For Leopold Gmelin (1788-1853), another forerunner of the periodic table, physical and chemical relations among simple substances (= elements) are important, but the structural basis for their classification lies in their electronegativity or positivity, as defined by Jöns Jacob Berzelius (1779-1848) in his *Lehrbuch* (1823).

Getting into the details of such early classificatory attempts falls outside the scope of this article. But we wish to highlight the motivation that guides them all: to find a form of representing observations of similarities and order among elements that could be *universally* accepted while containing all the relevant information known about the elements, their 'kinds' (grouping) and ordering.

This desire for universality sometimes surpasses the limits of chemistry. John Alexander Newlands (1837-1898) formulated in 1864 his "Law of Octaves", according to which the ordering of the elements accruing to increasing atomic weight reveals a periodic pattern of similarity after each interval of seven elements. Newlands' detection of periodicity was overlooked possibly because of the analogy he drew between chemistry and the musical scale, thought to be naïve and distracting. Striving for universality, Newlands tried to force all known elements to fit into his octaves – but some new discoveries (heavy elements) escaped the pattern. Also, James Blake (1815-1893) went beyond chemistry when he attempted to classify some elements based on their pharmacological effects (1848).[7] While such attempts were not well received, if one thinks of kinds as being natural, and not socially constructed, there is no reason to assume any periodicity would confine itself to conventional disciplinary boundaries.

THE PERCEPTION OF THE PERIODIC TABLE

Let us now focus on the mainstream periodic tables of Dimitri Mendeleev (1834-1907) and Lothar Meyer (1830-1895). Mendeleev ordered the elements according to their increasing atomic mass. He placed elements underneath other elements with similar chemical behaviour. For example, he placed sodium underneath lithium because both exhibited similar chemical behaviour: shiny and soft metals which react promptly with oxygen and violently with water.

Sometimes the atomic mass of an element would not be in the right order to put it in the group of elements with similar behaviour. He placed a question mark (?) next to its symbol to indicate he was uncertain the atomic mass had been measured correctly. Some other times the next heaviest element would not display the properties expected of the next element in the table, and he thought important to only group together elements with similar properties. He postulated the existence of an unknown element to occupy that place, and left blanks, allowing for (temporary) holes for undiscovered elements in the table. Mendeleev used dashes (-) to indicate the predicted mass of the element to be discovered. It was precisely this abductive reasoning that allowed for the future discovery of gallium (1875) and germanium (1882), for example, to be accommodated by the table. Germanium's fit in its group and its behavioural contrast with neighbouring elements gave Mendeleev's classification strong empirical support. As Kemp puts it: "Mendeleev's periodic table permitted him to systematise crucial chemical data. But its real triumph was as an exercise in theoretical modelling, allowing the prediction of the discovery of previously unknown elements."[8]

The table formulated by Mendeleev is a *tour de force* in terms of resilience. Since its first appearance 150 years ago the table has been able to accommodate the discovery of new elements (lanthanides), and groups of elements (noble gases, transuranic and transfermic elements). New theories and philosophical positions did not affect the solidity of Mendeleev's formulation, nor did the revolutionary empirical discoveries since the end of the nineteenth century: the discoveries of atomic divisibility and subatomic particles, radioactivity, artificial transmutation, and innovations generated by quantum mechanics. It is certainly this capacity to accommodate (and help predict) novelties, and withstand theoretical criticism, that gave Mendeleev's periodic table its iconicity and universal appeal. Eventually, it became a definitive representation of elemental periodicity.

It is interesting to note that none of the previous proposals for classifying the elements had more repercussion outside their context of creation than Mendeleev's. Its high degree of empirical adequacy gave Mendeleev's systematization the status of scientific law (Mendeleev's Periodic Law). Such status was later corroborated by what is now known as Moseley's Law (1913). Up until Moseley's work, the atomic number of an element was just its place in the table, and it was not associated with, or determined by, any known measurable physical property. But Moseley demonstrated that the frequencies of certain characteristic x-rays emitted by atoms are approximately proportional to the square of the element's atomic number. This discovery also supported Antonius Van den Broek's (1870-1926) and Niels Bohr's atomic model, according to which the atomic number is the same as the number of positive charges in the atom's nucleus. It is precisely this degree of consilience, i.e. this 'jumping together' (convergence) of evidence originated from different, unrelated sources, that help explain Mendeleev's success in formulating a definitive and universal representation of elemental periodicity.

The motivation for drawing a table of the elements was to find a way of representing them that could be universally accepted. Representations that were only based on analogies – and did not constitute scientific laws – did not achieve this objective. The discovery of periodicity, followed by Mendeleev's insight when grouping the elements according to their similar properties while allowing for gaps, did achieve universality and, ultimately, iconicity. In part, such iconicity is derived from the table's widespread use as a teaching tool. It is widely used by teachers to aid students with the abstractions necessary for a proper understanding of chemistry. Abstractions such as the ordering of a periodic system, systematization of possessed knowledge, prediction and projections involving new discoveries, chemical properties, correction of data, and finally understanding of the macro and microcosmos in terms of atoms, molecules and substances.

So, what we mean by the universality of the periodic table goes beyond geographic universality. It is endurance in time and space, and unity of meaning and form, of sign and concept. The universality of the periodic table of the elements is so pervading, that it is even capable of connecting intellectual ideas and human passions. In the words of S. Alvarez: "The periodic table of elements is the agora where art, science and culture meet to dialogue about matter, light, history, language and life. It is an extraordinary tool that allows us to find the connections between humanistic culture and science."[9]

The iconic table has a variety of uses:

- as a teaching tool;
- as a heuristic method for scientific practice;
- as an aid to classify and preserve chemical knowledge;
- as a theoretical foundation for the understanding of chemistry;
- as a research tool for other sciences, such as mineralogy;
- as a tool for the popularisation of chemistry;
- as an aesthetic component in the corpus of chemical knowledge;
- as a factor of integration between science and the Humanities;
- as a pop-cultural object.

MEYER'S AND MENDELEEV'S DIDACTIC PURPOSES

Both Mendeleev and Meyer developed their periodic tables confessedly for didactic purposes – the ordering of the contents - in writing their textbooks *Principles of Chemistry* (1869) and *The Modern Theories of Chemistry* (1864), respectively. Lothar Meyer's *Die modernen Theorien der Chemie und Die Bedeutung für die Chemische Statik* (Maruschke & Berendt, Breslau, 1864) is very concise. From the outset, the author makes it clear that he intends to systematise and order, among all available knowledge, those he considers more fundamental (greater reliability and precision). The starting point is the Berthollet *Essai de statique chimique* (1804). Meyer also accepted Dalton's atomic theory and some reductionism. As he writes: "The development followed by chemistry has brought with it the necessity of abstracting every theoretical point of view from a great deal of widely scattered detail."[10]

Speculations about the cause and essence of phenomena are various, and often conflicting points of view coexist.

What theories that remain and which ones will be rejected is a decision that belongs only to the opinion of today's active chemists, and only exceptionally and fragmentary in their writings [as the literature overestimates the amount of disagreement]. The struggle for the systematic ordering of chemistry's body of knowledge seems to be long over.[11]

In Meyer's view, the long-lasting dispute on whether the properties of a compound depend on its nature or on the arrangement of its components seems to be solved to the satisfaction of both parties, for probably no one in the right mind would categorically reject the atomic theory. The didactic aspect to which we refer in the text of Meyer is the systematisation in function of the choice of the most appropriate hypotheses for a rational exposition of the problems of chemistry. Meyer keeps a hypothesis only so long as it is useful.

Let us now focus on the didactic purpose that led Mendeleev to elaborate his classification to better order the contents of his *Principles of Chemistry* (1869/1871). When in 1867 he succeeded Alexander Voskresensky (1808-1880) as Professor of Inorganic Chemistry at the University of St. Petersburg, Mendeleev wrote: "I began to write [the Principles] when I started to lecture on inorganic chemistry at the university after Voskresensky and when, having looked through all the books, I did not find anything to recommend to students."[12] This direct association between Mendeleev's Table and his *Principles of Chemistry* was carefully examined by Bonifaty M. Kedrov (1903-1985).

In another analysis, Masanori Kaji (1956-2016) also considered social and scientific factors as motivations for the table's formulation. Kaji identified a close relationship between the periodic law and Mendeleev's concept of 'element'. Mendeleev participated in the Congress of Karlsruhe in 1860, and the ideas of Stanislao Cannizzaro (1826-1910) exposed there exercised great influence on his chemical thought. He accepted the atomic theory (with certain exceptions, for there were exceptions to the law of constant proportions), allowing him to establish a relation between the properties of the elements and the atomic masses, the origin of the "periodic law". Following in the footsteps of Cannizzaro, Mendeleev distinguished between "simple bodies" (material entities) and "element" (abstract entity). He would later refer to an element as a "chemical individual", highlighting the existence of multiple elements, consistent with his view of natural diversity (as opposed to there being a unity of matter).

In his "Faraday Lecture" (1889), Mendeleev claimed that the periodic law had been arrived at by inductive reasoning, i.e. "a direct outcome of the stock of generalisations and established facts which had accumulated by the end of the decade 1860-1870: it is an embodiment of those data in a more or less systematic expression."[13] Clearly, the more data the better basis for any generalisation. And "sound generalisations – together with the relics of those which have proved to be untenable – promote scientific productivity, and ensure the luxurious growth of science under the influence of rays emanating from the centres of scientific energy [scientific societies]."[14]

As for those who at the time hoped the periodic law would lend support to the notion of a unity of matter (such as Berthelot), Mendeleev showed little sympathy:

> *…the periodic law, based as it is on the solid and wholesome ground of experimental research, has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; and it has no historical connection with that relic of the torments of classical thought (…) None of the advocates of a unique matter has ever tried to explain the law from the standpoint of ideas taken from a remote antiquity when it was found convenient to admit the existence of many gods – and of a unique matter.*[15]

In this lecture, Mendeleev also defended the use of conceptual structuring as an important complement to the experimental method, foreshadowing much of the 20th century preoccupation in placing "agreement between theory and experiment" at the centre of scientific thought and method. Much of the iconicity of Mendeleev's table lies of course in its success in visually representing an agreement between an inductively identified regularity of nature and vast empirical chemical data. If properly used as a teaching tool, as Meyer and Mendeleev intended, the very same conceptual structuring would help rid the scientific world of obsolete metaphysical notions, and guide scientists towards scientific progress.

THE RECEPTION OF THE TABLE

About the reception of the Periodic Table by different scientific communities, Stephen Brush mentions that at the end of 19th century there were few and irregular citations of the Table. It is therefore difficult to say if it was widely accepted by chemists, or if only a specialised circle of chemists showed interest in the novelty. Brush mentions 236 citations of the Table during the period 1871-1890: 20 from 1871 to 1875, 72 from 1875 to 1880, 61 from 1881 to 1885 and 83 from 1885 to 1890. Concerning textbooks, we should not forget that usually many years elapse from the original inception of a new idea by the author and its inclusion in a textbook: 244 textbooks were published from 1871 to 1890, but only 76 of them mention the Periodic Table.[16]

First "modern" Periodic Tables were presented in Russia and in Germany, and we could suppose that in these countries such a powerful instrument would be accepted without any restrictions. History shows many drawbacks in accepting periodic classification because of singularities related to the scientific *milieu* of the two countries. In Russia, as Kaji and Brooks observe, the main difficulty was just the fact that the Periodic Table was presented by a Russian, deeply immersed in Russian intellectual and scientific atmosphere.[17] Despite a dispute about priorities between Mendeleev and Lothar Meyer (caused by Wurtz's criticism of a German translation of one of his books), Russian chemists of German descent (Friedrich Beilstein, Victor von Richter, Felix Wreden) did much towards the recognition of Mendeleev's system. An early presentation of Mendeleev's first paper at the St. Petersburg Academy of Sciences by Nikolai Menshutkin (1842-1907) was largely ignored. Nikolai Zinin (1812-1880) suggested that Mendeleev should devote himself to actual chemical lab work. After months of silence, Mendeleev's ideas began to be discussed in scientific meetings by important Russian chemists: Markovnikov, Butlerov and even Zinin. The first Russian textbook to include a Periodic Table was Victor von Richter's (1841-1891) "Textbook of Inorganic Chemistry, based on most recent theories" (1874). Most later textbooks included Mendeleev's classification.

In Germany, where precursors like Richter, Döbereiner, Gmelin, Kremers, Pettenkofer, among others, worked on classification before Mendeleev, the adoption of a Periodic Table was delayed.[18] Karl Seubert (1851-1942), Meyer's colleague in Tübingen, explains this delay by a generalised lack of interest by most chemists in Inorganic Chemistry, especially issues like "periodic classification": Meyer's explanations were too short and succinct, while Mendeleev's were deemed too complex and included non-chemical knowledge. Rudolf Fittig (1835-1910) in Tübingen and Eugen von Gorup-Besanez (1817-1878) in Erlangen mention the Periodic Table in 1873: Fittig in an encyclopaedia article, Gorup-Besanez in the 5th edition of his "*Lehrbuch der Arnorganischen Chemie*". G. Boeck considers Victor von Richter's German translation (1874) as the first German textbook to present a Periodic Table. Brush takes the third edition of Carl Rammelsberg's (1813-1899) *Grundriss der Chemie* (Lüderitz, Berlin, 1873; Brush mentions erroneously 1874) as the first textbook outside Russia to discuss periodicity.[19] August Michaelis' (1847-1916) *Ausführliches Lehrbuch der Chemie* (1878) and Karl Arnold's (1853-1929) *Repetitorium der Chemie* (1885) deserve mention. Most of the nineteenth-century college-level textbooks don't include Classification, the famous "Schule der Chemie" by Adolph Stoeckhardt (1809-1896), and not even the last editions from 1881 (19th) and 1919 (22nd).[20]

The introduction of Mendeleev's table in different scientific contexts, in central as well as in peripheral science, met some degree of opposition or reluctance. In many places, there were already prior classifications and tables, some of them with a long tradition and successful in their task in organising the content of textbooks. More pragmatic or theoretical scientific schools considered the efforts of looking for a periodic classification as useless. It is necessary to say that before Mendeleev's classification, other classifications, *e. g.* Thenard's "artificial" classification, or "classifications" not even taken as such, like that of Berzelius, entered the scientific literature of several countries: Thenard in the Latin world, and Berzelius in Germany. And, finally, some local scientific communities produced their own classifications, like those of Lewis Reeve Gibbes (1810-1894) in the United States (published in 1884) or of the Catalan pharmacist Josep Antoni Balcels (1777-1857) in Spain (1838).

In Great Britain, not even classifications suggested by English chemists, like William Odling (1829-1921), in 1865, or John Alexander Newlands (1837-1898), in 1864, were taken seriously.[21] There was little interest in Mendeleev or Lothar Meyer. But the discovery of gallium (1875) by Lecoq de Boisbaudran (1838-1912) changed the situation. After the awarding of the Royal Society's Davy Medal to Mendeleev and Meyer (1882) there was some revival of "Newland's octaves" (Newland's Davy Medal in 1887), but English scientists had little interest in "classifications", although they produced very important empirical data to confirm the "periodic law" as a scientific law (the discovery of noble gases, Moseley's work). First texts to include a Periodic Table were those of William Allen Miller (1817-1870), "Elements of Chemistry" (6th edition, 1876) and George Fownes (1815-1849), revised by his assistant Henry Watts (1815-1884) in 1877. S. Brush mentions Thomas Edward Thorpe (1845-1925) as author of the first English language textbook including Mendeleev's Table (1877).[22]

Also in France Mendeleev's table remained almost unnoticed, a "non-event" in the history of French chemistry in the opinion of B. Bensaude-Vincent.[23] But in the period of precursors of a classification we must remember contributions of Thenard (1813) and Ampère (1816), Dumas' numeric table (1851), as well as the exotic "telluric screw" of Chancourtois (1862) – the "screw" connects chemistry and geology, another example of the universality of the periodic table. The strong influence of Positivism and refusal to accept atomism by influential scientists like Marcellin Berthelot (1827-1907) explain why most French chemists looked for alternative classificatory systems, ignoring Mendeleev (the "equivalentists").[24] Berthelot agrees that Mendeleev's Table may have some practical utility, but for him, it is not a "law" or a theoretical argument, as this would undermine the empirical, logic and positive bases of science,[25] and could also lead to a return to mysticism. In 1885, in his *Les Origines de l'Alchimie*, Berthelot discusses the periodic system as an "artificial construction based on vague theoretical arguments".[26] Among the exceptions are notables like Charles Adolphe Wurtz (1817-1884), who dedicates an entire chapter of his "Atomic Theory" to Mendeleev, Edouard Grimaux (1835-1900) and Paul Sabatier (1854-1941). After 1890, Mendeleev's system began to gain some sympathy: Paul Schutzenberger (1829-1897) published the first French textbook containing the periodic classification (*Traité de Chimie Générale*, 1880). Georges Urbain (1872-1938) was perhaps the first to try to explain the opposition of equivalentists and atomists (1934).[27] Mendeleev himself was not truly an atomist, he used "equivalent weight" instead of "atomic weight".[28] In France, there was not only the opposition between positivists-rationalists but also the opposition between "natural" classifications (Ampère, Dumas) and "artificial" classifications (Thenard). Differently from what happened in Great Britain and in the United States, the discovery of gallium did not contribute to the acceptance of Mendeleev's ideas: Lecoq insisted that his discovery was due only to his skills as a spectroscopist and had nothing to do with Mendeleev's table 'blanks'.[29]

A recently unified Italy presented a fertile soil for the introduction of new scientific ideas. In the case of the Periodic Table this is exemplified by the almost immediate acceptance of Mendeleev's system by important Italian chemists, such as Augusto Piccini (1854-1905), who translated Richter's textbook into Italian (1885), and Giacomo Ciamician (1857-1922). It was accepted that former classifications were based on less reliable properties.[30]

In Spain, Thenard's text (*Traité de Chimie Élementaire*, 1813) and classification were largely used. Thenard's classification was also present in other French textbooks translated into Spanish, like that of Mateo Orfila (1787-1853). There is no reference to Mendeleev in the extensive text published in 1875 by Rafael Sáez Palacios (1808-1883), but there is such reference in a book (1880) by Santiago Bonilla Mirat (1844-1899).[31] Eugenio Mascareñas (1853-1934) published in 1884 in Barcelona "Introdución al estudio de la Química", discussing Mendeleev's work and presenting his own table.[32] Theoretical and speculative studies on periodicity were done by Ángel del Campo y Cerdán (1881-1944), suggesting interactions of protons with protons and with neutrons as the origin of periodicity (1927): "The properties of the elements seem to be simultaneously a periodic function of the masses of their atoms and the electric charge of their nuclei, that is, of the atomic masses and the atomic numbers."[33] As a consequence of Bohr's studies, Miguel Catalán Sanudo (1894-1957) presented a table relating periodicity to spectra (1923).[34]

Modern Portuguese science has its beginnings with the renovation of the University of Coimbra by the Marquis de Pombal (1699-1782) in 1772. A new reform followed in 1841, and since 1870 a strong influence of positivistic thought in scientific practice can be observed. Antônio Luís Ferreira Girão (1823-1876) did not mention Mendeleev in his *Teoria dos Átomos e os Limites da Ciência* (published 1879), but his student Agostinho de Sousa published (1880) in French *La Loi Périodique*, the first reference to Mendeleev in Portugal. This was later repeated in the 2nd edition (1895) of a textbook by Antônio Joaquim Ferreira da Silva (1853-1923).[35]

In Northern Europe, the reception of Mendeleev's Table occurred in different contexts. In Sweden, Berzelius' *Treatise on Chemistry* (1818) presented a classification of the elements based on their electronegative or electropositive character. In Denmark Julius Thomsen (1826-1909) worked out his own table (1887, 1895), in which he tried to turn more visible the relation between periodicity and atomic structure – a subject studied later by another Danish scientist, Niels Bohr (1885-1962). Lundgren suggests that in Sweden the reception of Mendeleev's system was by no means dramatic: no opposition, but also no enthusiasm.[36]

Swedish chemistry shows no difference before and after Mendeleev, it was a pragmatic and practical chemistry, with a reduced theoretical component (a theoretical revival took place with Svante Arrhenius after 1884). According to Lundgren, Sweden's only contribution to periodicity and the classification of the elements, Lars F. Nilson's (1840-1899) discovery of scandium (1879), was seen as an analytical problem. In Denmark, the situation was similar – a pragmatic, practical chemistry, some theory (Thomsen).[37] In Kragh's opinion, Thomsen presented in 1865 one of the "many incomplete anticipations of the periodic system", but in 1880 most Danish chemists already knew Mendeleev's and Meyer's systems. Odin Christensen (1851-1914) wrote the first Danish paper (1880) and textbook about the Periodic System (*Elements of Inorganic Chemistry*, 1890). The case of Norway is in some sense *sui generis* – linked to Sweden since 1814 but *de facto* independent since 1905, the country used its own chemical terminology and had a small but important scientific community (Peter Waage, Kristian Birkeland). Mendeleev's system had little effect on chemical practice and was introduced relatively late, with a textbook (1888) by Thorstein Hallanger Hiortdahl (1839-1925).[38]

A situation which deserves a wider and detailed study, even outside chemistry, is the reception of Mendeleev's periodic system in scientific communities which used their own language and had their own scientific evolution but were not independent nations at Mendeleev's times. This is the case of Czech and Croatian chemical communities, politically and economically linked to Austria-Hungary until 1918. Somewhat different is the Polish chemical community, spread throughout Russia, Austria and Germany, they did not constitute a united group of chemists. Using their own languages, terminologies and nomenclatures, not only in science but also in literature, philosophy and the humanities, Czech and Croatian scientists saw in Russia a leader, and positive reception of Mendeleev's system was an *a priori* decision.[39]

Use of one's own language in intellectual activities created and fortified emerging nationalisms in the 19th century. In the present Czech Republic,[40] until 1918 Austria's Kingdom of Bohemia, nationalism forced the creation in 1869 of a Polytechnic School (independent from the German Polytechnic) and the separation of the old Prague University (1348) into a German and a Czech University (1882). A textbook authored by Vojtech Safarik (1829-1902) was the first to mention the Periodic Table in the Czech language, but in Strbanova's opinion, the most important defender of Mendeleev's system in Czech lands was his personal friend Bohuslav Brauner (1855-1935). In the face of growing russophylia and anti-German sentiment, Brauner defended Mendeleev's ideas and vindicated the replacement of German scientific influence in Czech lands by Slavic influence. This case illustrates how nationalism and xenophobia may constitute a threat to the autonomy of science. There was some resistance to the acceptance of Mendeleev's work by Safarik (a Slovak), and by Jaroslav Formanek (1864-1936). Both wanted a 'natural' classification of Elements. Ambiguous behaviour of Czech intellectuals may be seen in Cermak's germanisation of his name, Gustav von Tschermak (1836-1927). Tschermak presents his own periodic table (1859), the first to draw attention to 'blanks'.[41]

In Croatia, until 1918 part of the Austro-Hungarian Empire, the reception of the Periodic Table was more straightforward.[42] Since 1861 school textbooks were published in Croatian, and since 1873 there was a University in Zagreb (then called Agram), but only in 1901, an academic textbook by Julije Domac (1853-1928) presented Mendeleev's system. A former text by Pavao Zulic (1831-1922), even in his second edition from 1877, omitted the periodic classification. The acceptance of Mendeleev's system in Croatia is largely due to the Czech chemist Gustav Janecek (1848-1929), whose text on the subject (1914) goes back to Döbereiner and other precursors.

Not only Czechs and Croats, but also other nationalities lived in polyethnic Austria-Hungary, maintaining their language, traditions and many centuries of their own cultural activities, like Hungarians. Since the *Ausgleich* from 1867, between the Emperor and the Hungarian government, Hungarian became the official language in schools, and Karoly Than (1834-1908) was designated chemistry professor at Budapest University. Than was the author of the most popular chemistry textbook in Hungary, *Elements of Experimental Chemistry* (1898), in which he presented Mendeleev's classification and systematisation.[43]

At the same time, in Serbia, a Slavic country *de facto* independent since 1867, with a University in Belgrade (1905), there was modest chemical activity. Frequently repeated information about a first non-Russian textbook on a Periodic System written by Serbian chemist Sima Lozanic (1846-1935) in 1874 (*Chemistry as Viewed by Modern Theories*) is incorrect. Lozanic included Mendeleev's System only in the second edition of his book (1897).[44]

Like Serbia, Bulgaria, another Slavic nation *de facto* independent since 1876 (Treaty of San Stefano) had modest scientific activity. A recent essay by Borislav Toshev suggests that all Bulgarian publications on Mendeleev are hagiographic, with the only exception being professor Dimitar Balarev's (1885-1964) *Significance of the Periodic System*, 1950).[45] Balarev himself designed a three-dimensional form of the Periodic Table.[46]

It is difficult to state precisely which Latin-American country first received the periodic system. Latin American historiography rarely refers to science, and when it does, it pays close attention to institutional history, or biographical data. Equally difficult to obtain information on Latin American contributions to the periodic system. It is however easy to ascertain that from the 1940s interest in the periodic table of the elements has spiked. It's great potential as a teaching tool was the main driving factor, as can be seen in Ceccon and Berner's monograph.[47]

The first record of the periodic system in Latin America is probably due to Álvaro Joaquim de Oliveira (1840-1922), professor at the Rio de Janeiro Polytechnic School. In his textbook *Apontamentos de Química* (1883) he critically examines the table under the influence of positivist dogmas.[48] Oliveira was one of the founders of the Brazilian Positivist Society (1876), but his views and interpretation of Mendeleev's work met strong opposition from his peers,[49] prompting another leading Brazilian positivist, Raimundo Teixeira Mendes (1855-1927), to publish an alternative textbook, *La Philosophie Chimique* (1898).[50]

There were different versions of the periodic table in use by Brazilian teachers. We mention, because of its originality, a contribution presented in 1949 by Alcindo Flores Cabral (1907-1983), professor of chemistry at the School of Agriculture in Pelotas. Cabral's spiral classification, elegant in its symmetry and use of colours, made use of what he called the 'differentiating electron'.[51] Another formulation of the table (1950) worth mentioning was made by professor Werner Gustav Krauledat (1908-1990), from Rio de Janeiro State University.

In Spanish speaking Latin America, a very successful table was designed in 1952 (and revised in 1962) by Gil Chaverri Rodrigues (1921-2005), a physicist and chemist from Costa Rica. His table follows a logical sequence derived from the sequence of atomic numbers and has done well in presenting lanthanides and actinides without disrupting the sequence of elements.[52] Like Cabral, Chaverri lectured at an agricultural school, which showed a widespread interest in periodic classifications.

Another successful table was that of Peruvian chemist Oswaldo Baca Mendoza (1908-1962), from Cuzco University, *Generic Laws of the Chemical Elements. A New Periodic System* (1953), inspired by the theories of his Spanish teacher A. del Campo y Cerdán.[53] Julio António Gutierrez (b. 1955) continued Mendoza's work (*Sistema Periódico Armônico and Leyes Genéticas de los Elementos*, 2004) on the 'quantification' of Mendeleev's table. Spaniard António García-Banús (1888-1955), creator of the great mural table in Barcelona, immigrated in 1938 to Colombia (1938) and lectured at the Bogotá National University, where he got involved with the periodic system.

In Uruguay, a chemical institute was created at the Faculty of Medicine in Montevideo (1908), where studies on periodicity largely focused on using the table as a teaching tool. During the decades of 1930 and 1940, there were some original ideas about the best position for the actinides in the table, and during the seventies, there were discussions about a new spiral design of the periodic system, but without a successful outcome.[54]

Western science found its way to Japan through Dutch textbooks used in "Dutch Studies": before the Meiji period, the Netherlands were the only western nation to have consistent contact with Japan. The first Japanese chemistry textbook, *Seimi Kaiso*, was written by Utagawa Yoan (1798-1846) around 1830 and included parts from Lavoisier's treatise.[55] Robert William Atkinson (1850-1929), an English chemist, the first western chemistry teacher in Japan, was interested in periodic classification but preferred Lothar Meyer's table. Naokishi Matsui (1857-1911), a professor in Tokyo, was the first to mention Mendeleev in a paper (1882), and Toyokichi Takamatsu (1852-1931) was probably the first to mention it in a textbook. Research on the subject was also done by Kikunae Ikeda (1864-1936) and Masataka Ogawa (1865-1930), the former from a theoretical point of view, and the latter in an empirical context.[56]

Of notable interest was the difficult introduction of the periodic table in Turkey. Two problems contributed to making this task complicated: an absolute lack of modern chemistry texts and the use of Arabic symbols for letters and numbers – Arabic texts are written from right to left, which turns writing formulas, equations and reactions even more difficult. Despite these difficulties, Vasil Naum (1856-1915) included Mendeleev's system in his book *Medical Chemistry*, with names of elements and numbers in Arabic characters (the official language of the Ottoman Empire). In 1914, the Turkish government decided to modernise its higher education system, and from 1915 to 1918 a group of German chemists lectured in Constantinople, headed by Fritz Arndt (1885-1969) – Gustav Fester (1886-1975) and Kurt Hoesch (1882-1932) were the other members of the mission. After facilities and equipment, Arndt's priority was the production of textbooks in Turkish language (Arndt was fluent in Turkish), and in his *First Medical Experiments* (1917) we find the second Turkish periodic table, with Latin characters used for the elements and their symbols, but with the text itself remaining in Arabic, read from right to left.[57]

In the United States, we distinguish between the reception of Mendeleev's system and the reception of several other classifications, some of them proposed by American chemists, a situation similar to that observed in Great-Britain and France. In 1854, Harvard professor Josiah Parsons Cooke (1827-1894) presented before the American Academy of Arts and Sciences in Boston a lecture *Numeric Relations between Atomic Weights and some Ideas about Classification of Elements*, considered by Edgar Fahs Smith (1854-1928) as the first serious attempt in studying this subject (1914).[58] Gustavus Hinrichs (1836-1923) published his textbook in 1874, but instead of Mendeleev's system he included his own spiral classification (worked out in 1867), not even mentioning Mendeleev's formulation.[59] Lewis Reeves Gibbes (1820-1896) published in 1886 a *Synoptical Table of Chemical Elements*, using an 'inverted' procedure with respect to Mendeleev's, arranging a great number of chemical proprieties and deriving from them a periodicity of atomic weights.[60] Stephen Brush could not find a single American textbook discussing Mendeleev's ideas until Lecoq's discovery of gallium in 1875. In 1877, Ira Remsen (1846-1927), from Johns Hopkins University, published his *Principles of Theoretical Chemistry*, the first text in the United States to mention Mendeleev.[61]

THE TABLE AS A RESEARCH TOOL

Mendeleev`s Periodic Table contains 'blanks' (though he was not the first to postulate their existence); all periodic tables presented after Mendeleev's also contained 'blanks'. The desire to replace such blanks with new discoveries strongly motivated chemical research.

The increasing number of elements discovered since 1800 (thanks to improved analytical techniques), the degree of uncertainty associated with many physical properties (such as atomic weights), the dispute on what properties to use as criteria of periodisation, and the inability to forecast how many elements remained to be discovered, all illustrate how the study of the 'blanks' became a powerful centraliser of experiments and discoveries. In one way or another, research activity revolved around the question: How many elements are there, and how can we best order them?

Let us detail two recent events in the history of chemistry related to 'blanks' in the periodic table: the troubled hunt for mysterious Element 43 (technetium, masurium), and the controversial discovery (1923) of hafnium, Element 72. It was precisely the discovery of three of the elements foreseen by Mendeleev (three 'blanks') which promoted the acceptance of Mendeleev's system: (eka-aluminium or gallium by Lecoq de Boisbaudran in 1875, ekaboron or scandium by Nilson in 1879, and ekasilicon or germanium by Winkler in 1886).

The epistemological status of these discoveries is still a matter of contention among philosophers of chemistry. Mendeleev considered the existence of nine unknown elements (including gallium, scandium and germanium), as well as the need to correct the atomic weights of five elements (including beryllium, tellurium and uranium). And as put by Mendeleev himself, "the confirmation of a law is possible only by deducing consequences from it, and by justifying those consequences by experimental proof."[62] But as highlighted by Scerri, the number of verified predictions equals the number of predictions which turned out to be false, so not a good score for the confirmation of the law of periodicity.[63] However, despite fewer than optimal numbers, Mendeleev's table had a predictive ability which was lacking in alternative formulations, such as the tables by Odling, Newlands, and Lothar Meyer, hence Mendeleev's eventual widespread acceptance.

How can the periodic table guide research? A simple example: by the position of the 'gaps' predicted by Mendeleev in the Table, one can predict in which minerals these new elements should be sought. In the 10th series, Group VII, from his second table (1872), Mendeleev predicted the existence of two elements still unknown below manganese, that would have atomic masses 100 and 190, respectively. He named them ekamanganese and dwi-manganese; eka- and dwi- are Sanskrit prefixes, meaning 'first' and 'second'. Mendeleev was a friend of German Indologist and Sanskrit scholar Otto von Böhtlingk (1815-1904), his colleague in St. Petersburg, which may explain his use of Sanskrit (Mendeleev did not know the language). Speculations on a possible analogy between the periodicity of the elements and the phonemes of Sanskrit are fantasies.

Elements with atomic masses 100 and 190 were really discovered: technetium (atomic Number 43) and rhenium (atomic number 75). For over two centuries chemical literature accumulated innumerable cases of spurious, never confirmed discoveries, i.e. 'discoveries' of already known elements or of mixtures of elements.[64] Unguided research rarely led to new discoveries. But the discoveries mentioned above were achieved by using the positions of the missing elements in Mendeleev's table as a guide. The most striking example of such a 'guided' discovery is the discovery of hafnium (1923) by Gyorgy de Hévesy (1885-1966) and Dirk Coster (1889-1950). Hafnium was Mendeleev's ekazirconium and was effectively obtained from zirconium silicate ($ZrSO_4$) extracted from the mineral alvite. Mendeleev's prediction was in this case strengthened by Bohr's theoretical arguments, and by the discovery of the new metal by mineralogist Victor Goldschmidt (1888-1947) in 1925.

The association between prediction and discovery is not obvious in the case of elements 43 and 75. Although Walther Noddack (1893-1960), Ida Tacke (1896-1978) and Otto Berg (1873-1939) published an article "Die Manganelemente" (1925), rhenium was actually discovered in the minerals molybdenite (MoS_2, today the most important source of rhenium), columbite [$(Fe,Mn)(Nb,Ta)O_6$] and gadolinite, and in platinum minerals.[65] Masurium, the supposed element 43, was never obtained from natural sources (there is a recent controversy on this issue), but allegedly identified spectroscopically in molybdenite. Properties of technetium and rhenium are more similar to molybdenum (element 42) than to manganese, but there are diagonal relations in the periodic table.

Chemists, historians and philosophers of science questioned the predictive capacity of the periodic table. Lothar Meyer doubted the possibility of making predictions based on classification. After the formulation (1913) by Henry Moseley (1887-1915) of what would be known as 'Moseley's Law', some have questioned whether these predictions had heuristic status since Mendeleev's times, or if it was Moseley's Law that was responsible for any heuristic value ascribed to the periodic system. Moseley predicted the existence of only 14 rare earths, one of them still unknown (element 61), and of six elements to be discovered – six 'blanks', in the periodic system (elements with atomic numbers 43, 61, 72, 75, 85 and 87). The 'criticism', while reasonable, seems exaggerated. One can justifiably say that Moseley's law and the discoveries that followed from it added to the stock of empirical data that ultimately offers support to the prior discovery of elemental periodicity.

The periodic table has also seen many uses in non-strictly chemical research. It is employed in fields such as mineralogy, geology and geochemistry.[66] The table itself benefited from the search for new minerals and still unknown elements in these minerals. Before ionic rays were known, isomorphism and so-called isomorphic substitutions were important for the 'periodisation' in mineralogy. This can be seen in the table by Vladimir Vernadsky (1863-1945), of the University of Moscow, considered one of the 'fathers' of geochemistry. The introduction of magnitudes such as atomic mass, atomic number and ionic radius allowed Norwegian mineralogist Victor Goldschmidt (1888-1947) to establish the substitutions in mineral series, such as the feldspars (Goldschmidt's rule).

PERIODICITY AND SOME PHILOSOPHICAL CONSIDERATIONS

In 1869, Mendeleev's Periodic Table, the model of all tables to come, appeared. Mendeleev's representation is not only the prototype, so often modified, of the record of all subsequent tables, but its own theoretical basis (the periodic law) – is the basis for all later tables. Mendeleev's classification should not be regarded, however, as the crowning of precursor classifications – the Russian chemist's table is grounded, *malgré lui*, on philosophical assumptions. Mendeleev initially did not consider philosophy important for the formation of chemists, but during his professional life, especially after the Congress of Karlsruhe (1860), he became himself a philosopher of chemistry.

His intellectual positions are original and difficult to fit into some philosophical school. But it is generally accepted that later in life, as an old man, Mendeleev would accept something like *Kantian* epistemology: the belief that humankind, even when well-equipped with the tools of science, was unable to comprehend the "thing-in-itself", i.e. substances as mind-independent entities. In fact, he would say that substances can only ever be studied by "their properties or by their relations to our organs of sense and to other substances and bodies" although he clearly accepted substances' independent existence "for there is something in its nature which is self-existent."[67]

Such a view was also dear to Goethe, namely, that experience is, to an important extent subjective – every scientist experiences phenomena in a way that is only his/her, not being able to see through the eyes of someone else. It is according to this Kantian framework that Mendeleev considers himself to be a realist (although it must be said that there is a less prominent interpretation of *Kantian* ontology which places the German philosopher closer to idealism). According to Vucinich:

> *To Mendeleev being a realist meant denying the ontological unity of the universe and rejecting revolution as a source of natural and social change. It also meant recognising not only the powers of science but also its limitations. But above all, it meant adopting a philosophical outlook untrammelled by metaphysics.*[68]

So, despite being a self-declared realist of some sort, positivists, nihilists and Marxists alike all attempted, in vain, to exhibit Mendeleev's ideas were in agreement with their intellectual frameworks (and political agendas) and count him as one of their own.

Several of the periodical classifications presented during the nineteenth-century show relations with philosophy, relations only sometimes explicit. But it was Mendeleev's periodic system that most aroused the attention of philosophers of science, not forgetting the 'philosophy of science' implicit in the work of Mendeleev himself – which for some is empirical, for others theoretical, or even empirical/theoretical). Also, his table is sometimes considered just a classification based on experimental data, and sometimes a representation of a law or theory.

It is necessary to separate the theoretical bases of chemical periodicity together with experimental data from the experimental data of the philosophical aspects involved in the periodic law and the resulting table. A supposed dialectical materialism that would permeate Mendeleev's science is a fiction by Friedrich Engels (1820-1895), for whom the periodic classification was a victory of dialectical materialism, an unconscious application of Hegel's law of transformation (though Marx explicitly states that his dialectic differs and opposes that of Hegel) concerning the transformation of quantity into quality. Engels's analysis of 1890 was made in the absence of Mendeleev himself, who never accepted this interpretation by Engels and Marx, or even Heraclitus's principle of transformation as a universal principle.

For Mendeleev, and in accordance with leading ideas from his time, "the elements are constituents of nature, essentially unique, *permanently fixed* and genetically discrete, irreducible to a primary matter."[69] Richard Feynman (1918-1988) would later say about something seeming permanently fixed: "To our eyes, our crude eyes, nothing is changing, but if we could see it a billion times magnified, we could see that from its own point of view it is always changing: molecules are leaving the surface, molecules are coming back."[70]

Mendeleev, after the discussions at the Karlsruhe Congress, approaches the issue later raised by Feynman with surprising insight, solving the problem inherent in atoms and molecules in three stages; at the macroscopic level, at the microscopic level, and in the relationship between the macroscopic and the microscopic. On the macroscopic level, it is necessary to distinguish in current chemical language between 'body' and 'substance'; at the microscopic level, to distinguish between 'atom' and 'molecule'; and finally, to establish a relationship between the two levels." He expands on this:

> *It is evident that water does not contain gaseous oxygen or oxygen in the form of ozone; it contains a substance capable of forming oxygen, ozone and water... It is necessary to distinguish the concept of a simple body from that of an element. A simple body substance, as we already know, is a substance, which taken individually, cannot be altered chemically by any means produced up until now or be formed through the transformation of any other kinds of bodies. An element, on other hand, is an abstract concept; it is the material that is contained in a simple body and that can, without any change in weight, be converted into all the bodies that can be obtained from this simple body. A similar definition of an element and the same argument for the need to distinguish clearly between an element and simple body were later presented in the first part of Principles."*[71]

An immediate perception by the senses refers to macroscopic phenomena, it is a perception of the transformations that occur in 'bodies'. But 'bodies', necessary to understand the transformations that occur, refer to the idea of 'substance' (= element). As Gaston Bachelard (1884-1962) would later say, the experiment never puts us in contact with the 'substance', but without the notion of 'substance' it is impossible to understand experiments (which refer to 'bodies'). It proceeds at the microscopic level, differentiating atom from molecule:

> *We call a 'molecule' the quantity of 'substance' that reacts with other molecules, and which occupies in the vapor state volume equal to two weights of hydrogen [...] 'atoms' are the smallest quantities of chemical masses indivisible from the elements, which form the molecules of simple and compound bodies.*[72]

For more than 60 years our high school teachers, capturing the essence of Mendeleev's argument, taught students that 'atom' is the smallest part of an element that conserves its properties, and 'molecule' is the smallest amount of a substance that retains its properties. In a similar fashion, 'element' is the set of all atoms of the same atomic number (atomic weight, in the time of Mendeleev): the simple substances coal, graphite and diamond are formed by atoms of the element carbon. Mendeleev's simple but ingenious innovation related macroscopic and microscopic levels:

> *A simple body is something material endowed with physical properties and capable of chemical reactions. The term 'simple body' corresponds to the idea of 'molecule' ... The name 'element' should be reserved for the particles which form the simple and compound bodies, and which determine how they behave from the point of physical and chemical view.*[73]

Fritz Paneth (1887-1958), one of the few chemists to philosophise, rationalised these concepts along with ontological and epistemological considerations. The word 'element' refers to the idea of 'atom'. The element, the *Grundstoff*, belongs to the transcendental world and is not observable. The simple substance, *einfacher Stoff*, is observable because it belongs to the world of 'primitive' or 'naive' realism. The *Grundstoffe* are, therefore, the entities that fill the 'squares' of the periodic table. Still on this subject, American chemist Benjamin Harrow (1888-1970) offered much earlier (1930) a very simple, perhaps too simple, anthropomorphic explanation:

> *This periodic Law is really more complicated than our exposition would lead the reader to believe; but for our purpose [diffusion of scientific knowledge] all complications can here be discarded. For us the important lesson that the periodic law teaches is that since there are family relationships among, since there are brothers and sisters, there must be fathers and mothers, from which we conclude that there must be a 'something' in the universe simpler and still more fundamental than the elements – a 'something' out of which the elements themselves are built.*

This 'something', recent studies have shown, is the proton and the electron, the positive and the negative particles of electricity. All atoms are made up of protons and electrons. The atoms of any element, such as gold, are practically alike, but an atom of gold is different from an atom of chlorine. On the other hand, the protons and electrons, so far as we can tell, are the same, whether they are found in an atom of gold, in an atom of chlorine, or in any atom of the 92 elements.[74]

Harrow certainly knew Moseley's law: there is no direct evidence of this, but reference to anthropomorphic "brothers" and "mothers" must have been inspired by the radioactive decay series. Mendeleev himself explained Harrow's 'something' in 1869 when he referred to carbon, diamond and coal. In the following quote, we can identify Paneth's classification of *Grundstoff* and *einfacher Stoff*:

> *It does not matter how the properties may change, something remains unchanged, and when these elements form compounds, this something acquires a material value and establishes the properties of the element containing compounds. With respect to this, we know only one property characteristic of each element, the atomic weight. The magnitude of the atomic weight, according to the very essence of matter, is a number unrelated to the degree of division of simple bodies but related to the material part common to the simple body and its compounds. The atomic weight does not refer to coal or diamond, but to carbon.*[75]

Finally, it may prove useful to verify if the concept of the element has remained unchanged over the years, or whether it has undergone some sort of 'reconceptualization'. Going to back to Lavoisier, we can see that the French chemist introduced a pragmatic concept of element: a substance which cannot be further subdivided by any chemical means. This pragmatic, empirical and operational approach to the definition of 'element' can be traced back to Condillac and even to Locke, and it can be singled out as one of the probable causes of Lavoisier's inability in elaborating a philosophy of chemistry.

The alternative to the pragmatic approach can be found in classic metaphysics: the element is a 'substance' (from the Greek *ousia* = being). *Substantia* (Latin) is that which 'grounds' things like attributes or properties. Substances, in generic philosophical terms, can therefore, be said to be the fundamental entities of reality. According to this definition, if atoms are the basic things from which all else is constructed, then atoms are (or are like) substances. There is an obvious realist interpretation of reality here, substances – the basic building blocks of reality – are real, and so are all instantiated properties.[76]

Philosophical schools such as logical positivism or pragmatism (i.e. those which consider metaphysics a simple matter of convention) would deny the reality of substances. For the antirealist there can be no fact of the matter about the foundation of reality, so substances, atoms, elements, or any candidate to what can be ontologically basic, lose their objective status. It must also be said that one can coherently think of a substance in different terms. It can be said to be a kind of entity, like an object. And an object can perhaps be thought of as a bundle of properties, in which case 'object' is not basic, or simple. The same reasoning could be applied to an atom or even element.

Mendeleev's views, according to Martin Labarca and Alfio Zamboni, seem to somehow combine pragmatism with a metaphysical approach to substance, what they call a dual sense.[77] Elements are foundational, abstract and real, but deprived of properties. 'Operational' elements are 'simple' substances (like atoms) which possess properties. One could think of such a hybrid approach used by Mendeleev – in contrast to other classifications – as vulnerable to challenges originating from Soddy's definition of isotope. But Paneth, in the 1930s, sustained that isotopy does not modify chemical properties (hydrogen being the exception), so no revision of the chemical periodic table would be necessary. Each new isotope would be a new 'simple substance', and not a new abstract element. Paneth's arguments convinced the IUPAC to substitute the atomic mass as characteristic of each element by the atomic number (1923), a property of the abstract (real) element.

But with the discovery of the neutron (Chadwick, 1932) some adaptations were indeed necessary: for each element, there is an upper and lower limit of the number of neutrons, and of atomic mass, to ensure the atom's stability. An up-to-date representation of periodicity would be based not just on the atomic number, but also on the number of neutrons. Labarca and Zamboni propose to reconceptualise the element as: "a certain class of entity constituted by a 'fundamental substance' [metaphysical concept] which exhibits two representative properties, the atomic number and the limits for the atomic mass, with contingent proprieties varying case-by-case."[78] The primary criterion for the classification of the elements, they propose, would be the number of neutrons, whereas the second criterion would be the electronic distribution – and not the atomic number. Nevertheless, even under such a reconceptualisation, the periodic system maintains most of Mendeleev's conception.

THE PERIODIC TABLE AND AESTHETICS

Georges Urbain (1872–1938), a chemist interested in so many arts and involved in filling the "blanks" or "voids" left by Mendeleev in his table, said in one of his non-chemical works: "from an intellectual point of view, the sage and the creative artist are twin brothers."[79]

It is also often the case that scientists regard the products of their work (theories, models, proofs) as holding aesthetic value. But the precise nature of the relationship between science and aesthetics is difficult to grasp, and often involves confusion of categories. As an example, one could refer to a rather cryptic quote from the engineer who turned physicist and philosopher, Abraham Moles (1920-1992):

> *In the act of creation, the scientist does not differ from the artist: in principle, there is no difference between artistic creation and scientific creation, they work with different materials of the Universe […] creation is an act of spirituality, which, using all 'dimensions' of spirituality, all its planes of freedom and phenomenological apprehension, cannot be limited to a logical Universe, to a ludic Universe of gratuity, but must include all aspects of spiritual freedom, […] there is only one unique intellectual creation.*[80]

It is one thing to say there can be beauty in the products of scientific investigation, or in the tools used to represent scientific knowledge (such as the periodic table), quite another to say there is beauty in the 'act' of creation. Intermingling aesthetics with spirituality does not do Moles any favours either. Furthermore, in science, there is often talk of discovery, instead of creation, so where and when scientific creation occurs must be specified.

Several aspects of science may hold aesthetic value. It is possible that aesthetic considerations play a role in theory choice – for example, in a situation of empirical underdetermination of theories: when having to choose between empirically equivalent rivals, one could appeal to aesthetic properties of one theory to favour it over the other. Or, it could be said that valuing simplicity as a heuristic guide is yet another instance of science intermingling with aesthetics.

More importantly, as singled out by Ivanova, "beauty is also often taken to stand in a special epistemic link to truth. Many scientists argue that a beautiful theory is more likely to be true."[81] To assign an epistemic role to aesthetics is difficult. Can we ever justify confidence in the truth of a theory as arising from its beauty? Any aesthetic judgement is secondary to empirical adequacy, which remains to this day the main criterion theory acceptance.

Furthermore, it seems unlikely that beauty can ever be a predictor of scientific success. One could easily challenge the association between aesthetics and scientific progress (or truth, or empirical adequacy) and claim it to be arbitrary and misleading. One could do so by pointing out cases of 'beautiful' theories that turned out to be false (such as *Newtonian* mechanics), while highlighting the success of theories which lack any aesthetic appeal. As Ulianov Montano points out, aesthetic values such as simplicity and unity are not [usually] instantiated by highly successful theories.[82]

However, if one considers not truth but understanding to be the aim of science, then it may be easier to assign an epistemic role to aesthetics. For Henri Poincaré (1854-1912) aesthetic values, Ivanova reminds us, reduced in the case of science to simplicity and unity, work as "regulative ideals to be followed because they are linked to the ultimate aim of science, namely, gaining an understanding of the relations that hold among the phenomena." Therefore, aesthetic value gains an epistemic role because it shows how, given a certain theory, "apparently disconnected phenomena are unified under a simple framework."[83]

We may now return to the case of the periodic table. While its acceptance is clearly owed to its success in predicting the discovery of a few elements, our appreciation of it as an object possessing important aesthetic value can be said to be the result of its excellent capacity to unify phenomena under a simple framework, therefore facilitating our understanding of, among other things, periodicity.

It falls outside the scope of this essay to address the question of whether aesthetic judgements in chemistry or science in general, may have objective validity. We wish to highlight, however, that there is consensus among the scientific community that the periodic table exhibits aesthetic properties that are widely regarded as desirable, such as unity and simplicity. This helps explain why different representations of the table exist outside chemistry or academia.

So, let us now focus on less abstract digressions, and briefly survey the periodic table's existence outside chemistry books. It can be found in works of art around the world, ranging from gigantic murals or monuments to postal stamps.

In fact, the first homage of the Periodic Table on a postal stamp was issued by the Spanish mail in 2007 (centenary of Mendeleev's death). Created by inorganic chemist, Javier Garcia-Martinez (Alicante University), it was designed to transmit a "modern and positive image of chemistry" and "to catch the attention of stamp users and collectors alike with a colourful and highly geometric design." Garcia-Martínez was inspired by Dutch painter Piet Mondrian (1872-1944), whose abstract expressionism, geometric expression, and judicious use of colours help detail the 'voids' in the table.[84] On the verse of the stamp, there are mural tables and printed tables in laboratories and classrooms.

Over the years, some representations of the periodic table acquired notoriety or made the news – like the one recently discovered at St. Andrews University, printed in Vienna (1885) and brought to Scotland by Thomas Purdie (1843-1916). The oldest preserved printed table (1876) can be found in the Museum of the University of St. Petersburg. The historically most interesting case of mural tables is the large mural (2,2 x 2,7m) existing in an auditorium in the old building of the University of Barcelona (Taula de García-Banús), painted in 1934 by commission of professor Antonio Garcia-Banús (1888-1955). Historians later discovered that it was a reproduction of the table conceived in 1926 by Bonn professor Andreas von Antropoff (1878-1956), a popular table at the time,[85] but abandoned in 1945 because of Antropoff's ideological positions. Some historians refer to *Bauhaus* and *de Stijl* influences in Antropoff's table. Recently rediscovered by Philip Stewart (b. 1939), the table was carefully restored in 2008 by professor Claudi Mans i Teixidó.[86] Mans would say this is a unique case in the history of chemistry: a republican and socialist professor adopted a table created by a national-socialist professor, which was restored during a fully democratic government, after surviving Franco's dictatorship. J. Marshall suggests Antropoff's table was situated halfway between Mendeleev's classic short table and Alfred Werner's (1866-1919) "long" table from 1905, and that the resulting practicality was responsible for the popularity of Antropoff's table, even in the United States.[87]

It would probably be best if ideologies never intervened in the progress of science. But ideologies often accompanied Mendeleev's career: his prestige in tsarist Russia was enormous, *malgré lui* a national hero of the Soviet Union, although he did not see himself as socialist and despite his criticism of popular demonstrations after failure of the 1905 Revolution. Mendeleev, in Brooks' opinion, was always loyal to the tsarist regime, although there were frequent disagreements between the scientist and lower-ranked bureaucrats.[88]

Another classic table, very popular in the 1920s and 30s, was the one designed by American chemist Henry David Hubbard (1870-1943), from 1901 to 1938 secretary of the *United States National Bureau of Standards*. Hubbard modified Mendeleev's table (1924), giving it a more compact form, suitable for use in class. It has been updated several times, 12 editions until 1936, 18 until 1963, sponsored by *Sargent & Welch*, Buffalo, manufacturers of teaching material. Hubbard's was the most widely used periodic wall table in American schools. It was also well received in Brazil during the 1930s, the so-called "Hubbard's Brazilian Table" from the former *Escola Nacional de Engenharia* (now the Polytechnic School of the Federal University of Rio de Janeiro), a table 'rediscovered' by Sir Martyn Poliakoff, of Nottingham University. Hubbard's Brazilian Table includes dated symbols, like Cb (columbium ^{41}, instead of niobium), Ma (masurium ^{43}), Il (illinium ^{61}), Ab (alabamine ^{85}), and Vi (virginium ^{87}), among other curiosities, none of which were recognized discoveries.[89] In an era of atavistic nationalism, Hubbard's table clearly illustrates the reluctance to abandon elements 'discovered' in the United States, even though these were not recognised by the international chemical community and would later have to be removed from the table.

In past centuries chemists had different, often subjective, views on the structure of matter, which reflected on their teaching of chemistry. The same can be said of chemistry teachers and their subjective views on how best to present the periodic table. In some cases this personal exploration of the table by teachers was incredibly creative, and quoting Bertomeu-Sanchez (*et al*):

> *The most creative books were not necessarily the great treatises written by creative academic chemists. Obscure chemistry teachers, who were not necessarily active in scientific research, attempted innovative and ambitious systems of elements in order to satisfy both didactic and scientific constraints. Textbook writing remained a creative activity. By creative, we do not necessarily imply innovation or great discovery. They were creative in a more modest way as they expressed original and ambitious interpretations of the foundations of chemistry.*[90]

This idea is exemplified by one of the few Brazilian contributors to represent the periodic system, Alcindo Flores Cabral (1907-1982), professor at the School of Agriculture Eliseu Maciel (nowadays part of the Federal University of Pelotas), in 1946. Examining a mysterious mural at the entrance of the chemistry building in Pelotas, professor Eder Lenardão rediscovered his table (2001).[91]

In the case of a few talented chemists the necessity to write more engagingly and creatively – often inspired by episodes from their personal and professional lives – was responsible for the production not just of textbooks, but high-quality, transcendent or poetic literary pieces. Two examples deserve special attention: "Il Sistema Periodico" by Primo Levi (1919-1987), published in 1975, and the biographical "Uncle Tungsten – Memories of a Chemical Boyhood" (2001) by neurologist Oliver Sacks (1933-2015). For Sacks:

> *The Periodic Table is incredibly beautiful, the most beautiful thing I had ever seen. I could never adequately analyze what I meant here by beautiful – simplicity? Coherence? Rhythm? Inevitability? Or perhaps it was its symmetry, the comprehensiveness of every element firmly locked into its place, with no gaps, no exceptions, everything implying everything else.*[92]

The elements in Primo Levi's "Il Sistema Periodico" become symbols and metaphors for the various phases of the author's life, so that a summation of elements becomes his life story or a memoir. On such metaphorical usage Luigi Dei (b. 1956) concluded that "we can say that the properties of the elements often reflect the properties of life itself: volatile, inert, lustrous, precious, poisonous, brittle, explosive..."[93]

In the chapter dedicated to iron, Levi thus refers to the Periodic Table:

> *That the nobility of Man, acquired in a hundred centuries of trial and errors, lay in making himself the conqueror of matter, and that I had enrolled in chemistry because I wanted to remain faithful to this nobility. That conquering matter is to understand it, and understanding matter is necessary to understanding the universe and ourselves: and that therefore Mendeleev's Periodic Table, which just during those last weeks we were laboriously learning to unravel, was poetry, loftier and more solemn than all the poetry we had swallowed down in liceo, and come to think of it, it even rhymed! That if one looked for the bridge, the missing link…*[94]

Most of such literary pieces portray the periodic system in a positive light. This need not always be so. In the poem "The Periodic Table of Elements", Australian poet Bruce Greenhalgh shows his disenchantment with the table:

> *…that it listed more/and less/than earth, wind, fire and water, [but 118 elements are] arranged by atomic number/ in an obscure scheme/of electrons and abbreviations, [without any] reflect/on sodium/or potassium/or Byzantium [in reference to Yeats's poem], no flair, no mystery, no poetry, nothing for me", [poet and periodic table] have gone our separate ways.*[95]

Chilean poet Nicanor Parra (1914-2018), professor of theoretical physics in Santiago, has a similar, if more ironic, take on the table. In his long poem "Los Profesores" ("The Teachers"), he speaks of "teachers turning us mad/with questions which do not matter" – including the periodic table.

One may be tempted to explain why, given the success of the table in systematizing existing knowledge and predicting new elements, a chemist would react negatively to it. One could speculate that the table, for some people, may fall victim to its own success. It would be very difficult for a chemist to attempt any different form of systematisation today, which some would see as a limitation to creativity. The table also indicates what possible new chemical discoveries may be like, which may lessen our sense of amazement when progress is indeed achieved.

Finally, some chemical elements, isolated or classified by the table, inspired musical compositions as well. Edgar Varèse (1883-1965) honoured platinum with a piece for flute solo (1936), "Density 21.5" (the density of the metal), and the composer and theorist Andrew Stiller (b. 1946) composed in 1988 "A Periodic Table of the Elements" for 14 wind and percussion instruments.[96]

This brief survey of the table's presence in non-chemical or academic contexts goes to show that some scientific achievements, when consolidated through a universally accepted form of representation, have the tendency, or at least the potential, to become iconic – in the sense defined at the beginning of this essay. More on this in the next section.

THE PERIODIC TABLE AND POP CULTURE

The periodic table is the object of this essay, so let us define less rigorously what after all is 'popular culture'. Also, the definition of "science fiction" differs from author to author; let us adopt here the definition given by Darko Suvin (b. 1930): "... a literary genre or verbal construct whose necessary and sufficient conditions are presence and interaction of estrangement and cognition, and whose main device is an imaginative framework alternative to the author's empirical environment."[97]

Science Fiction does not necessarily deal with the actual Periodic Table, but often invents (sometimes even foresees) fantastic and fanciful imaginary elements in an environment artificially constructed, but still plausible and credible. Hans Dominik (1872-1945), engineer, in his time famous as author of many science fiction stories and novels conceived in *Atomgewicht 500*, published in 1934, artificial elements with very high atomic weights.

At the time he wrote it uranium had the highest atomic weight, 238. Dominik's scientific views are no longer valid, but the author's utopian vision with respect to the future of nuclear chemistry is worthy of note. Some lines from the book: "The most important! You know what I mean. Atomic weight? Two hundred and forty-two! Four unities more than the atomic weight of uranium. Congratulations, Slawter! You were the first to obtain a substance non-existent on Earth and in terrestrial conditions"[98]. Transuranic and transfermic elements exceed this weight; the heaviest known element to date is oganesson (Og, atomic number 118 - first synthesised in 2002 at the Joint Institute for Nuclear Research in Dubna, Russia, by Russian and American scientists), with an atomic weight of 294.

With the probable completion of the ninth series of the table, we will surpass the value 300 ... will these imaginary elements one day become reality? Suze Kundu wrote in N*ature*: "scientists and non-scientists alike have long been dreaming of elements with mighty properties. Perhaps the fictional materials they have conjured up are not as far from reality as it may at first seem."[99] In face of "Atomic Number 500" and the ongoing study (a reality) of the Periodic Table, may we expect an upper limit for this "expanded" Periodic Table? Or a lower limit? What will this limit be? Sima Lozanic speculated about a limit already in 1906. Niels Bohr (1885-1962) in 1922 expanded electronic configuration to element 118, but in 1924 he concluded theoretically that it would be difficult to surpass atomic number 137.[100] Beyond the "island of stability" around atomic masses 290 – 300, perhaps atomic number 128 will be the limit, or, for Albert Khazan (b. 1934), this figure would be 155.[101] Pekka Pyykkö (b. 1941) and Burkhard Fricke, on the basis of mathematical calculations, suggest a limit of $Z = 172$ (suggesting a noble gas)[102], and for Walter Greiner (1935-2016) there is no limit for the Periodic Table.

On the chemical properties of aluminium (an element already known but still unused at the time), Charles Dickens (1812-1870) wrote in 1856:

> *Within the course of the last two years [...] a treasure has been divined, unearthed and brought to light [...] what do you think of a metal as white as silver, as unalterable as gold, as tough as iron, which is malleable, ductile, and with the singular quality of being lighter than glass? Such a metal does exist and that in considerable quantities on the surface of the globe.*[103]

Dickens' 'treasure' element did become reality. Another contemporary of Dickens, English chemist and industrialist John Carrington Sellars (1840-1916), in an attempt to popularise chemistry and find connections with Christianity, published in 1873 a curious and rather long poem titled *Chemistianity*, "an oratorical verse, in poetic measure, on each known chemical element [...] in the universe."[104] Each of the 63 then-known elements received symbolic names. Dickens's wonder metal aluminium, for instance, was called 'Ktyon', and about it Sellars says: "Aluminium, the Bright Star of Metals,/ The principal metal in common clay/In extremely light, bright, and silver-like/It does not oxidise in exposure to Air..."[105] Sellars described in 'oratorical verse' the properties of the element. According to van der Krogt, Sellar's book (today very rare and collectable) was well-received at the time of publication.[106]

On the other hand, there is a perceptible trend in more recent fictional writing in which plausibly imagined chemical knowledge gives way to fantastic, far-fetched chemical worlds – as can be seen in superhero comics (Captain America, Wolverine), or in Tolkien's fantasy books, and even in Janet Kuypers' poetry: "I wracked my brain, 'wait a minute,/I know osmium, it's the densest metal/in the Periodic Table. But Diburnium?"[107]

J. Ober and T. Krebs include amongst their favourite fictional elements the *mithril* of the Hobbit, by J. R. Tolkien (1892-1973), the *dilithium* from the universe of Star Trek, and the *vibranium* of Captain America's shield.[108] *Mithril*, made by dwarves, resembles silver, but it is lighter and stronger than steel. *Dilithium*, a mineral found on different planets of the Star Trek universe, regulates the reaction between matter and antimatter. *Vibranium*, originating from Wakanda (Africa) exhibits a powerful capacity to absorb, store, and release vast amounts of kinetic energy. One cannot help but wonder whether reality will meet fiction at some point, and whether we will be able to say of a new element something similar to what Dickens said of aluminium.

Still, in the genre of popular culture, the musician, comedian and Harvard professor of mathematics Tom Lehrer (b. 1928) authored a song containing all the elements of the periodic table. The song was based on comic opera "The Pirates of Penzance" (*aka* "The Slave of Duty"), by Sir Arthur Sullivan (1842-1900).

In the case of cinema, probably one of the most efficient vehicles of mass communication, there has been little interest in the periodic table and its creator, Mendeleev. He has not been the subject of any movies, figuring only in documentaries such as "The Mystery of Matter" (2014). This is in sharp contrast to the cinema's interest in the lives and works of many notable scientists, such as Pasteur, Marie Curie, Ehrlich, Paracelsus, Copernicus, and even Julius Robert Mayer.

FINAL REMARKS

On November 2nd, 2017, the 39th General Conference of *UNESCO* in Paris proclaimed 2019 the *International Year of the Periodic Table*. This is, of course, a result of the table's iconicity and universal appeal. Such recognition does not mean that the table itself, or even the discovery of periodicity, are the most important innovations in the history of chemistry. One could think of Dalton's quantitative atomic theory, or Lavoisier's oxygen theory, as better candidates for most important breakthrough moments. Yet, most are quick to recognise the table as chemistry's most important icon.

Michael Mingos (b. 1946), from Oxford University, resumes the real possibilities of the Periodic Table:

> *The Periodic Table is neither a biblical tablet of rules nor a monolithic Rosetta Stone, which provides accurate translations of chemical trends and properties. It does, however, offer a flexible two-dimensional mnemonic for recalling the important characteristics of the 118 known elements and the structure of their constituent atoms. [...] It thereby provides a way of thinking for chemists which also reflects the individual's unique history and personality.*[109]

The table has undoubtedly been the most successful tool for the popularisation of chemistry and, by extension, scientific knowledge and practice. This cannot be explained just as a response to the discovery of periodicity. But perhaps it can be explained by the table's success in both, accommodating and systematizing existing knowledge (theories and data) and predicting new discoveries. As is always the case in science, empirical adequacy was the primary reason for the table's worldwide adoption as the best representation of what is known about the elements, atoms and their structure. But there were also other reasons for its positive reception in different countries.

Finally, we hope to have shown that it is the dual nature of the table – its capacity to enclose the totality of chemical and physical knowledge about the elements, and its usefulness as a research and teaching tool – that give it iconicity. And such iconicity is revealed by the table's appeal in domains outside of chemistry, such as the arts. By quickly surveying such domains, it shall be clear that the table's role as a main vehicle of scientific communication to the broad general public remains unchanged.

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Discovering Elements in a Scandinavian Context: Berzelius's *Lärbok i Kemien* and the Order of the Chemical Substances

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Abstract. During the Eighteenth century Sweden was a propitious context for the discovery of chemical substances and elements. At the beginning of his scientific career Jöns Jacob Berzelius contributed by his experimental research and discoveries to the preservation of the high scientific profile of his native country. Electrochemistry and chemical atomic theory marked Berzelius's scientific life and organized his vision of chemistry and his classification of substances. Berzelius used his *Lärbok i Kemien* to spread his discoveries and to frame his conception of chemistry. Focusing on Berzelius's textbook of chemistry the paper tries to enlighten a specific vision of chemical science which was very influential in the first half of the XIX century.

Keywords. Swedish science, Berzelius, textbooks of chemistry, communicating science.

1. CENTER AND PERIPHERY IN EIGHTEENTH CENTURY CHEMISTRY

The traditional reconstructions of Eighteenth century chemistry focused on the scientific relationships between Paris and the British research centers with some incidental reference to various German political contexts. The recent historiography of science has started to pay attention to peripheries and to their interactions with the main scientific centers, and such a new perspective has allowed to draw some richer and more complex pictures, to locate forgotten paths of knowledge, and to reconstruct some actual networks of personal and institutional relationships. Thanks to these current approaches, new light has been cast on theories and experimental pratices of Eighteenth century chemistry.

In the Eighteenth century Swedish science played a major role as regards the development of mineralogy, metallurgy, chemistry, and of the natural and experimental sciences. At the beginning of the Eighteenth century, losing the Great Northern War, the Kingdom of Sweden was no longer a military, imperial power,[1] it was a minor power but still played a significant role owing to its metallurgical activities and its production of guns. Chemists and mineralogists of the *Bergkollegium* (Board of Mines), chemists at Uppsala

University and members of the Royal Swedish Academy of Sciences were an important reference to the scientific culture of that time.[2]

Johan Gottschalk Wallerius (1709-1785), Torbern Olof Bergman (1735-1784) and the pharmacist Carl Wilhelm Scheele (1742-1786) were the protagonists of the Swedish scientific scene, particularly with respect to the interpretation of the discoveries of airs or gases. In the rich landscape of Enlightenment chemistry it is possible to identify French Stahlism, British experiments and discoveries of gases but also a true Swedish theory which Lavoisier himself considered a primary critical reference.[3] Swedish naturalists were famous for their discoveries of minerals and chemical elements, for some refined theories of gases by Scheele, and of the chemical affinities by Bergman. The translations into various languages of Wallerius's, Scheele's and Bergman's papers demonstrate their ideas were spread all over Europe. In Italy it was customary to say that sciences were migrating into cold Northern Europe.

At the end of the Eighteenth century Sweden had seemingly lost that very high position of prestige enjoyed during the Enlightenment; the second edition (1796; the first one had been edited by Bergman in 1775) of Henrik Teofilus Scheffer's *Chemiske föreläsningar* (chemical lectures) contained a traditional, pre-lavoisian chemical theory; the brief *Inledning till chemien* (1798) by the Finn Johan Gadolin (1760-1852), professor at the University of Åbo (Turku), presented a concise exposition of antiphlogistic chemistry (*antiphlogistiska systemet*) which was shaped according to the highly popular *Philosophie chimique* (1792) by Antoine-François Fourcroy.[4]

The history of Swedish chemistry is unavoidably connected to the name of Jöns Jacob Berzelius (1779-1848), a dominating authority of European science during the first half of the Nineteenth century. Berzelius was highly successful; he was the discoverer of many chemical substances and four elements, an impressive experimental scientist, a theorist of stoichiometry and chemical atomism, a prolific writer and editor of several journals. Jenny Beckman has recently reconstructed Berzelius's publication strategies emphasizing his efforts to spread his discoveries and conceptions, and his plan for preserving the status of European scientific language in the Swedish tongue.[5]

It is generally argued that the development of organic chemistry and the birth of unitary theories made Berzelius's dualistic theory obsolete, but it must be stressed that Berzelius's influence continued during the whole century, as demonstrated by Stanislao Cannizzaro who suggested to read and read again Berzelius's works and papers.

2. A CENTER FOR CHEMICAL RESEARCH: SCIENTIFIC PILGRIMAGES TO STOCKHOLM.

In 1815 Christian Gottlob Gmelin (1792-1860), a young German naturalist who was to become the professor of chemistry at the University of Tübingen, left his native land moving to Stockholm in order to improve his knowledge of chemistry. He remained one year in Sweden and paved the way for some other German naturalists. In the background of the chemists of the first half of Nineteenth century the specialization in Stockholm was a common trend for many German naturalists. In the map of the Nineteenth century chemistry Stockholm was next to Paris (the Lavoisian school), London (Humphry Davy) and Manchester (John Dalton). Gmelin's path was followed by Eilhard Mitscherlich (1794-1863), Heinrich Rose (1795-1864), Gustav Rose (1798-1873), Gustav Magnus (1802-1870) and Friedrich Wöhler (1800-1882), and the latter became the grand and noble father of German chemistry. At the beginning of his career Justus Liebig planned to go to Stockholm, but eventually choosed to go to Paris.[6]

This new scientific pilgrimage to Stockholm was caused by Berzelius. From 1812 to 1819 thanks to the patronage of Wilhelm Hisinger, a naturalist and industrialist, Berzelius founded a laboratory of chemistry in Stockholm; in 1819 he became the permanent Secretary to the Royal Swedish Academy of Sciences, and founded a new laboratory at this institution which was then located at *Stora Nygatan* in the ancient part of the city (*Gamla Stan*), and here the young German chemists went to improve their knowledge. Since 1829 the laboratory of chemistry was in Drottinggatan, next to *Adolf Fredrik Kyrkan*, where there was the new seat of the Academy, and this laboratory continued to be one of the crucial places of the history of European chemistry.

If we want to draw an exemplary picture of chemistry in the first half of the Nineteenth century we must have recourse to Berzelius: the portrait of Berzelius as a young, poor student of medicine at Uppsala University can be compared with one of the official portraits of the old, noble Berzelius, laden with medals, reputation and fame. This comparison can give the image of the surprising career of an orphan boy from a Swedish provincial district, but it also proves that between the end of the Eighteenth and the beginning of the Nineteenth century the science of chemistry could offer the opportunity for prestigious and social redemption.

To Berzelius we owe a surprising series of experimental discoveries, a new chemical nomenclature, the development of electrochemistry, the establishment of chemical atomism, the discovery and verification of stoichiometric laws, the dualistic theory, the formulation of the concept of isomerism, and the beginnings of a proper organic chemistry. In the light of some crucial experimental discoveries Berzelius could renew, invent, and organize the whole domain of chemistry.

At the end of the Nineteenth century Henrik Gustaf Söderbaum (1862-1933) published in German the first historical reconstruction of Berzelius's chemistry,[7] and at the beginning of the Twentieth century he started publishing manuscripts, travel diaries, correspondence (*Bref* or *Brev*), and from 1929 to 1931 a three volume *Levnadstecking*, that is a biography of Berzelius.[8] The publication of the correspondence offered the historian a fundamental resource, and the mammoth correspondence between Berzelius and Wöhler, edited by Otto Wallach (1847-1931) and published in 1901, gave a unique opportunity for understanding some main chapters of the history of chemistry in the first half of the Nineteenth century.[9]

The new established international history of science and of scientific thought has favoured a revival of interest in Berzelius's work. In 1981 Evan H. Melhado published a volume on *Jacob Berzelius. The Emergence of His Chemical System* which contains a detailed reconstruction of the background of Eighteenth century chemistry, an explanation of Berzelius's debt to Lavoisier's theory and of the differences between Lavoisier's system and Berzelius's. The second part of this volume, devoted to *The Berzelian Theory of Salts*, presents a detailed historical analysis of the genesis and structure of the Berzelian system of chemistry.[10]

Berzelius contributed to the cultural and philosophical controversies of his time and he severely criticized F.W.J. Schelling's natural philosophy, and the *Naturphilosophie* which was welcomed in Sweden by naturalists, physicians, philosophers and theologians. In 1992 Melhado and Tore Frängsmyr edited a volume on *Enlightenment Science in the Romantic Era. The chemistry of Berzelius and its cultural setting*, which is the best recent, overall work on the Swedish chemist. Among the contributions to this volume one must point out the papers by Anders Lundgren on *Chemical Atom*, and by Alan J. Rocke on *Berzelius's Animal Chemistry*. Melhado's *Novelty and Tradition in the Chemistry of Berzelius (1803-1819)* is a wide-ranging detailed reconstruction.[11]

The *Afhandling om Galvanismen* (1802) and the *Föreläsningar i djurkemien* (1806-1808) mark the beginning of Berzelius's scientific career which is characterized by the publications of papers in Swedish and in German in the Acts of the Swedish Academy of Sciences and in German scientific journals. The German texts were the basis for translations into French and English.

Colin A. Russell reconstructed Berzelius's electrochemical theory, Lundgren has clarified the question of the Berzelian chemical atomism,[12] and thanks to the contemporary historiography of chemistry one can schematize the main stages of Berzelius's stochiometric research in the following way: in 1811 Berzelius published in the Paris "Journal de Physique" his outstanding *Essai sur la Nomenclature chimique*;[13] the same year he started publishing in Ludwig Wilhelm Gilbert's "Annalen der Physik" the first part of the *Versuch, die bestimmten und einfachen Verlhätnisse aufzufinden, nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind* (1811-1812);[14] in 1819 in Paris Berzelius published his *Essai sur la Théorie des Proportions Chimiques et l'influence chimique de l'Électricité* which contains a *coup d'oeil* on the theory of chemical proportions, the order of chemical substances, the method to calculate the relative number of atoms in chemical combinations, some observations on nomenclature, the classification of substances starting with the oxides, and one hundred and twenty alphabetical tables of the atomic weights of the main substances.[15] These publications confirm the impressive quantity of experimental research that Berzelius made in his laboratory for establishing the true order of the well-known and newly discovered chemical substances.

Here, I do not want to resume Berzelius's discoveries and theories, I only hope to show some aspects of his work, in connection with the history of his chemical textbook because my aim is to clarify the Berzelian image of science which was so influential during the Nineteenth century. Through a consideration of his chemical textbook, it can be appreciated the interactions in his thought between didactics of science and strategies of communication. Berzelius built a network of personal relationships which became an instrument of information and controversy, and he used the Stockholm Academy of Sciences as an arena for the dissemination of a specific, Swedish image of chemistry.

3. A FAVOURITE CHEMICAL TEXTBOOK.

In 2000 Anders Lundgren and Bernadette Bensaude-Vincent edited a volume on *Communicating Chemistry*, devoted to *Textbooks and their Audiences, 1789-1939*. It is a very important collection of essays aimed at understanding the value and historical meanings of the chemical textbooks. In his *Introduction* to *The Study of Chemical Textbooks* John Hedley Brooke clarifies the main problems which are met in the study of scientifc textbooks, and notwithstanding many methodological complications this study reveals that textbooks can be more enthralling than their unglamorous image might suggest. [16]

A historical analysis of Berzelius's various *Försök* and *Versuche* allows to clarify the genesis of his discoveries, the formulation and modifications of his conclusions, in short the construction of a science. A study of his highly popular textbook of chemistry may be useful for giving a picture of his didactics of science and of the structure of his chemistry, but the origin and the development of this textbook comprise a very complicated history which reveals all the difficulties in defining a stable body of scientific knowledge when the science is making daily progress and is the focus of controversies and diverging approaches. In *Communicating Chemistry* there is an important paper by Marika Blondel-Mégris devoted to Berzelius's textbook and to its multiple translations, but the center of her study is the German context and Wöhler's editions.[17] The vicissitudes of this textbook appears to be still more complex in Germany and when its fate in France, Italy, Spain and the Netherlands is made clear.

At the very beginning of the Nineteenth century Berzelius was dissatisfied with the chemical textbooks of his time. We must keep in mind that he was a self-taught man in chemistry, and he studied this science by reading Lavoisier's *Traité élémentaire de chimie* (1789) and Christoph Girtanner's *Anfangsgründe der antiphlogistischen Chemie* (1792), two works which marked the shift from the theories of phlogiston to the antiphlogistic approach. In Germany Lavoisier's chemistry was not welcome, and many German chemists used it because it was clear but they did not believe that it was also true.

In 1808 in Stockholm the first volume (*Förra Delen*) of Berzelius's *Lärbok i kemien* appeared. It opened with the author's statement that since Sweden has not had a complete textbook of chemistry written in Swedish for a long time, and such a textbook was necessary because Swedish young people cannot use the *utländska Lärböker*, foreign textbooks. Berzelius also states that he has tried to treat chemistry in all its generality (*i allmänhet*).[18] This first volume confirms Berzelius's belonging to Enlightement philosophy, because it presents a very simple definition of chemistry, which remained unchanged in all the other editions, and underlines the recent status of chemistry as a recognized science, notwithstanding its very long history.

The writing of the *Lärbok* was a very hard task because Berzelius used his textbook both to encode knowledge, that is to reorder accepted science, and to present his new experimental discoveries. The second volume could only be published in 1812, the third one in 1818, but in 1817 the second edition of the first volume (*Första Delen*) was published, and it was an improved and partially rewritten text (*omarbetad och betydlygt tillökt*). In the Preface of this second edition no reference to Swedish young people was made; Berzelius only emphasized that chemistry had made great progress in the past ten years, mentioning the decomposition of alkalis, the doctrine of chemical proportions and the importance of electricity as a chemical agent.[19] Berzelius put aside the Swedish destination of his textbook, he remained faithful to the Swedish tongue but at that time he was aware of the diffusion of his text in Germany. It is important to note that a comparison of the title pages of the 1808 and 1817 editions shows a significant increase in Berzelius's accademic qualifications, and this growth confirms his successful professional and scientific achievement.

In the Enlightenment cultural setting the French editions of a scientific text were the groundwork for the translations into English or Italian, whereas German or Russian texts and local academic translations continued to use Latin which guaranteed their circulation. In the case of Berzelius's textbook the German versions became the reference texts for the translation into French, and from French into other languages, so a novelty developed: the German texts were used for the dissemination of the Swedish science outside Sweden. On the 19th of October 1825 from Berlin Wöhler informed Berzelius that the capital of Prussia "ist jetzt ein wahrer Sammelplatz für Scandinaver" (a true place of reunion for Scandinavians), because together with the Swedish chemist Carl Palmstedt (1785-1870) there were some other Swedes and four Norwegians: the Scandinavian naturalists carefully considered the German scientific context.[20]

Together with Mitscherlich, Wöhler was the official voice of Berzelius in Germany and the main protagonist of the diffusion of his textbook, but before Wöhler started translating from Swedish, Berzelius's work had already gained some attention. Historians do not usually recall that in 1816 Johann Georg Ludolph Blumhof (1774-1825), a naturalist of the Grand Duchy of Hesse, published in Leipzig the translation of the first volume of the *Lärbok* with the title of *Elemente der Chemie der unorganischen Natur*. In Blumhof's *Vorbericht* it is stated that Berzelius is famous for his literary productions and for his outstanding observations and discoveries which make the first two volumes of his *Lärbok* a reference text. Blumhof underlines that Berzelius deals with chemistry "bloss in Allgemeinen", without references to its pratical applications, but he thinks that the teaching of chemistry permits an application of knowledge by those naturalists who are interested in industry and in the practical arts.[21] The *Elemente* is a useful text to chemists because it contains all the discoveries of the present age; it is therefore an updated textbook, but it is also written "im ächt philosophischen Geiste", which is missing in the other "chemischen Lehrbücher".[22] To Blumhof, a precise description of the laboratory experiences, an up-to-date presentation of chemistry, a philosophical spirit that shapes the writing and the structure of the topics are the peculiarities which make Berzelius's text a fundamental contribution to science.

Blumhof's translation was limited to the first Swedish volume of 1808. In 1820 in Dresden, for K.A. Blöde's edition of the first volume of Berzelius's *Lehrbuch der Chemie* the translator used the second Swedish edition.[23] The second volume was translated by Palmstedt and the third one by Wöhler; the three volumes were reprinted in Reutlingen in 1821, 1824 and 1828. In 1825 in Dresden the first volume of the *Lehrbuch der Chemie* was published in a new translation by Wöhler, and on the front page it is stated that Berzelius had changed in Swedish the Blöde-Palmstedt translation and that Wöhler had translated it and included Berzelius's modifications. In fact, the volume opens with a long *Vorerinnerung* signed by Berzelius and dated Stockholm, July 16th, 1825, in which are listed all the novelties compared with the original plan of 1807, for instance Davy's discovery that alkalis can be reduced to metals, the properties of the new metals, the newly discovered properties of known metals, the discoveries of new radicals, new earths, and so on.[24]

In a letter from Berlin dated the 25th of July, 1825 Mitscherlich informed Berzelius that Wöhler had checked the translation from Swedish into German of the additions, declared that Wöhler understood Swedish, and the Swedish chemical books, better than his other former pupils, and suggested his Master and Friend a full involvement of Wöhler in the German editions of his textbook.[25] Wöhler's editions from 1825 to the fourth, grand edition of 1835-1841 in ten volumes contain updates and additions directly furnished by Berzelius. In the last years of his life Berzelius, unable to carry on laboratory research, prepared a new German edition of his textbook, published in 1843-1848. In 1843 he wrote the Dutch chemist Mulder that "Je poursuis toujours avec assiduité le travail pour refondre mon Lehrbuch".[26] A comparative and detailed study of these editions is very difficult owing to the mammoth quantity of printed materials which they contain, but it could surely furnish much information about the knowledge added by Berzelius to the various German editions of his textbook.

Wöhler was the official spokesman for Berzelius in Germany, and from Germany to the remaining parts of continental Europe, but the historical relevance and the scientific impact of the Berzelian textbook is confirmed by a three volume edition published in Stuttgart and edited by Heinrich F. Eisenbach and Carl August Hering. The title of *Lehrbuch*, adopted in 1820, is conserved but on the front page it is stated tha that Stuttgart edition contains some updates relating to new research and discoveries and this statement explains why chemists were so attentive to the novelties coming from Stockholm. The editors declare that Berzelius's volumes could be used for *Vorlesungen* (Lectures) and *Selbstudium* (personal learning) by numerous groups of people: physicians, pharmacists, administrators, agronomists, craftsmen, and industrialists.[27] This specification shows that chemistry was by then socially relevant as a science, and a science able to favour some productive activities, so a sort of continuity was established between modern chemistry and the seventeenth century project by Johann Rudolph Glauber (1604-1670) for the use of a *chimistry* which could favour *Dess Teutschlands Wohlfahrt* (*Prosperitatis Germaniae,* 1656-1661).[28]

The German edition of 1832-1833 confirms Berzelius's deserved reputation and his importance in the history of modern chemistry. In the presentations of the various editions of his textbook which I have been able to study, it is always stated that the Swedish chemist is so famous that a translation of his textbook needs no justification or explanation. In their *Vorrede* Eisenbach and Hering write that the plan of the textbook is what "die Natur der Sache" requires: a general introduction containing some notions derived from physics, the chemistry of inorganic substances, which follows the order of salts and their bases, and the doctrine of chemical combinations which closes the inorganic chemistry and opens to the organic chemistry.[29]

In his *Vorrede* to the 1835 German edition Berzelius states that it is not an easy enterprise to outline a good plan for a *Lehrbuch* because a textbook has a different aim from a *Handbuch* whose main feature is a strict systematic order. In a *Lehrbuch* this order is to be carefully sought because the exposition of the science is to begin from the most simple concepts that can be easily kept in mind. The writing of a chemical textbook is very demanding and the attention of the reader is to be captured, and when the stated goal is reached, the study of a science does not prove to be hard. Berzelius acknowledges that he has not adopted a perfect systematic order because he wants to introduce in science that lightness which is helpful to a beginner.[30]

Many different needs and preoccupations converge around Berzelius's textbook: the pedagogical aim is connected with the project of a book which could present an orderly system of chemistry, but this science was in such a dynamic state that updates, corrections and adjustments of the book were continuously required.

In order to further illuminate the historical meaning of Berzelius's textbook it is appropriate to recollect some data concerning the other editions.

On November 1828 Berzelius received a letter from A.-J.-L. Jourdan, a French physican, who was charged by the Paris printer Didot to translate the *Lehrbuch*. Jourdan discussed the French title with Berzelius, who preferred that of *Éléments de Chimie*, asked him to send updates and modifications in comparison with the German edition.[31] This request is common to every translator who wanted to include chemical novelties the planned edition, and therefore the various translations are full of Berzelius's experimental and theoretical changes. From Berzelius's correspondence it can be understood that he sent some updates in Swedish (*tilläg*) to Wöhler, who translated them into German (*Zusätze*) in order to assure their dissemination in Europe. The first volume of the *Traité de chimie traduit par A.J.L. Jourdan* was published in Paris in 1829,[32] and aroused Berzelius's violent protests because of translation errors; these protests are documented in Berzelius's letters to Pierre-Louis Dulong.[33] In June 1829 from Stockholm Berzelius recalled that in Berlin he had asked the advice of Mitscherlich, Heinrich and Gustav Rose, Magnus and Wöhler before accepting Didot's and Jourdan's proposal for a French translation of his textbook,[34] and this episode confirms that Berzelius's German pupils composed a true, compact Berzelian school of chemistry. Jourdan was replaced by Melchior Esslinger and the publication of Berzelius's *Traité* in eight volumes was completed in 1833.

The Paris edition is not the only French version; in Bruxelles in 1839 the first volume of the *Traité de chimie* was published. Jean-Benôit Valerius (1807-1873) was the translator taking his text from the fourth German edition. In the *Avis des Éditeurs* there is, besides the customary homage to Berzelius and the emphasis on his scientific relevance, the statement that this new traduction was made "pour ainsi dire sous les yeux de l'auteur" because it contained the *Zusätze* of the fourth German edition, and therefore it was different from the Paris French translation.[35] It is stated that the textbook is addressed to professional chemists and above all to those who are beginners in the science. The Bruxelles edition was completed in 1846 in four volumes, and the existence of two French translations gave rise to different destinies of Berzelius's textbook in Spain and in the Ancient Italian States.

In 1845 Rafael Saez y Palacios and Don Carlos Ferrari y Scardini, first and second chemists at the General Hospitals in Madrid, published the first volume of the Castilian translation of Berzelius's *Lehrbuch* with the title of *Tratado de Química*; their translation was based on Valerius's French translation. In their presentation the two *Traductores* underlined that chemistry, after its inclusion among the sciences by Lavoisier, has not produced a more important textbook than Berzelius's. They used Valerius's edition because it was the most up-to-date version but made note of the fact that "la química no ha quedado estacionada en estos últimos años", owing to surprising and continous discoveries.[36] The second volume was published in 1845, but this literary undertaking started changing with the third volume because the title was modified to *Tratado de Química Mineral, Vegetal y Animal*[37] and the following thirteen volumes – the translation was completed in 1851 – were translated using the second French edition that in 1845 Esslinger and Ferdinand Hoefer started publishing in their unending search for the latest version.

In the first half of the Nineteenth century many cities of the Ancient Italian States produced translations of scientific textbooks in a competitive system of book trade. From 1826 to 1828 in Milan a translation of Berzelius's textbook was published in four volumes with the title of *Trattato elementare di chimica teorica e pratica*.[38] During the Eighteenth century Venice and Naples played a major role in the spread of European science and in these cities two different editions of Berzelius's work were published. In Venice, the printer Antonelli charged the chemist Francesco Du Pré, who contributed to the debates on antiphlogistic theory, to translate the Berzelian textbook from the French Jourdan-Esslinger version. The Venice edition was published in eight volumes between 1830 and 1834 and it was entitled *Trattato di chimica*.[39] In Naples in 1838 Giovanni Guarini started publishing a new translation of Valerius's edition[40] which was completed in nine volumes in 1845. In the Italian States chemistry was not officially established but an Italian reader at least had at her/his disposal some updated Italian versions of Berzelius's textbook.

The Dutch version must be considered because it marked the involvement of a physician and chemist of Rotterdam and Utrecht in the network of Berzelius's scientific relationships. On the 24th of June 1834 Gerardus (Gerit) Johannes (Jan) Mulder (1802-1880) wrote to Berzelius sending him the plan of a Dutch translation of his textbook compiled by Mulder's three pupils (A.S. Tischauser, B. Eickma, A.F. van der Vliet), and informed him that he was using the Berzelian text for his lectures to forty young students. He also informed Berzelius that such an editorial enterprise was very risky because the Netherlands were a small country where people could read foreign languages. Mulder asked Berzelius for some unpublished notes in order to enhance the diffusion of the Dutch version.[41] Berzelius was proud of this translation and promised that he would send Mulder some unpublished notes prepared for the fourth German edition. In November Mulder thanked Berzelius and informed him that the editorial enterprise had started, and highlighted the relevance of the unpublished notes. In a letter dated 1835 Mulder informed Berzelius about the poor state of chemical research in the Netherlands and his choice of the Berzelian text in order to favour the growth of the socio-cultural perception of chemistry as an outstanding science.[42]

The first volume of the *Leerboek der Scheikunde* was pubblished in Rotterdam in 1834 and on title page it was stressed that the translation was based on the third German edition but improved (*en vermeerderde oorspronkellike uitgave*) by some unpublished portions, and Mulder's *Voorberigt* underscored their scientific relevance.[43] The Dutch version was completed in 1841 in six volumes. Subsequently, Mulder became one of Berzelius's most faithful correspondents, and organic chemistry was their favourite topic. Mulder and Berzelius were both interested in the chemical composition of proteins, and they had a common aversion to Liebig. The work of Liebig on the radical of benzoic acid, his study of animal chemistry and the applications of chemistry to agriculture are epoch-making, but Liebig had a zealous, upbeat character which was the antithesis of Berzelius's philosophical calm. In March 1838 facing Liebig's criticisms, Berzelius confessed that "nous [Berzelius and Liebig] cherchons tous les deux la vérité, c'est une beauté pour laquelle il faut se battre d'une manière honnête".[44]

My review of the translations of Berzelius's *Lärbok* – one must note the lack of a translation into English – contains a sequence of data and may be considered dry and boring,[45] but it was necessary for understanding the genesis and spread of that specific image of chemistry which Berzelius had constructed. Berzelius drove home his chemistry by using different strategies of communication and transmission because he wanted his Swedish chemistry to be rooted in the chemical communities of the European continent, in spite of the presence of contrasts and controversies. The surprising fate of the *Lärbok* allows the historian to observe the vicissitudes of Swedish science from a particular point of view. But Berzelius's textbook was not the only resource at his disposal to describe scientific progress and to weigh in on his own vision of the state of the chemical sciences.

4. A PRESTIGIOUS ARENA

At the end of November 1818 Berzelius, who was then in Paris, was elected perpetual Secretary to the Royal Swedish Academy of Sciences. This institution founded in 1739 had always used Swedish for its academic transactions (*Kongl. Svenska Vetenskapsacademiens Handlingar*, then *nya Handlingar*) because scientific knowledge and technical expertise major tools in the development of the economy of the Kingdom of Sweden. The use of Swedish did not deter the dissemination of these transactions in Europe because partial translations into various languages were available, and up until 1792, the mathematician Abraham Gotthelf Kästner (1719-1800) translated the whole series into German. After 1792 many difficulties arose due to the decline of the cosmopolitan cultural climate of the Enlightenment, and to the Napoleonic campaigns, which limited the reception of scientific news from Stockholm. So, in December, 1820, reforms were introduced into the statutes of the Academy, and Berzelius became the prime mover of the reappearance of scientific communication from Northern Europe.

The reforms determined that on the 31st of March of each year, an official and solemn session of the Academy would take place, during which the Secretary was to present an annual report on the status of science. In March, 1821, Berzelius presented his first report which came to 150 printed pages. It is the first volume of Berzelius's *Årsberättelse om Framstegen i Physik och Kemi*, that became a yearly journal, whose first series (1821-1840) amounts to twenty volumes, while the second series, in seven volumes, finishes in 1847,[46] the year before Berzelius's death. Firstly Berzelius aimed at treating all the sciences, and then he focused on chemistry, physics, geology and mineralogy. Composing the reports was a heavy duty and his reports became more and more bulky: the report of March 1845 concerning chemistry and mineralogy consists of 692 printed pages.

The preparation of the reports obliged Berzelius to systematically read all European scientific activity, therefore enabling him to collect an impressive mass of information. The stated aims of the *Årsberättelse* were two: the first one was pedagogical; the second one was cultural and social. Berzelius vigorously supported the improvement of students' chemical preparation; with regard to his chemical textbook, the reports obviated the need for new editions of a massive textbook because they provided an operative, annual update of scientific progress. In presenting his reports Berzelius also wanted to reach a general and wide reading public in order to stimulate a social and institutional interest in science.

Berzelius was not just a historian or a *rapporteur* because the topics he dealt with were the objects of his own personal research. Therefore, the reports contain his critical considerations, and his strong criticisms. The official position of Perpetual Secretary of the Academy did not constrain his polemic spirit when the topics were chemistry and mineralogy.

The two series of *Årsberättelse* were not limited to a chapter in Swedish science because Berzelius's German former pupils got involved in disseminating the contents of the reports beyond Sweden. The first three volumes were translated by Gmelin; then the faithful Wöhler started translating all the yearly volumes with the title of *Jahrbericht*, and he was even able to excise the censorial expressions Berzelius used when he criticized German scientists. Thanks to his Swiss assistant Philippe Plantamour, Berzelius witnessed his reports published in French in Paris, and the first volume (1841) contains the statement "traduit du suédois sous les yeux de l'auteur".[47]

Årsberättelse was conceived as an instrument of renewal of the Academy of Sciences but it became an arena, an extraordinary literary place which Berzelius occupied in order to accomplish two main goals: the communication of knowledge, and of his research; and the severe criticism of certain philosophical and scientific trends of the culture of his time.

5. A BRIEF CONCLUSION

Sweden, Stockholm, and the Academy of sciences are very important places in the history of the development of chemistry from the Eighteenth century to the first half of the Nineteenth century because they were the context of some extraordinary chapters in the adventurous history of modern chemistry.

Berzelius is a symbol of Swedish science. He was aware that the growth of science was a difficult, but essential task, and he became both a steadfast, experimental researcher and a brilliant controversial figure who had committed himself to elucidate the ongoing progress of science. He adopted various strategies of communication, i.e. the writing of a textbook and of annual academic reports on science, and the creation of a network of personal relationships with students and other followers; these strategies allowed him to keep attention on his ideas and research alive.

Berzelius contributed to the success of chemistry in the Nineteenth century, but his ideas were slowly put aside, and together with his dualistic theory his project of a continuous, public information resource about science disappeared.

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Mendeleev's "Family:" The Actinides

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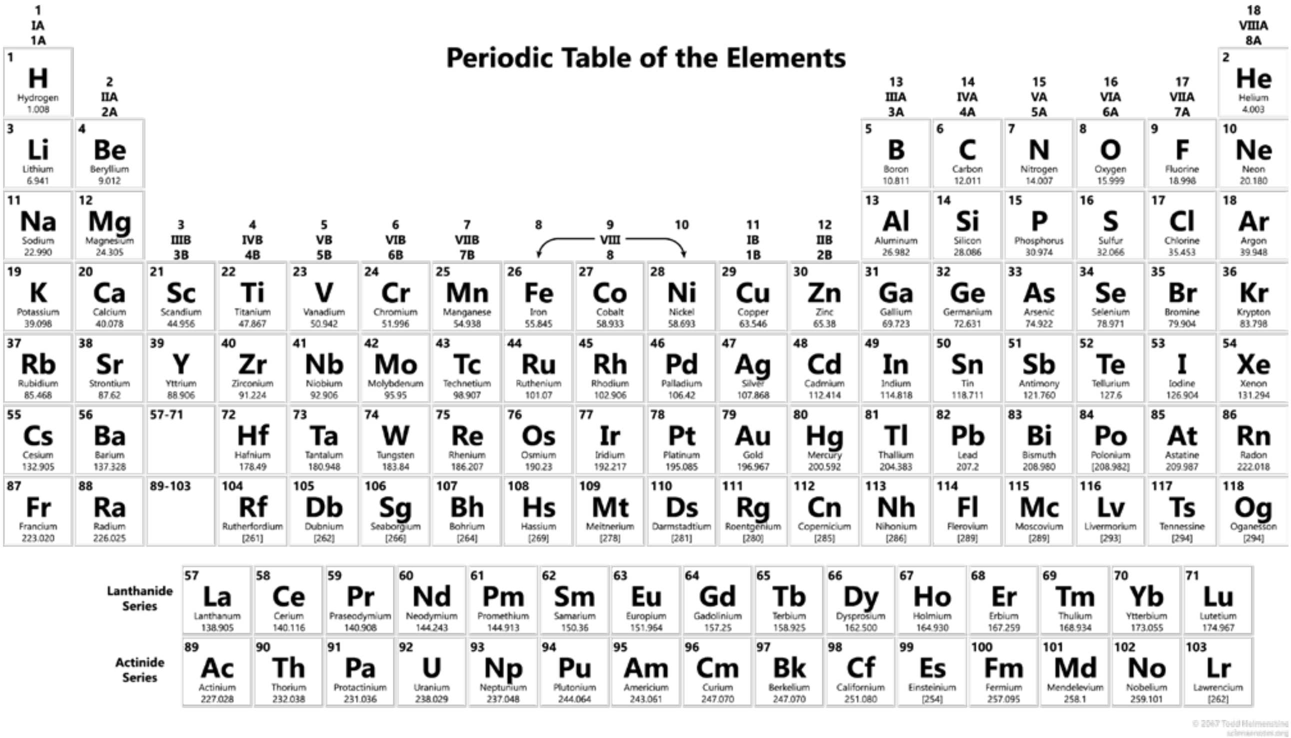
Abstract. When Dmitri Mendeleev laid out his ordered grid of the then-known elements in 1869, he could not have predicted the overwhelming and all-encompassing effect that his idea would have on scientific theory for the next 150 years. Nevertheless, he knew, presciently and from the start that he had conceived and laid claim to a powerful predictive tool that would bring some kind of order to a seemingly random set of fundamental substances. It is not within the scope of this paper to detail how the thought currents of his day were converging, little by little, on the realization that the universe was an intrinsically ordered one, nor is it our purpose to award to Mendeleev the title of sole "discoverer" of the periodic system. We wish merely to point out that he now occupies a well-deserved place within the system under the title of "mendelevium," element 101, and that, by this attribution, he belongs to a special "family," the actinides. How this family was uncovered, grew, and developed is the topic of this essay.

Keywords. Discovery, Fission, Intergroup Accommodation, Priority, Radioactivity.

INTRODUCTION

One glance at any modern periodic table (Figure 1) will superficially show that the actinides belong to a group of elements, from atomic numbers 89 to 103, that occupy the "southern plateau" offset from the main body of the periodic table and directly under the rare earths. How and why this "geography" came about is a tale to be told, fraught with both theoretical and experimental implications.

The first caveat is that this form of the table is one that Mendeleev himself never saw, nor even dreamed of. His table[1] took form from a set of cards on which Mendeleev had written the names and properties of all 63 of the then-known elements. Arranging them in order of increasing atomic weight, many of which were erroneous, he began nevertheless to see a pattern.[2] The genius of the arrangement was (1) spaces were presciently left open for presumed missing elements based upon obvious large gaps in atomic weights and physical properties; (2) anomalous pairs that threw the atomic weights out of order were retained in groups with similar valences instead; (3) as an afterthought, Mendeleev flipped his chart 90 degrees to the right, giving us



Periodic Table of the Elements

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

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Figure 1. The standard medium-long form of the periodic table.

the arrangement that persists to this day. By acknowledging an implied motif known only to Nature, he conferred a predictive quality on his table that bore fruit in the discovery of three of the missing elements within the following 20 years. His acceptance of the anomalous order of some elements left wiggle room for attempts to determine more accurate atomic weights and at the same time to allow this mystery to unfold into the discovery of isotopes many years later. His 90-degree "flip" eventually made the elemental groupings and trends in their properties more visible. Since this first table appeared, more than 700 others have found their way into print.[3]

The table shown in Figure 1 has headings with group numbers. Group numbers have been a bone of contention for years, leading to confusion for both practicing chemists and for students. In 1983, the American Chemical Society decreed the now-familiar 18-column numbered sequence version[4] and in 1988 the International Union of Pure and Applied Chemistry (IUPAC) followed suit, acknowledging that the system actually had been proposed as long ago as 1956 by Stockholm chemistry professor Arne Ölander (1902-1984).[5]

Over the course of the sixty years following Mendeleev's attempt,[6] a series of discoveries were made that began to reveal the modern picture of the structure of the atom. In chronological order these were cathode rays, emission spectra, canal rays, X-rays, radioactivity, the electron, α, β, and γ rays, Planck's Law, the photoelectric effect, the atomic nucleus, isotopes, Bohr model of atomic structure, atomic number, and the neutron. It gradually became clear that the number of nuclear protons equaled the nuclear charge and conferred on each atom its unique identity. This allowed scientists to determine how many elements existed in nature, theoretically 92. It also allowed them to devise experiments to push the envelope beyond 92 – to actually create new elements by bombarding and combining existing atomic nuclei, thus expanding the original periodic table to 118 elements. The impact of these discoveries has changed the course of history. The story of Debierne's discovery, actinium, and the fourteen elements that follow it are the subject of this article.

WHAT ARE THE ACTINIDES?

"Discovery is new beginning. It is the origin of new rules that supplement, or even supplant, the old…Were there rules for discovery, then discoveries would be mere conclusions."[7] The history of the discovery of the actinides, the 15 elements that comprise the second f-block row of the present periodic table of the elements, is peppered with rules: new rules, old rules transformed, new rules broken and remade – not necessarily by those doing the research, but often by Nature itself. Furthermore, if we consider the ways in which discoveries are made, they often fall into the categories of planned research, trial and error, or accidental discovery. Add to this a creative and observing mind[8] and you can encompass virtually all of the discoveries, and the methods used to further understand and gain more information about how the discovery can be exploited. It would be useful to analyze the following story for these characteristics for this is the discovery that set in motion the train of events that would expand and change the periodic table forever. As our exploration continues, we will discover that the actinides themselves, just like any family, have their share of rugged individuals, lawlessness, disruptive behavior, problem children, nonconformists, and law-abiding citizens.

In 1896, Henri Becquerel (1852-1908) reported that the double sulfate of potassium and uranium, formulated by him as $[SO^4(UO)K{\cdot}H^2O]$ using the superscript notation common at the time, emitted radiation capable of penetrating light-opaque paper to expose silver salts. He realized that the so-called phosphorescent material was emitting this radiation by its very nature and not because of becoming phosphorescent by exposure to light.[9],[10] Subsequent work showed that the radiation could also penetrate thin sheets of aluminum and copper. Becquerel realized at this stage that the radiation was analogous to the newly-discovered Roentgen rays.[11] Five additional notes in the same volume of the journal follow the course of his further experiments to show, beyond doubt, that the radiation was spontaneous and due to the uranium component of the salt. This conclusion is succinctly summarized in Becquerel's Nobel Lecture:

> *The phenomenon could be ascribed to a transformation of solar energy, like phosphorescence, but I soon recognized that the emission was independent of any familiar source of excitation...We were thus faced with a spontaneous phenomenon of a new order...[My experiments] showed that all uranium salts, whatever their origin, emitted radiation of the same type, [and] that this property was an atomic property connected with the element uranium.*[12]

It was Marie Curie (1867-1934) who eventually named the new phenomenon "radioactivity."

Radioactivity, discovered in a uranium salt, was to dominate the scientific, political, economic, and social scenes of the first half of the 20th century. And during that century, all the rest of the actinides were to be discovered.

Using radioactivity as the signature by which radioactive atoms could be detected, scientists began to bombard targets with particles such as α-particles and neutrons as they became available, and then to identify the products of these reactions. They gradually surpassed the limit of atomic number 92 imposed by nature to venture onto an unknown sea, not knowing where it would lead. So far, the journey has led to the discovery of 26 elements beyond uranium, completing the seventh row of the periodic table. This has involved massive amounts of funding, dedicated and persevering work on the part of genius-level individuals, and a surprising degree of international cooperation even during the Cold War. It has led to spectacular discoveries, overturned assumptions and theories, and given glimpses of a Nature full of unexpected surprises.

A simple definition of the actinides is: the elements beginning with actinium, with atomic number 89, and ending with lawrencium, element number 103. None of these elements possesses a stable isotope; every actinide is radioactive with half-lives that vary from billions of years, like thorium, ^{232}Th, with a half-life of 1.41×10^{10} y, to microseconds, like polonium, ^{214}Po, with a half-life of 1.62×10^{-4} s. The electronic structures of the actinide elements are complicated and still a subject of both theoretical and experimental research, although the latter is hindered due to the nature and scarcity of the atoms being studied. They are thought to all have a $7s^2$ outer electronic configuration, with variable and irregular occupancy of the 5f and 6d subshells. Table 1 lists these 15 elements (occupying about 12.7% of the periodic table) in order of atomic number. However, the chronology of discovery does not follow from this order.

The first actinide to be discovered, in 1789 by Martin Heinrich Klaproth (1743-1817), was uranium; a century later it was, as well, the first element recognized to be radioactive. Klaproth's alertness to detail accompanied by his pure love of science[13] no doubt prepared him to recognize a new substance when he dissolved the mineral pitchblende in nitric acid, and then neutralized the solution with a strong base and observed the formation of a yellow precipitate. Using the tried and true method of heating the precipitate in the presence of a reducing agent, he obtained a black powder that he took for the element, which he named uranium in honor of the newly-discovered planet, Uranus.[14]

A glance at Table 1 is quite informative regarding discovery. The first three actinides to be discovered were "lone wolf" affairs: a single discoverer is named, and that brings us to the end of the 19th century. It is an entirely different matter for the entire 20th century: discovery is a team affair, often with long lists of multi-

Table 1. Discovery of the Actinides.

Atomic Number	Symbol	Name/Symbol	Discoverer	Date of Discovery	Place of Discovery
89	Ac	Actinium	A. Debierne	1899	Paris, France
90	Th	Thorium	J. J. Berzelius	1829	Stockholm, Sweden
91	Pa	Protactinium	O. Hahn, L. Meitner, K. Fajans F. Soddy, J. A. Cranston, A. Fleck	1917	Berlin, Germany Karlsruhe Glasgow, Scotland
92	U	Uranium	M. H. Klaproth	1789	Berlin, Germany
93	Np	Neptunium	E. McMillan, P. Abelson	1940	LBNL*, USA
94	Pu	Plutonium	G. T. Seaborg, A. C. Wahl, J. W. Kennedy	1940	LBNL, USA
95	Am	Americium	G. T. Seaborg, L. O. Morgan, R. A. James, A. Ghiorso	1944	LBNL, USA
96	Cm	Curium	G. T. Seaborg, R. A. James, A. Ghiorso	1944	LBNL, USA
97	Bk	Berkelium	S. G. Thompson, A. Ghiorso, G. T. Seaborg	1949	LBNL, USA
98	Cf	Californium	S. G. Thompson, K. Street, Jr., A. Ghiorso, G. T. Seaborg	1950	LBNL, USA
99	Es	Einsteinium	G. Choppin, S. G. Thompson, A. Ghiorso, B. G. Harvey	1952	LBNL, USA
100	Fm	Fermium	G. Choppin, S. G. Thompson, A. Ghiorso, B. G. Harvey	1952	LBNL, USA
101	Md	Mendelevium	G. Choppin, S. G. Thompson, A. Ghiorso, B. G. Harvey, G. T. Seaborg	1955	LBNL, USA
102	No	Nobelium	G. Flerov & others	1958	JINR*, Russia
103	Lr	Lawrencium	A. Ghiorso, A. E. Larsh, T. Sikkeland, R. M. Latimer	1961	LBNL, USA JINR, Russia

*LBNL = Lawrence Berkeley National Laboratory; JINR = Joint Institute for Nuclear Research.

ple authors: we have entered the age of "big chemistry," characterized by specialized and expensive equipment in a national laboratory. It is easy to see that the Lawrence Berkeley National Laboratory (LBNL) exercised a monopoly on actinide discoveries, completing the list with element number 103, lawrencium, in 1961.

THE PLACE OF THE ACTINIDES IN THE PERIODIC TABLE

The modern periodic table is a grid consisting of seven rows (periods) and eighteen columns (groups). Periods 6 and 7 exceed the 18-column model with thirty-two groups each in the long form, and two offset rows of fifteen elements each in the traditional, or medium-long, configuration, used for convenience so that the table will fit on a normal printed page, as shown in Figure 1.

The grid, originally arranged in order of increasing atomic weights of the elements, is now arranged in order of increasing atomic number (the number of protons in the nucleus of an atom, often abbreviated Z) in one dimension, and in order of similar chemical properties in the second dimension to form the groups. This grid actually defines the way electrons arrange themselves in atoms in terms of principal energy levels and sublevels that they occupy, the so-called s, p, d, and f blocks. Not only has it brought order out of the chaos of so many elements with so many different properties, but it also functions as a theoretical tool, a "marvelous map of the whole geography of the elements."[15]

The two rows offset as "footnotes" from the main body of the periodic table each consists of fifteen elements. The top row, from lanthanum (Z = 57) to lutetium (Z = 71), along with two elements in the main body of the table, scandium and yttrium, are termed the "rare earths." The fifteen rare earths in the offset sit below yttrium with properties so similar to one another that the Czech chemist, Bohuslav Brauner (1855-1935), once proposed that they should all occupy the same space.[16]

Today, we take the placement of the actinides in the table for granted. However, initially, the first-discovered members of this group were placed in the main body of the table with actinium in the yttrium group, thorium under hafnium, protactinium under tantalum, and uranium under tungsten. Any transuranium elements to be yet discovered were expected to fall into place to complete period 6, with the last element in the row, Z = 104, fitting under radon.

The differences in chemical properties between, say, tungsten and uranium, soon made this assumption untenable. It was Alfred Werner (1866-1919) who first suggested that the heavier elements beyond uranium might need an intergroup accommodation similar to that of the rare earths.[17] Decades later, in 1940, when Edwin McMillan (1907-91) and Philip Abelson (1913-2004) discovered element 93, and shortly afterward, Glenn Seaborg (1912-99) and his team discovered element 94, they had a surprise waiting. Chemical tests revealed that the properties of both new elements were more similar to those of uranium than to their supposed homologs, rhenium and osmium.[18] At this point in the group's struggle to place the new elements in the periodic table, its extreme utility became spectacularly evident as both a flexible and predictive theoretical tool: Seaborg took up Werner's old idea and made it his own:

> *"I began to believe it was correct to propose a second lanthanide-style series of elements …[starting]…with element number 89, actinium, the element directly below lanthanum in the periodic table. Perhaps there was another inner electron shell being filled. This would make the series directly analogous to the lanthanides, which would make sense, but it would require a radical change in the periodic table…[I was told] that such an outlandish proposal would ruin my scientific reputation. Fortunately, that was no deterrent because at the time I had no scientific reputation to lose."*[19]

So the initial stages of discovery of the transuranium elements gave rise to a reconfiguration of the periodic table. The two new elements were appropriately named neptunium and plutonium after the two planets that lay beyond Uranus in the solar system. The rest of the actinides, as they were discovered, fell right into place under their rare earth homologs, and the transactinides, from atomic numbers 104 to 118 populated period 7 to its completion. It remains to be seen how the future treats the super-actinides beginning with atomic number 121.

THE PRE-URANIUM ACTINIDES: ACTINIUM, PROTACTINIUM, AND THORIUM

The Discovery of Thorium

Element number 90, thorium, was the first of this trio to be discovered in 1829. One of the most famous chemists of the time, Jöns Jacob Berzelius (1779-1848), Professor at the Karolinska University, Stockholm, in examining a curious mineral sent to him by Jens Esmark (1763-1839), a Norwegian mineralogist, thought he could discern the presence of a new element. He isolated the impure metal by reducing its fluoride salt with elemental potassium, and named it thorium, after the Scandinavian god, Thor. The mineral subsequently was called thorite.[20] In 1898, working independently, Marie Curie and Gerhard C. Schmidt (1865-1949) reported almost simultaneously that thorium, like uranium, was radioactive.[21,22]

The Discovery of Actinium

Seventy years were to pass before the announcement of the discovery of actinium (Z = 89), the element that gives its name to the entire actinide series.[23] Parisian André-Louis Debierne (1874-1949) began his studies at the École de Physique et de Chemie and began to study mineral chemistry following the death of his mentor, Charles Friedel (1832-99). Welcomed into the Curies' laboratory, he began to treat the enormous quantities of pitchblende they supplied to him until he soon discovered a new element; he was one of the youngest chemists ever to do so.[24] He called it actinium from the Ancient Greek word, *aktinos*, meaning beam or ray.

The year 1913 was a landmark one for science: in that year H. G. J. Moseley (1887-1915) conferred a number and identity on every atom by reason of its number of nuclear protons, and Frederick Soddy (1877-1956) discovered isotopes, atoms with differing neutron numbers in atoms with like atomic numbers. He also formulated the law of chemical displacement: α-emitters produce a daughter product two atomic numbers lower and β-emitters one atomic number higher. Moseley's work defined the list of elements still missing in the periodic table, namely elements 43, 61, 72, 75, 85, 87, and 91.[25] Soddy's work solved the puzzle of the myriad of new "elements" spawned by radioactive decay and his chemical displacement law had predictive properties. All of these facts figured weightily in the discovery of protactinium over the period from 1913 to 1917.

The Discovery of Protactinium

The hunt was now on for the missing element 91. Kasimir Fajans (1887-1975) and Ostwald Helmuth Göhring (1889-1915?) took up the challenge. Fajans was the first to succeed in deciphering the radioactive decay cascade of ^{238}U as the following:

$$\mathrm{U_I} \xrightarrow{\alpha} \mathrm{UX_1} \xrightarrow{\beta-} \mathrm{UX_2} \xrightarrow{\beta-} \mathrm{U_{II}} \xrightarrow{\alpha} \mathrm{Io} \qquad \text{[Eq. 1]}$$

which translates in modern terminology to:

$$^{238}\mathrm{U} \xrightarrow{\alpha} {}^{234}\mathrm{Th} \xrightarrow{\beta-} {}^{234}\mathrm{Pa}^{m} \xrightarrow{\beta-} {}^{234}\mathrm{U} \xrightarrow{\alpha} {}^{230}\mathrm{Th} \qquad \text{[Eq. 2]}$$

They found that the substance UX$_2$, a β-emitter with a very short half-life of about one minute, did not correspond to any radioisotope already known, realizing that it should occupy a vacant space in the periodic table. Due to its short half-life, they named this new element *brevium*.

Soon after Fajans's announcement, Otto Hahn (1879-1968) and Lise Meitner (1878-1968), working in Berlin, began to search for longer-lived isotopes of this same element. Hampered by the outbreak of World War I, especially by Hahn's conscription, Meitner carried on alone with a miniscule sample (21 g) of pitchblende, doing preliminary separations. It was only a year later that she received a kilogram sample of radioactive salts from which she was able to isolate an isotope of element $^{231}91$ with a half-life of about 32,700 y.[26] They named it protoactinium (later changed to protactinium by IUPAC in 1949), recognizing it as the mother substance of actinium.

In June of that same year, Frederick Soddy and his young student, John Arnold Cranston (1891-1972), published the results[27] of their heat treatments of pitchblende that yielded small sublimated amounts of protactinium for which they were unable to characterize the decay scheme. Obviously, the case of protactinium, with multiple publications claiming priority over a period of several years, was a complicated one. Eventually the priority was awarded, by custom, to the team that had discovered the isotope with the longest half-life, Hahn and Meitner,[28] but not without dealing delicately with the aggressive character and imperious temperament of Kasimir Fajans, who eventually withdrew his claim.[29] Cranston and Soddy, having published their papers three months after those of Hahn and Meitner, immediately recognized their priority.[30,31]

While it is beyond the scope of this paper to single out one element on which to discourse on chemical properties, we beg this little exception. Because protactinium's electron configuration is such that an energy crossover between its 6d and 5f orbitals results in nearly degenerate states, its bonding characteristics deviate drastically from its neighboring actinides. For this reason, protactinium's chemistry has been described as puzzling, peculiar, mysterious, and even smacking of witchcraft![32]

This little protactinium story was told at some length because it presages the multiple contentious priority disputes to follow: who gets the recognition for the discovery, and who gets to name the new element? The naming, in the end, came to be the most controversial issue, for as paleobotanist Hope Jahren (b. 1969) observes:

> *The scientific rights to naming a new species, a new mineral, a new atomic particle, a new compound, or a new galaxy are considered the highest honor and the grandest task to which any scientist may aspire.*[33]

DISCOVERY OF URANIUM FISSION

Enrico Fermi's Neutron Bombardment Experiments

The facts that uranium was discovered in 1789 and its radioactivity was recognized in 1896 seem almost trivial in light of the shattering discovery of its most important, and most all-encompassing property: its ability to undergo nuclear fission with the consequent release of immense amounts of energy. This property was undreamed of, and in fact dismissed, when Enrico Fermi (1901-54) and his team, the legendary "Ragazzi di via Panisperna," began to bombard uranium with neutrons. Fermi, convinced that knowledge of the atom was in large part complete, decided to investigate the properties of the atomic nucleus. He was one of the first to recognize the tremendous importance of artificial radioactivity, discovered by Frédéric Joliot (1900-58) and Irène Joliot-Curie (1897-1956), and for which they received the Nobel Prize in Chemistry in 1935.[34] Not possessing a cyclotron, and therefore lacking sufficient irradiated material, he decided to attack the atom with neutrons, discovered only two years previously by James Chadwick (1891-1974), instead of with α-particles. Since neutrons had no electric charge, Fermi reasoned, they would not be repulsed by the nuclear charge and might easily penetrate the nucleus itself. But since neutrons are not spontaneously emitted by radioactive isotopes, he had to obtain them by bombarding lighter elements, like beryllium, with α-particles emitted by natural substances, like radium. The neutron yield was low: just one per every 100,000 α-particles emitted, but undeterred, Fermi personally built the detectors necessary for counting atomic disintegrations. Success only came when, after bombarding all the lighter elements, fluorine and aluminum exhibited neutron-induced radiation.[35] After that, the list of nuclei susceptible to neutron irradiation grew.[36, 37, 38] Seven months later, in October, Fermi announced a second crucial discovery: the braking effect of hydrogenous substances, like water, on the radioactivity induced by neutrons. This amounted to the first step towards the utilization of nuclear energy.

Meanwhile at Rome, Fermi procured a very precious treasure, 1.6 grams of radium chloride from which he could extract *emanation* (or radon) that would be necessary for the production of neutrons. Further work by Fermi and his team led to seemingly two new elements with atomic numbers 93 and 94[39] due to neutron absorption by ^{238}U, and subsequent double-β-emission according to the following schemes:

$$^{239}\text{U} \longrightarrow {}^{239}93 + \beta^- \longrightarrow {}^{239}94 + \beta^- \qquad \text{[Eq. 3]}$$

Radiochemical tests showed that the activity of ^{239}U produced particles with properties that did not belong to any elements that preceded them in the periodic table. Believed to be eka-rhenium and eka-iridium, they were placed in period 7 of the table.

Criticism of the Fermi Group's Interpretation of Results

The Fermi group's announcement raised sharp criticism in scientific circles. In addition to the two "transuranic elements" they thought they had identified, they had found a good half-dozen others with a variety of chemical properties difficult to place in the periodic table since they had to be untangled from uranium's ongoing normal decay producing its own short-lived daughter products.[40] In fact, a chemist at the University of Fribourg, Ida Tacke Noddack (1896-1978), criticized Fermi's experimental judgment in only searching for elements in the neighborhood of element 92. She said that all elements should be searched for, even lighter ones. She did not hesitate to declare that she strongly doubted that the products Fermi identified were transuranium elements, but suggested nuclear fission instead.[41] This idea was unacceptable in the physics world, deemed highly speculative and lacking a theoretical basis. "Everyone knew" that atoms just did not fly apart in such a manner!

Things remained unresolved. A year later, Otto Hahn and Lise Meitner repeated Fermi's experiments using better facilities and they confirmed Fermi's results. Furthermore, according to them, they were also able to observe traces of elements 95, 96 and 97 that they provisionally called *eka-iridium*, *eka-platinum*, and *eka-aurum*.[42] However, as time went on, Irène Joliot-Curie and her Yugoslavian co-worker, Pavle Savić (1909-1994), published some papers documenting their concentration on only one of the products of neutron irradiation, that with a half-life of 3.5 hours, and after a few false starts conclusively stated that the product in question strangely resembled lanthanum, an already known element lodged in the middle of the periodic table. However, they never declared that they had actually found lanthanum, only a possible transuranic element that resembled lanthanum![43, 44] They could not imagine that they actually had lanthanum. Reality was hidden in plain sight!

Fission at Last!

The last of these papers made Hahn sit up and take notice: perhaps the almost forgotten suggestion by Ida Noddack was right after all. So later in 1938, after more experimentation and re-thinking, Hahn and his colleague Fritz Strassmann (1902-80) finally admitted that, as chemists, they realized they were dealing with radiobarium and radiolanthanum, but as physicists they added, "we cannot bring ourselves to take such a drastic step, which goes against all previous laws (a word that Hahn later changed to "experiences") of nuclear physics."[45]

Hahn communicated his conclusions by letter to Lise Meitner who was in exile in Sweden, fleeing the Nazi racial persecution, and she, with her nephew Otto Frisch (1904-79), in their famous walk in the woods, worked out a theory whereby the positive charge of the uranium nucleus was large enough to overcome the effect of the nuclear surface tension almost completely, allowing the nucleus to fall apart at the slightest provocation. They also worked out the fact that the mass loss on nuclear division would be about one-fifth the mass of a proton, exactly equivalent to the correct and enormous energy predicted by Albert Einstein's (1879-1955) relationship, $E = mc^2$.[46, 47]

Meanwhile, Enrico Fermi had already received his Nobel Prize in Physics for 1938, awarded

> *for his demonstrations of the existence of new radioactive elements produced by neutron irradiation, and for his related discovery of nuclear reactions brought about by slow neutrons."*[48]

The citation is very cautious in using the words "new radioactive elements," initially interpreted erroneously by Fermi as transuranium elements. But in the light of subsequent interpretations, he had actually discovered nuclear fission without knowing it, and actually produced new radioactive isotopes of elements previously known!

The Impact of Uranium Fission on the Modern World

By the irony of fate (or, some would say, of blindness), Enrico Fermi, in looking for transuranium elements, found nuclear fission. At the about the same time, physicist Paul Scherrer (1890-1969), working in Zurich, had an even closer encounter with fission.

> *He bombarded thorium...with neutrons and saw the fission fragments that Meitner and Frisch had identified. But Scherrer wouldn't believe his eyes. He thought his Geiger counter was malfunctioning. What wasn't expected wasn't seen.*[49]

Fermi, working in Fascist Rome in 1933, or Scherrer working in Switzerland, could have handed (or have seized from them) the information the Nazis would need to build a super-weapon six years earlier than the actual recognition of fission and its potential had they realized the evidence that was right before their eyes. Their "slight oversights" had a profound and beneficial effect on the rest of the world.

When word of the reality of nuclear fission broke upon the world, Niels Bohr (1885-1962) in Copenhagen struck his head with his fist and exclaimed. "Oh, what fools we were that we did not see this before."[50] And in Paris, Irène Joliot-Curie cried out, "What fools we were!"[51]

In 1941, just two years after the discovery of fission, Hans von Halban (1908-64) and Lew Kowarski (1907-79), two French exiles from the Curie Institute working in Cambridge but under the mentorship of Frédéric Joliot in France, were the first to establish that it was possible to sustain a chain reaction starting with uranium.[52] Simultaneously, two other Cambridge physicists, Norman Feather (1904-78) and Egon Bretscher (1901-73), hypothesized that the chain reaction could have military applications. By now it was recognized that the fissionable nucleus was the ^{235}U isotope of element 92, only seven parts in 1,000 in naturally occurring uranium. They also hypothesized that the more abundant isotope, ^{238}U, could be transmuted by neutron absorption into a new, hitherto unknown, element which would not only be fissionable, but would also have a long half-life according to a pathway almost identical to Eq. 3:

$$^{238}\mathrm{U} + n \longrightarrow {}^{239}\mathrm{U} \longrightarrow {}^{239}93 + \beta^- \longrightarrow {}^{239}94 + \beta^- \quad \text{[Eq. 4]}$$

What would follow from these discoveries was an international race for the ultimate weapon carried on in wartime under the shroud of utmost secrecy. Although research on the peaceful uses of atomic energy was also on the docket, it had low priority when it came to building the atom bomb. Heavy water, deemed essential for the propagation of a chain reaction due to its moderating (slowing down) properties on neutrons, was in short supply. The largest production plant, Norsk Hydro, was in the hands of Nazi Germany. Although many top scientists abhorred the idea of such a weapon, the Allied governments knew that they could not allow Germany to beat them in the race and use this weapon for world domination. As Frederick Soddy remarked presciently in 1904:

> *The man who put his hand on the lever by which a parsimonious nature regulates so jealously the output of this store of energy would possess a weapon by which he could destroy the earth if he chose.*[53]

THE BERKELEY HEGEMONY

To understand how the University of California at Berkeley eventually became the epicenter of discovery of the transuranium elements, it is necessary to describe some institutional facilities and historical events that came together to form a collaborative whole which led to the completion of the actinide series at this single and unique location.

The Invention of the Cyclotron

It is often said that the three landmark scientific inventions that gave the impetus to discovery of new elements, in chronological order, were the voltaic pile, the spectroscope, and the cyclotron. The voltaic pile, devised by Alessandro Volta (1745-1827), began the age of electricity, the energy source that drives the modern world, as well as the disciplines of electrodynamics and electromagnetism.[54] Its use by Humphry Davy (1778-1829) led to the discovery of numerous elements such as sodium, potassium, magnesium, calcium, strontium, barium, and boron. Similarly, the spectroscope, invented by Gustav Kirchhoff (1824-87) and Robert Bunsen (1811-99), changed the face of analytical chemistry, making possible the myriad instruments available today for purposes as varied as archaeological characterizations and medical diagnoses.[55] It also was the instrumental method in the discovery of thallium, indium, rubidium, and cesium. Perhaps the cyclotron (see Figure 2), invented in 1929 by Ernest Orlando Lawrence (1901-58) and

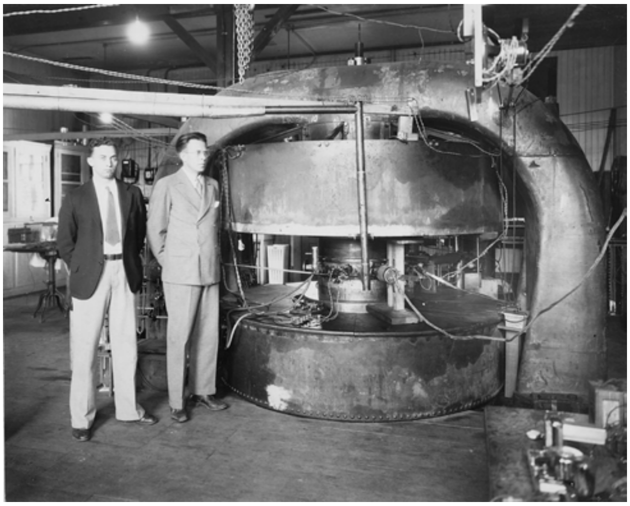

Figure 2. M. Stanley Livingston (L) and Ernest O. Lawrence in front of the 27-inch cyclotron at the old Radiation Laboratory at the University of California, Berkeley.

M. Stanley Livingston (1905-86), was the most prolific invention of all in terms of element discovery: 25 new elements and still counting!

With his ever-larger and more powerful cyclotrons, Lawrence pioneered what is now known as "Big Science," an approach that required large and expensive instrumentation, teams of researchers, interdisciplinary (chemistry, medicine, engineering, physics) collaboration, and consequently, a rather complex bureaucracy. He not only probed and illuminated some of the darkest mysteries held by Nature but also invented a new approach to the problem of studying Nature.

When Lawrence traveled to the centers of science in Europe during a belated "*Studienreise*," he was astounded at the groundbreaking discoveries European scientists, such as Marie Curie and Ernest Rutherford (1871-1937), were making with the most rudimentary equipment. He did not realize that high quality research and solid theoretical reasoning were the key to scientific advances – not necessarily glitzy equipment. As if to give the lie to the "small science" approach he had witnessed, Lawrence experienced a seminal moment in 1929 when he read an article in the obscure *Archiv f*ür *Elektrotechnik* which outlined a general approach on how to accelerate ions. By 1930 he was up and running, empirical trial and error running ahead of theory as well, until he discovered the two fundamental principles that would make his ideas work: the "cyclotron principle," as particles gain speed their paths spiral wider, and the "resonance principle," that protons keep time with the oscillator even as they accelerate. Putting these principles together accompanied by lots of hard work with prototypes eventually led to success.[56]

Eventually, with his cyclotrons running around the clock, Lawrence was a sort of overseer of workers, each one focused on bombarding only one element's nucleus to see what secrets it would reveal. He attracted great talent and enormous funding with a panache that would soon attract a Nobel Prize, for physics, in 1939 with the citation:

> *for the invention and development of the cyclotron and for results obtained with it, especially with regard to artificial radioactive elements.*[57]

World-Class Theoreticians and Experimentalists

In 1912, Gilbert Newton (G. N.) Lewis (1875-1946) moved from M.I.T. to take up the chairmanship of the chemistry department at Berkeley, at that time viewed by the eastern establishment as a scientific backwater. Of the five chemistry faculty in the department, Lewis retained three and managed adroitly to purge the other two. He then began to populate the department with people of his choice beginning with Joel Hildebrand (1881-1983), Kenneth Pitzer (1914-97), and Wendell Latimer (1893-1955). Some of his recruits went on to win Nobel Prizes, such as William Giauque (1895-1982), Willard Libby (1908-80), Melvin Calvin (1911-97), and Glenn Seaborg. Lewis imprinted his educational philosophy on his faculty: educate for chemical understanding and not rote learning. He required every faculty member to run undergraduate labs as part of their departmental duties; he promoted research, especially in physical chemistry, and eventually in nuclear chemistry. Much of Lewis's own work, especially on thermodynamics, and acids and bases, is still taught in undergraduate courses today.[58] Gilman Hall, the seat of Berkeley's chemistry department, was named a National Historic Chemical Landmark by the American Chemical Society in 1997.

Across the road in the physics department, a similar trajectory was in progress: game-changing research, pioneer scientists, and world-class students. In addition to Ernest Lawrence, recruited from Yale to run the Radiation Laboratory, such notables as Emilio Segrè (1905-89), Owen Chamberlain (1920-2006), J. Robert Oppenheimer (1904-67), Charles Townes (1915-2015), and Luis Alvarez (1911-88) were changing the world as we know it by their historic discoveries.

What Motivated the Research?

In addition to scientific curiosity and national pride, there were three other reasons for pursuing heavy ion research with a view to extending the periodic table. The first was to verify the validity of the periodic table itself as a theoretical tool. By forming elements of higher atomic number one by one and by examining their chemical properties, one could see examples of the trends predicted for the naturally occurring elements among the artificial ones. The second reason was to reach the theoretically predicted "Magic Island of Stability" in which, in the contest between half-life and spontaneous fission, half-life wins out. The third reason, which took pride of place during the years of World War II, was military and commercial exploitation of atomic energy.

THE FIRST TRANSURANICS: NEPTUNIUM, PLUTONIUM, AMERICIUM, CURIUM, BERKELIUM, AND CALIFORNIUM

Neptunium

Although it turned out to be upstaged by its long-lived and fissile daughter, plutonium, neptunium remains the first synthetic transuranium element. It is somewhat ironic that it was discovered accidentally during an experiment to study nuclear fission. Working with Berkeley's 37-inch cyclotron, Edwin McMillan bombarded uranium with neutrons and began to examine what he thought were the fission products. He detected two interesting ones, the first with a half-life of 2.3 d and the other with a half-life of 23 m. He was able to identify the latter as ^{239}U, but the longer-lived product was puzzling. McMillan, working later in partnership with Philip Abelson, realized that the isotope did not resemble any known element and that it had chemical properties similar to those of uranium. This was the first definitive proof that the new element, and presumably those to follow, would behave like the rare earths rather than its supposed homolog, rhenium, in the main body of the periodic table. Theoretically interpreted, there was an inner 5f electron shell that was being filled in, with the outer shells remaining the same, thus explaining the similar chemical properties. They published their results immediately, but only later named it neptunium, after the next planet out in the solar system. Since McMillan and Abelson were the only discoverers, there was no controversy over either the discovery or the name.[59] Element 94, about to make its debut, turned out to be completely unique. To appreciate its uniqueness, it is important to digress on two additional topics: a theoretical model of the atomic nucleus and the criteria for the discovery of new chemical elements.

The Liquid Drop Model

Ever since people began to believe in the existence of atoms, prior to Dalton, as a matter of fact, the idea of an atom was that of an impenetrable, hard sphere. Newton, in his treatise *Opticks* expressed this model of the atom in this way: "It seems probable to me that God, in the beginning, form'd matter in solid, massy, impenetrable particles…even so hard as never to wear or to break into pieces, no ordinary power being able to divide what God Himself made one."[60] With this model fixed in mind for centuries, it was a great break with tradition when, in the late 1920s, the theoretical physicist, George Gamow (1904-68) advanced a simplified liquid-drop model of the nucleus; it was extended in the mid-1930s by Wilfrid Wefelmeier (1909-1945), a student at Berlin-Dahlem, who proposed the idea of a non-spherical lump, or *Kernwurst*, with more exposed surface area to allow for the ejection of nuclear particles.[61] Otto Frisch found this model helpful in determining the parameters of fissile (fissionable) nuclei, especially the concept of nuclear surface energy, E_S, as a stabilizing force which was crucial to understanding it. There are two antithetical forces that determine the conditions under which an atomic nucleus will be fissile: the Coulomb energy, E_{Coul} and the surface energy, E_S. The model predicts that when E_{Coul} exceeds twice the value of E_S, a nucleus will undergo fission. When a liquid drop is perturbed by a little energy, it will just jiggle; there is a threshold energy that will engender a split between roughly two equal halves of the drop to give a bi-lobar, or dumbbell-shaped drop; applying the critical energy, E_C, exceeds the threshold energy and results in fission. E_C is directly proportional to the product of the atomic numbers of the separating nuclei, and inversely proportional to the sum of their radii. A potential energy vs. reaction coordinate diagram similar to those used to track ordinary chemical reactions (Figure 3) can be used to illustrate this effect.

As the mass number and atomic number increase, E_C generally decreases, but since this is a complex term, other factors such as odd or even numbers of nucleons, also determine the value. Table 2 illustrates this with some selected nuclei. Since the isotope ^{235}U is known to be fissile, any nuclides with E_C values lower than 6.5 MeV would also be fissile.

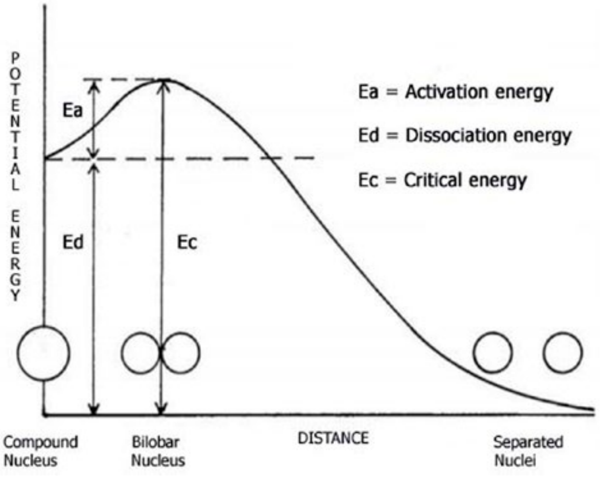

Figure 3. Model Illustrating Conditions for Nuclear Fission.[62]

Table 2. Critical Energies of Some Representative Nuclei.

Nucleus	^{232}Th	^{238}U	^{235}U	^{233}U	^{239}Pu
E_C	7.5 MeV	7.0 MeV	6.5 MeV	6.0 MeV	5.0 MeV

Criteria for the Discovery of New Chemical Elements

Now that it is evident that the periodic table can undergo expansion, it becomes necessary to define what forms of experimental proof must be offered to establish one's claim to having discovered a new element. An international group of scientists identified these criteria in a 1979 paper drawing upon the experience of many members of the group.[63] The most important criterion for asserting discovery is to confirm, without doubt, that the element possesses a unique atomic number, Z, different from all other elements known. At the same time, it is not necessary to establish the mass number unless evidence for it is directly related to the means by which the atomic number was determined. Establishing Z can be done in a variety of ways, and preferably using multiple ways: chemical identification, which is an ideal proof if the chemical procedure is appropriate, such as ion-exchange adsorption and elution; identification of characteristic X-rays that accompany the new element's decay, determination of the half-life, and measurement of the precise, unique energies of the emitted α-particles; or proof of a genetic decay relationship through an α-particle decay chain in which the isotope of the new element is identified by the observation of previously known decay products.

These criteria would prove to be extremely important in adjudicating competing claims in the decades that followed. These criteria, despite the claim by Neil Rowley that physicists alone were responsible for expanding the periodic table beyond element 92,[64] left room for either chemists or physicists to establish the identity of a new element.

Plutonium

The creation of neptunium turned out to be the stepping-stone to plutonium. The team involved did not include Abelson, who was only temporarily working at Berkeley, nor McMillan, who was called away for "war work," although he received co-authorship on the first paper announcing the discovery.

This time, using the Radiation Laboratory's 60-inch cyclotron (referring to the diameter of the poles of the electromagnet), Glenn Seaborg, Joseph W. Kennedy (1916-57), and Arthur C. Wahl (1917-2006) bombarded uranium with deuterons (^{2}H) and succeeded in replacing one of uranium's neutrons with a proton to yield neptunium which in turn decayed by β-emission to yield an isotope of element 94 with a half-life of about 90 y:

$$^{238}\text{U} + {}^{2}\text{H} \longrightarrow {}^{238}\text{Np} + 2\,{}^{1}\text{n} \longrightarrow {}^{238}94 + \beta \qquad \text{[Eq. 5]}$$

This work was done in 1941, but was not published until 1946[65] due to wartime secrecy, in force at the time. The content of the paper is much understated since the researchers did not feel that they had sufficient proof to say they had discovered a new element.

Chemical characterization proved to be the most difficult part because the element was not susceptible to the ordinary oxidizing agents. They finally used the strongest oxidizing agent known, peroxydisulfate with a silver ion catalyst, and finally obtained proof that the material they had made was different from all other known elements.[66]

The isotope signaling the existence of plutonium for the first time, not yet named, was ^{238}Pu, which, due to its even number of protons and neutrons, was not fissile. The isotope of interest in this regard was ^{239}Pu which was identified and characterized as a nuclear energy source in the spring of 1941 – cloaked in secrecy due to the military potential of fission. However, microgram quantities, invisible and almost immeasurable, were all that could be produced after weeks of bombardment of a uranium target in the cyclotron. Glenn Seaborg estimated that at that rate, it would take 20,000 years to produce a kilogram of plutonium! On August 20, 1942, a several-microgram sample of plutonium was isolated and for the first time, a synthetic element was visible to the human eye. It was up to the physicists to figure out how to do a billion-fold scale-up, a task that got an excellent start by Enrico Fermi when he built the first atomic "pile" with 400 tons of graphite, 6 tons of elemental uranium, and 50 tons of uranium oxide. And it was up to the chemists to separate out purified plutonium from the many other products in the mix – a very daunting task that required not only perseverance but creativity and clever ideas in dealing with problems never encountered before.

After U.S. scientists succeeded in producing enough ^{235}U and ^{239}Pu to make the bombs that would eventually be dropped on Hiroshima and Nagasaki respectively, the world as a whole fell into a period of horror mixed with anger, recrimination, and reflection. Russia stepped up its nuclear program and had a working bomb within a few years; other countries wanted to join the nuclear club immediately. It soon became apparent that this terrible weapon of mass destruction was here to stay and everyone wanted it, if only to use it as a deterrent against aggression. It had "drastically reordered the global hierarchy after World War II and continued to amplify some of the darker pulls of humanity: greed, vanity, xenophobia, arrogance, and a certain suicidal glee."[67] Eventually terrorist groups and rogue states discovered that one did not need to do years of research to develop explosive fissile material – one only needed the black market to obtain some grams of uranium, perhaps slightly enriched in ^{235}U, but not necessarily, to create a "dirty" bomb – one with the impact of an ordinary bomb that would scatter long-lived radioactive material over a wide area, rendering it uninhabitable for years, or perhaps centuries. No matter how this two-edged sword would be used in the future, it was clear that there was no turning back. Actinide discoveries changed the course of history forever.

Americium and Curium

Once the Berkeley scientists had learned the trick of producing elements 93 and 94, they felt that numbers 95 and 96 would soon follow – but such was not the case. The working assumption was that these elements should behave chemically like plutonium, but it took two years of work for the team to realize that their assumptions were off base. Any new element in the series, unlike plutonium, had a stable +3 oxidation state and could not be oxidized further.

The breakthrough occurred in midsummer, 1944, when ^{239}Pu was bombarded with 32-MeV helium ions:

$$^{239}\mathrm{Pu} + {}^{4}\mathrm{He} \longrightarrow {}^{242}96 + {}^{1}\mathrm{n} \qquad \text{[Eq. 6]}$$

The new element, 96, an α-emitter, was identified by detecting its decay daughter, ^{238}Pu with a half-life of 162.9 d.

Element 95 followed shortly thereafter, in late 1944 and early 1945, when the transplanted Berkeley team, now working in Chicago as part of the war effort, produced it by successive bombardment and neutron capture by ^{239}Pu,

$$^{239}\mathrm{Pu} + {}^{1}\mathrm{n} \longrightarrow {}^{240}\mathrm{Pu} + \gamma \qquad \text{[Eq. 7]}$$

$$^{240}\mathrm{Pu} + {}^{1}\mathrm{n} \longrightarrow {}^{241}\mathrm{Pu} + \gamma \qquad \text{[Eq. 8]}$$

followed by β^- decay to yield element 95 with a half-life of 432.7 y:

$$^{241}\mathrm{Pu} \longrightarrow {}^{241}95 + \beta^- \qquad \text{[Eq. 9]}$$

Subsequent characterization of both elements determined that they chemically resembled their rare earth homologs, europium and gadolinium, named respectively in honor of the European continent and of the pioneer chemist, Johan Gadolin (1760-1852), who discovered the first rare earth element. So it was only deemed fitting that the two new elements be named americium, in honor of the American continents, and curium, in honor of Marie and Pierre Curie, the pioneers of radioactivity.[68] The existence of both of these elements was "published" informally in a most unusual way: in a question-and-answer session between Glenn Seaborg and a young participant on the nationally broadcast radio show, "The Quiz Kids."

Berkelium and Californium

Production of the next two elements was simple enough, although this depended upon a supply of fairly large amounts of americium and curium to use as targets. Element 97 showed up in late 1949 as the product of α-particle bombardment of ^{241}Am:

$$^{241}\mathrm{Am} + {}^{4}\mathrm{He} \longrightarrow {}^{243}97 + 2\,{}^{1}\mathrm{n} \qquad \text{[Eq. 10]}$$

Then in early 1950, bombardment of a few micrograms of ^{242}Cm with high-energy α-particles yielded element 98:

$$^{242}\mathrm{Cm} + {}^{4}\mathrm{He} \longrightarrow {}^{245}98 + {}^{1}\mathrm{n} \qquad \text{[Eq. 11]}$$

What makes these two elements unusual is that there was so little of them, estimated at under 10,000 atoms and with very short half-lives, that classical chemical means of identification could not be used. In each case, separation and detection methods had to be vastly improved, work that took years to develop. Eventually, both elements were detected by ion-exchange techniques, a first in transuranium element methodology.

Naming these elements proceeded along the logical lines of naming americium and curium. Element 97's rare earth homolog was terbium, one of four elements named after the Swedish hamlet near the Ytterby mine, where the rare earth ores were first extracted. Although by this time, Berkeley was not exactly a hamlet, it seemed appropriate to name 97 after a town, and hence it became berkelium. The homolog for element 98, dysprosium, presented some difficulties. The name, meaning "difficult to get" in Greek, was certainly also appropriate for 98. So in deciding to call element 98 californium, the researchers pointed out "that the searchers for another element (Au) a century ago found it difficult to get to California."[69, 70]

In 1950, a challenge from a Russian group headed by A. P. Znoyko (1907-1988) and V. I. Semishin signaled that the LBNL was not alone in claiming discoveries among the actinides. The Soviets claimed that they had the right to name element 97 on the basis of their prediction of its radioactive decay products, and proposed calling it mendelevium in honor of the father of the periodic table.[71] Although their "discovery by speculation" was rejected as having no merit, the Americans realized that they were no longer the only players in the field.

Einsteinium and Fermium: Children of a Blast

Elements 99 and 100 burst on the scene "full blown from the head of Zeus," so to speak.[72] Both were unexpectedly found in debris from a thermonuclear blast that took place at the Eniwetok atoll in the Pacific in late 1952. This incredible unplanned event[73] revealed that uranium was capable of absorbing numerous neutrons when subjected to a high enough neutron flux. Scientists immediately began searching the debris for transcalifornium elements and immediately found element 99, $^{253}99$, an α-emitter with a half-life of 20 d. A few weeks later, element 100 appeared in the coral that had been mined from the test site in sufficient quantity to identify such a short-lived isotope: $^{255}100$, an α-emitter with a half-life of 22 h. The method of identification once again was ion-exchange.[74] [75]

Subsequent to the initial discoveries, it was clear that the amounts found in the bomb debris were not sufficient, so scientists mined tons of coral reefs that surrounded the explosion site in a pilot-plant operation. Credit for all this work goes to scientists participating in a large cooperative project at LBNL, Argonne National Laboratory (ANL), and Los Alamos National Laboratory (LANL).

When it came time to name the elements, for element 99, the groups suggested the name einsteinium in honor of Albert Einstein, whose famous equation supplied the theory behind nuclear power. Enrico Fermi's turn came and appropriately so since he had ushered in the atomic age. When he was on his deathbed suffering with stomach cancer, Al Ghiorso (1915-2010) failed to communicate directly his intention to name element 100 after him. In April, 1955, five months after Fermi's death, he wrote a letter to Mrs. Fermi conveying the good news.[76] The two names were also a symbol of the openness of the research groups: any number of American scientists could have been chosen to be honored. Although Einstein and Fermi were both American citizens, both had been naturalized from countries that were at war with the United States. In addition, these names did not come without a certain amount of discord. The LANL people pushed hard for recognition by suggesting the name *losalium* (after Los Alamos), among many others, and the Argonne group proposed the name *anlium* (after their acronym, ANL). Many other suggestions came from other sites, even from places and publications that had nothing to do with the initial discoveries. A great deal of mediation was required to settle the matter, a premonition of the naming rights and priority disputes that would occur with virtually every other element soon to be discovered. The halcyon days of LBNL would soon be over.

Another ending of consequence was the fact that fermium would be the last element that it was possible to synthesize by utilizing neutron capture reactions. It was also clear that if fermium could only be produced in the amount of about 200 atoms; the heavier elements soon to come would require much more than large neutron fluxes or small particle bombardment of a given target. It would soon be necessary to devise reactions using heavier bombarding particles and to produce larger quantities of target material in order to move beyond the necessity of characterizing newer elements one atom at a time. And ever more powerful accelerators!

THE FIRST TRANSFERMIUM ELEMENTS OR THE LAST OF THE ACTINIDES: MENDELEVIUM, NOBELIUM, AND LAWRENCIUM

Mendelevium

A first for mendelevium, element 101, was its production and identification one atom at a time. The exciting story is told in the first person by the discovery team of Albert Ghiorso, Bernard G. Harvey (1919-2016), Gregory R. Choppin (1927-2015), and Stanley G. Thompson (1912-76). They started out by bombarding element 99, einsteinium, with helium nuclei, producing element 101 plus a neutron:

$$^{253}\mathrm{Es} + {}^{4}\mathrm{He} \longrightarrow {}^{256}101 + {}^{1}\mathrm{n} \qquad \text{[Eq. 12]}$$

The target was very small, not more than about 3 X 10^9 atoms, and any atoms of element 101 formed were caught on a gold foil placed directly behind the target. Once caught, a relay race of sorts took place: to first separate the one or two atoms of element 101 from the billions of atoms of einsteinium, and then to record the pulse of current from the detector as the atom decayed – all within about a half-hour, which was the estimated half-life of the isotope. The team remarked,

> *It is typical of these elusive heavy elements that we cannot positively identify an atom until the moment that it ceases to be that element and disintegrates into something else. It's rather like the man who only counts his money as he spends it.*

They continued,

> *In the first experiment, we waited more than an hour before the pen shot to mid-scale and dropped back, marking a line that meant the disintegration of the first known atom of mendelevium. Since this was quite an event…we connected a fire bell in the hallway to the counters so that the alarm would go off every time an atom of element 101 disintegrated. This was a most effective way of signaling the occurrence of a nuclear event, but quieter means of communication were soon substituted, following a suggestion put forth by the fire department. We found only about one atom of mendelevium in each of our first experiments, We repeated the experiment perhaps a dozen times, and our grand total was seventeen atoms of the new element.*[77]

We think Mendeleev himself would have approved of the fire bell.

Surprisingly, mendelevium was a maverick in a group of well-behaved newcomers to the periodic table (also a Mendeleev characteristic?). It exhibited electron capture, a process intuited by Al Ghiorso, and subsequently verified, which enabled the group to identify it by its fissile daughter, ^{256}Fm:

$$^{256}\text{Md} \xrightarrow{\text{EC}} {}^{256}\text{Fm} \longrightarrow \text{spontaneous fission} \qquad \text{[Eq. 13]}$$

In naming the new element mendelevium, the discoverers had obviously revisited the reasons put forth by the Russians five years earlier, but also proved to be very open and accommodating given the fact of the Cold War. Selecting a Russian to be honored certainly went against the grain of conventional attitudes at the time, but it brought unexpected political capital as well. At the September 1958 Atoms for Peace Conference in Geneva, the French chemist Moïse Haïssinsky (1898-1976), who had often had combative disagreements with Glenn Seaborg, pulled him aside and confided in him that his choice of the name mendelevium did more for international relations than everything that the U.S. Secretary of State had done in his entire career.[78]

The Convoluted History of Nobelium

By 1956, in order to overcome the barrier presented by the small masses of bombarding particles used up to this time, only three particle accelerators able to accelerate heavy ions existed: LBNL, Kurchatov Institute in Moscow (later JINR), and the Nobel Institute for Physics, Stockholm. All three were hard at work, and in that same year, a team in Moscow led by Georgy Nikolayevich Flerov (1913-90) produced element 102 by bombarding ^{241}Pu with ^{16}O. They proposed naming the element *joliotium* after Irène Joliot-Curie, although Flerov himself noted that the data were inconclusive and thus not widely disseminated. Then, in the following year, the Nobel Institute for Physics, in collaboration with ANL and the Atomic Energy Research Establishment, Harwell, UK, announced the production of either ^{251}102 or ^{253}102 (they were not sure) by bombarding ^{244}Cm with ^{13}C.[79] They immediately proposed the name nobelium in honor of the great Swedish philanthropist, Alfred Nobel (1833-96), and the name stuck because it received immediate approval by IUPAC. However, within the year, the group at LBNL were able to show that the Swedish claim was erroneous and in new experiments reported success by fusing ^{244}Cm and ^{12}C to produce ^{254}102.[80]

Now it was the Soviets' turn to disparage the LBNL results, claiming that they had erred in their half-life and isotope assignments, and therefore could not have produced element 102. And they continued to insist on their choice of name, *joliotium*. Spurred by the criticism, the LBNL group re-examined their data and realized their errors. Their revised analysis supported the data from the Soviet group, but continued to agitate for "naming rights" even though they allowed that they would be satisfied with the name nobelium.[81] The Soviets ignored all the claims made and continued to insist on their rights.

It should at this point be recognized that everyone involved in heavy ion nuclear research was feeling their way along a path that they were creating themselves.

> *It is important to remember that the methods used for nuclear identification at this time were still being developed so that it was not unusual for mistakes of interpretation to be made by all groups working in the field.*[82]

This standoff lasted for decades, prompted IUPAC to finally re-evaluate the discovery of all transfermium elements to date, and finally, in 1993, they attributed priority to the Flerov group at JINR,[83, 84] which had in the meanwhile published their own version of events.[85] Flerov and his group insisted that the expenditure of material and personal resources in the discovery of elements should result in the group's right to name the discovery. They also criticized the make-up of the IUPAC committee, peopled with persons without the expertise to judge the validity of claims. They cited as well a lack of objectivity in developing the criteria for judging the claims.[86] LBNL stubbornly rejected the JINR objections and the IUPAC decision, but the Berkeley hegemony was finally over.

In retrospect, Berkeley repeated the Stockholm method for producing number 102 ($^{244}Cm + ^{13}C$), using an identical reaction, and yet each group came up with different half-lives for what was presumably the same isotope. Add to this mystery the fact that the Stockholm group was assuming that 102 exhibited a preferred 3+ oxidation state, whereas in reality, it is more thermodynamically stable as the 2+ ion, so they would have missed it in their ion-exchange elution protocol.[87]

Despite all the controversy, the one fixed fact is that the name nobelium is here to stay: in 1997, the IUPAC confirmed the name nobelium with the symbol No.

Lawrencium

In 1958, LBNL lost its Director and founder, Ernest Orlando Lawrence, following a brief illness. It fell to Glenn Seaborg, who, by now, was Chancellor of the University of California at Berkeley, to select a new Director. Luis Alvarez pre-empted Seaborg's choice by first, indicating that he was not a candidate, and secondly, that he would highly recommend Edwin McMillan for the post. Seaborg happily accepted Alvarez's intervention, and McMillan took over soon afterwards.

A few years later, in 1961, element 103 was identified in the following fashion: about 3 μg of a mix of californium isotopes were bombarded with heavy ion beams of ^{10}B and ^{11}B at the Berkeley HILAC. An α-emitter with a half-life of 4.3 s due to $^{258}103$ was detected, and immediately named it lawrencium in the title of the publication announcing the discovery.[88] The new element, given the symbol Lw (later changed to Lr by IUPAC), honored the inventor of the cyclotron, the machine that had led to the discovery of so many new elements. Although the Berkeley team was acknowledged as the discoverers, in 1965 the JINR at Dubna identified the longest lived isotope, ^{256}Lr with a half-life of 28s, and established the genetic decay sequence as well. In its review of the decade-long efforts of both groups, and their substantial contributions to the correct identification and the properties of element 103, the Transfermium Working Group (TWG), in 1992, recommended that the two groups share credit for the discovery. It also reconfirmed the name, lawrencium, and the symbol, Lr.

SOME CHARACTERISTICS AND USES OF THE ACTINIDES

Electronic Structure of the Actinide Elements

Due to the radioactivity, toxicity, and lack of large numbers of sample atoms for many of these elements, theoretical calculations of atomic characteristics play an important role. However, due to spin-orbit and scalar relativistic effects, open-shell electronic structures, and likely covalent bonding of the 5f shells, among other considerations, ordinary crystal field calculations are unsuitable. The relativistic effects, particularly, are most important because the velocity of the electrons is directly proportional to increasing atomic number; these effects, in fact, overshadow the periodic trends that are characteristic of the lighter elements. *Ab initio* quantum chemical calculations utilizing relativistic multireference wavefunctions can help enormously in understanding the actinide elements' complicated electronic structures.[89]

Actinides in Medicine

The use of radioactivity in medicine got its start when Henri Becquerel realized that uranium was capable of producing images on a photographic film. This discovery was almost simultaneous with the discovery of X-rays by Wilhelm Conrad Röntgen (1845-1923) who, with them, produced an image of his wife's left hand. Thus, diagnostic imaging with high energy electromagnetic radiation became the first application of actinides in medicine. Radiotherapy came next, both external, and internal by brachytherapy and targeted radionuclide therapy (TRNT). The chief actinides in use were naturally occurring uranium and thorium and reactor-generated isotopes of actinium, thorium, and uranium, useful as radionuclide generators for the production of lighter elements such as ^{99m}Tc. Cost and availability of the actinides severely limit development of their use in clinical applications.[90]

Actinides in Catalysis

Developments in organoactinide chemistry have spurred the use of these compounds as potential catalysts in areas calling for chemoselectivity on sterically demanding substrates. Most catalytic studies have centered on Th^{4+} and U^{4+}, but U^{6+} has recently come into the limelight. One feature of organoactinides is the possibility of forming high coordination number complexes due to the large ionic radii of the actinides' 5f orbitals. Determination of bond disruption enthalpies to understand the thermodynamic factors responsible for catalytic turnover utilizing organoactinides has been found useful. This is a rapidly developing field.[91]

CONCLUSION

We can comfortably assert that the actinides and the rare earths share some similarities, both chemical and historical, but there are also some significant differences between the two groups. They are both set apart from the main body of the periodic table, chiefly for spatial convenience in accommodating their 4f and 5f orbital representations. They both take their group names, lanthanides and actinides, from the name of the first member of each group. Four of the actinides, Am, Cm, Bk, and Cf, received names analogous to those of their lanthanide homologs, Eu, Gd, Tb, and Dy. Discovery stories for both groups are peppered with priority disputes and contention over naming rights. However, we cannot discern many other points of likeness. It took almost 150 years to discover all of the rare earths; if we exclude uranium and thorium, the completion of "Mendeleev's family" took only 40 years of purpose-driven research.

Historically, we observe that the American contribution to lanthanide discoveries was marginal, as in the case Charles James (1880-1928),[92,93] and if not even fallacious, as in the case of John Lawrence Smith (1818-1883).[94] On the contrary, with respect to the actinides, the American laboratories exercised a hegemony for several decades that was not easily challenged. Using the enormous resources of their federal budget, they invented new ways of producing and identifying radioisotopes, resulting in almost routine new element discovery every couple of years. Eventually, their absolute domination of the field crumbled in the face of Russian, Swedish, Japanese and German expertise, ushering in a new age of collaboration, rather than of competition.

For Mendeleev, a scientist who formed the nexus between ancient Greek philosophy and the new 19th century discoveries, his periodic arrangement was a Kantian "categorical imperative." He was constrained to dismiss Julius Lothar Meyer's (1830-1895) notion of the unity of matter wherein all the elements were multiples of hydrogen (or possibly of some simpler entity) as simply a relic of classical thought.[95] Mendeleev based his own table on the idea of the "plurality of matter," by which all the elements are different, and yet are connected. He recognized "the existence of multiple elements as the basis of material reality. He never accepted the idea of "prime matter" maintained by Prout, and the possibility of reducing all the elements to a single element, hydrogen."[96] In his 1976 analysis of Mendeleev's thought,[97] Yuri Solov'ev makes it clear that the exact formulation of the periodic law did not spring forth suddenly from Mendeleev's head (as from the "head of Zeus"), but only after he had processed and clarified the fundamental concept of his system of the elements.[98] He says that there can be no doubt that the fundamental content of the law (the principle of periodicity) was quite clear to Mendeleev from February 17, 1869, and that it served as a guide to expand upon the system of the elements. By 1871, two fundamental concepts on the theory of periodicity had been definitively established and announced by Mendeleev. He emphasized that "every natural law gains its particular scientific significance when it is possible to derive practical consequences from it, that is, logical conclusions that explain what has not yet been explained, pointing out phenomena unknown from the beginning, and above all by the possibility of carrying out controllable predictions by experiment." The results of particular significance in the promulgation of the law was the prediction of the existence of "eka-aluminum" (gallium, discovered by Boisbaudran in 1875), "eka-boron" (scandium, Nilson, 1879) and "eka-silicon" (germanium, Winkler, 1885). The discoveries of these elements, and first of all that of gallium, decisively changed the attitude of the scientific world with respect to the periodic system of the elements. In 1879, in his letter to G.A. Quesneville,[99] Mendeleev had every right to affirm: "It is now evident that the periodic law leads to consequences that preceding systems did not dare to predict. At first there was only a scheme, a grouping according to determined facts, while the periodic law renders the facts subsidiary to itself as the principle, and aims at understanding more deeply the philosophical principle that governs the mysterious nature of the elements." Mendeleev states further "This trend is in the same category Prout's Law, but with this essential difference: that Prout's Law relies on mere numbers, whereas the periodic law draws its authority from a series of mechanical and philosophical laws which constitute the character and brilliance of the present impetus of the exact sciences."

He later stated that the periodic law is a direct outcome of a collection of experimental data and that experiment must take precedence above all else, seemingly a categorical dismissal of the idea of the unity of matter, an idea that comes not from experiment but from speculation.[100]

As Mendeleev's work marks the beginning of the modern chemical world, so the actinides mark the starting point for the expansion of periodic table chemistry, whose end, even up to today, it seems impossible to fix with any certainty.[101] This is a trajectory that doubly fascinates chemists: firstly as scientists, and secondly for the iconic meaning that the periodic table represents for them.

As we have already demonstrated, the early actinides are a subgroup unique among the elements. All radioactive, some naturally occurring, and in great abundance, and many fissionable, they have been the backbone of the nuclear energy industry, both in war and in peace. But, as far as their chemistry is concerned, actinide research fell into the doldrums in the late 20th century. A surprisingly recent resurgence of interest in actinide chemistry can be attributed to the realization that nuclear power can help to curtail carbon emissions and understanding actinide chemistry is vital in dealing with nuclear waste. In addition, the lighter actinides are increasingly being scrutinized, as noted above, for possible catalytic and medical applications, especially in terms of indirectly delivering hard-to-get radioisotopes as part of their decay chain. The mid-actinides pose another problem: availability. Unless more than a few milligrams of these cyclotron-produced elements can be available long enough for studies, let alone for commercial or medical use, they will remain in the backwater. But progress is being made: a research team in Japan has recently succeeded in measuring lawrencium's ionization potential. We should see much more activity in this area in the coming decades.[102]

In 1869, Dmitri Mendeleev literally started a family of elements. Now he is an honored part of it.

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Controversial Elements: Priority Disputes and the Discovery of Chemical Elements

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Abstract. There are only a limited number of chemical elements and to be credited with the discovery of a new one is therefore considered of great importance. Adding to the honour and fame is that traditionally the discoverer has the right to name the element in question. For these and other reasons, element discoveries are often followed by controversies regarding priority. While some of these are contemporary with the discovery process, others occur much later and are attempts to rewrite history. But what is a scientific discovery, more precisely, and why does it sometimes become controversial? From a scientific point of view, does it really matter who is recognised for the discovery of a new element? These are some of the questions considered in the paper, together with a few concrete cases from the history of chemistry. As shown by the recent disputes concerning the discoveries of synthetic elements at the end of the periodic system, modern priority disputes differ in some ways from the disputes of the past. On the other hand, there are also significant similarities.

Keywords.Discovery, chemical elements, controversy, priority, periodic system.

1. INTRODUCTION

The subject of this paper is priority controversies related to the discoveries of chemical elements. In order to discuss the subject rationally it will be useful to introduce and clarify the meaning of two key terms, namely “discovery” and “priority controversy,” in a general way that does not necessarily relate to the chemists’ elements. These are concepts that are often taken for granted, but scientists, philosophers and historians actually use them with different meanings, such as will be discussed in the following two sections. Nor is the meaning of “element” self-evident as it has changed through different phases of history to be explicated in Section 4, where a historical classification of element discoveries is suggested. In the last sections I look at aspects of three discovery cases from different periods and with different characteristics. The chosen cases are aluminium from the pre-Mendeleev era, lutetium from the early twentieth century, and nobelium from the transuranic age.

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2. WHAT IS A SCIENTIFIC DISCOVERY?

Much of the discussion about scientific discoveries can be traced back to different conceptions of what constitutes a discovery.[1] It is generally assumed that a scientist (or a group of scientists) has discovered X if he or she has convincingly established that X exists or is the case. X may be an object, a phenomenon, or a significant relation between empirical data. In the latter case it may consist of a structural organisation of data, where all or some of the data may be known in advance. An example from the history of chemistry is the Dulong-Petit law of 1819 correlating the specific heats of elements and their atomic weights. Another and more important example is Mendeleev's periodic system fifty years later. Although Mendeleev's system did not originally rely on new discoveries of objects and their properties, he discovered the system in the constructive sense that he organised known data into a new conceptual framework.

It may seem obvious that only objects which really exist can be discovered. When we say that William Ramsay and Lord Rayleigh discovered argon in 1894, it implies that argon really exists as a component of the atmosphere. As the philosopher Peter Achinstein has argued, truth and discovery go together: "Discovering something requires the existence of what is discovered. You cannot discover what doesn't exist."[2] Of course, one can *claim* to have discovered a non-existing object, and the claim may even be broadly accepted for a period of time, but in that case the claim does not count as a proper discovery.

Although Achinstein's view may seem to be common sense, from a historical perspective it is problematic to reserve the category of discovery for what is presently accepted as true. From this perspective one may legitimately speak of the discovery of non-existing objects or phenomena, namely if the discovery claim received wide recognition at the time it was announced. Phlogiston does not exist and yet the substance was believed to exist for half a century or so. It makes sense to say that Georg E. Stahl discovered phlogiston in about 1720 and also that Joseph Black discovered the heat substance called caloric in the 1730s. These non-existing entities were discovered and later de-discovered. There is another reason why Achinstein's claim is problematic, namely that it seems to presuppose that objects exist in nature prior to their discovery. But there are objects, such as the artificially produced superheavy elements, that only come into existence *with* their discovery. The so far heaviest known element, oganesson with atomic number 118, was not discovered because it existed. It exists because it was discovered.

A chemical element is not a specific and localisable object of the same kind as, say, a planet. The chemist cannot point to a piece of sodium and claim that "*this* is sodium" in the same sense as the astronomer can point to a planet and claim that "*this* is Neptune." On the other hand, to say that something is or contains the element sodium involves the *concept* of an element, just like the identification of Neptune as a planet involves the concept of a planet. The discovery of a new element is thus to demonstrate convincingly the elemental nature of some substance, which is a conceptual discovery, and also to find this substance in nature – or perhaps to synthesize it in the laboratory. The latter is an empirical discovery.

For something to be a discovery it is normally assumed that it must be a novelty, and for this reason it cannot be made twice at different times. On the other hand, there are many examples in the history of science of so-called rediscoveries, a concept which typically refers to insights that originally attracted very little attention and at a later time were unknowingly duplicated.[3] The rediscovery will almost always be in a different form than the original discovery. An example from the history of chemistry is provided by the discovery of vanadium, which was first isolated by Andrés Manuel del Río in 1801 and rediscovered by Nils G. Sefström thirty years later.[4]

If a discovery is little known and exerts almost no impact on the scientific community, the rediscovery is more effective than the one with which the discovery is often associated. The useful concept of the "effective discovery of an element" was introduced by the Danish chemist Edmond Rancke-Madsen, who referred to the cases of hydrogen (Henry Cavendish, 1766), oxygen (Joseph Priestley, 1775) and chlorine (Carl W. Scheele, 1774) as examples.[5] According to Rancke-Madsen, for a scientist to be the effective discoverer of an element, he (or she) must have observed the existence of a new substance "which is different from earlier described substances, and this new substance is recognized by him *or later by scientists* as being elemental" (emphasis added). Moreover, the discovery of the new substance must have been announced publicly and attracted attention among contemporary scientists. Notice that according to this view, the effective discoverer does not need to have recognised the substance as an element; what matters is only that it was granted this status by later scientists and that this is still its status today.

The notion of an effective discovery underlines that a discovery cannot be a private matter or limited to just a few persons. Not only must the discovery claim be publicly available, it must also be known and accepted by at least a substantial part of the relevant scientific community. It must be communicated, usually in a journal article although it can also be in the form of a well-publicized lecture or a press conference. The Swedish chemist and historian of chemistry Jan Trofast offers the following definition of the discovery of a chemical element:

> *A discovery is established when the scientist has shown new properties of the new element in form of e.g. a number of salts and clearly and unambiguously shown that it is a new element. … Further the time of discovery is said to be when the first publication (could be in the form of a letter to a colleague) is available and not when the first observation is made or when the first suspicion was aroused in the laboratory.*[6]

However, to include a private letter under the label "publication" is too wide an interpretation of the term. Communication by letter does not secure dissemination to the scientific community but at most to a few members of it. Only in exceptional cases, namely if the letter is copied or its content otherwise circulated to a large number of scientists, can this form of communication be of a public or semi-public nature. The scientist who makes an observation of something new, but reports it only in his diary or in a letter, has not made a discovery and that even though he may have recognised the novelty and significance of what he has observed. According to Alan Gross, "There is no such thing as a private discovery… A scientific discovery, then, is the public attribution of novelty to a claim regarded by a relevant scientific community as possible and as the consequence of following appropriate methods."[7]

Consider the case of plutonium which was identified in nuclear reactions by Glenn Seaborg and his team in late 1940 (Pu-238) and early 1941 (Pu-239). As a result of the unusual political circumstances of World War II the discovery paper submitted on 7 March 1941 to *Physical Review*, only appeared in print five years later.[8] Although plutonium thus became publicly discovered only in 1946, it is customary and reasonable to date the discovery to the year 1941. Incidentally, in this case there was no priority controversy as the discovery was unanimously assigned to Seaborg and his collaborators.

According to the individualist or "heroic" model of discovery widely favoured by scientists and journalists, one can identify the moment a discovery occurred and also the individual who should be credited. However, historical studies demonstrate that in many cases this is not possible and, generally, that the model is inadequate. Rather than focusing on the discovery itself some historians and sociologists of science argue that what matters is not so much the discovery's intellectual history as its social history. How and why does a discovery claim become accepted as a *bona fide* discovery by the scientific community? According to this view discoveries are retrospective judgments which are socially defined and constructed. They are labels attributed *post hoc* to some discovery claims but not to others. As one author puts it, "Discoveries do not simply 'occur' or 'happen' naturalistically, but are socially defined and recognized productions."[9]

While the importance of the social history is beyond doubt in discovery studies, it does not follow that it offers a sufficient account of discoveries and their receptions. Moreover, the social analysis is not incompatible with a more traditional, intellectual analysis. The two approaches are supplementary and none of them is sufficient alone.

Discoveries are often thought to be purely empirical, meaning that the first observation of an object or phenomenon X constitutes the discovery of X. However, philosophers have long pointed out that this is too simplistic a view and that a discovery involves an active mental process as it relies on theoretical preconditions. A scientist may observe or perceive X without identifying it *as* X. Or to put it differently, there is a crucial difference between "seeing that" and "seeing as."[10] For example, in experiments with iron and dilute strong acids Robert Boyle and other seventeenth-century chemists observed an "air" without recognising it to be new or elemental. They observed what became known as hydrogen, but they did not discover hydrogen. This view is contrary to the one of Rancke-Madsen as cited above.

The idea that discoveries involve changes in the theoretical or conceptual framework was a leading theme in Thomas Kuhn's influential essay dating from 1962. Using the discovery history of oxygen as a lead example Kuhn argued that "Observation and conceptualization, fact and assimilation of fact to theory, are inseparably linked in the discovery of scientific novelty."[11] Moreover, he distinguished between two classes of discovery, namely those which could be predicted from accepted theory in advance and those which could not. Kuhn found the second class – "discovery by accident" – to be more interesting, as this kind of discovery would typically force scientists to organise known data into a new conceptual framework. As a result an existing paradigm might be challenged and give rise to a revolutionary phase in science.

With respect to discoveries of the first class, such as the elements predicted or anticipated from the periodic system, Kuhn wrote that "There have been few priority debates … and only paucity of data can prevent the historian from ascribing them to a particular time and place." However, this is definitely a misconception. After the acceptance of the periodic system the frequency of priority controversies did not diminish nor did they become less serious. On the contrary, conflicts of this kind rather increased in number and intensity.

3. CONTROVERSIES OVER PRIORITY

In his *History and Present State of Electricity* dating from 1767, Priestley suggested that "mistakes, misapprehensions, and altercations" should have no place in the annals of science. According to him,

> *All the disputes which have no way contributed to the discovery of truth, I would gladly consign to eternal oblivion. Did it depend upon me, it should never be known to posterity, that there had ever been any such thing as envy, jealousy, or cavilling among the admirers of my favourite study.*[12]

Yet it is all too clear that controversies of various kinds do play an important and often fruitful role in science and have always done so. They are sometimes instrumental in defining the disciplinary boundaries related to a new subfield, such as exemplified by the emergence of physical chemistry in the late nineteenth century.[13]

As Robert Merton pointed out in a pioneering paper of 1957, not only are controversies abundant they also contribute – contrary to what Priestley thought – to scientific progress.[14] To be involved in a scientific controversy whether as a winner or loser, may cause a loss in reputation, but this is not generally the case. Priority controversies, in particular, may have the effect of increasing the competitive pressure and forcing the participants to study the subject in question more extensively and in greater depth than if the controversy had not existed. This kind of controversy goes far back in time, certainly to the age of Galileo if not earlier. One reason why the assignment of credit is important is that it helps in understanding the historical dynamics in the discovery process. Assigning the wrong credit for a discovery may distort the picture of how and why the discovery occurred.

There is no generally accepted definition of a scientific controversy, but it is useful to distinguish the concept from other forms of communicative disagreement, such as debate, discussion, polemics and dispute.[15] First, for a disagreement to qualify as a *scientific* controversy, evidently it should centre on a scientific issue and involve scientists as key participants. While some controversies are "pure," meaning that they are concerned almost exclusively with scientific questions, others are "mixed." The latter category refers to cases where political, environmental and ethical concerns enter significantly, such as the use of flame retardant chemicals.[16]

Whether belonging to one class or the other, typically a controversy is of some duration, it is expressed in public, and it takes place by means of arguments and counterarguments. Contrary to what is the case in a debate or discussion, the parties involved in a controversy must be committed to one of the opposing views. Being more than a quarrel between two individual scientists a controversy involves the relevant scientific community, and it is only if the community considers the disagreement worth taking seriously that it will develop into a proper controversy. In some if not all cases major parts of the scientific community will be engaged on both sides of the disagreement, although often disproportionally.

There are different kinds of controversies. Following a proposal of Ernan McMullin, one may distinguish between controversies of fact, of theory, and of principle.[17] In the present context dealing with element discoveries the first category is the most important. Here scientists disagree on whether a claimed entity or property actually exists. Does the substance claimed to be a new chemical element really have the status of an element? The two other categories relate to different theoretical views and methodological principles, respectively. The three categories are not mutually exclusive and may in some cases appear together, such as was the case with the much-discussed discovery history of oxygen.[18]

Disputes over priority mostly concern either factual or theoretical disagreements as in the discovery of objects or theories. They may also be about names which, in the case of new elements, have often provoked controversy if of a different kind. The accepted name of an element may directly or indirectly refer to the discoverer and thus suggest which scientist is to be credited with the discovery. Consider a scientist X who proposes the name A for a new element he claims to have found, while scientist Y independently finds what he names B and believes is the same element. In this case a dispute about the name reflects a controversy about discovery (see Section 6). Naming controversies have been common for the transuranic elements and in particular for those named after a scientist. The most controversial of the names was the one of element 106, seaborgium, but there were others as well.[19]

As controversies appear in different forms, so they terminate in different ways. A controversy may be resolved, meaning that the two parties come to agree, by means of scientific arguments, that one of the competing claims is after all superior to the other. The Irish chemist Richard Kirwan had for long defended the phlogiston theory and criticized Lavoisier's oxygen alternative, but in 1792 he gave in. "I lay down my arms and abandon the cause of phlogiston," he wrote.[20] A controversy may also terminate by withering away, perhaps by lack of interest or simply because the protagonists of one of the competing views disappear from the scene. Finally historians and sociologists speak about termination by closure if political or other non-scientific factors force the controversy to end.

In most cases priority controversies take place simultaneously with the discovery claims and involve the competing scientists as the main contenders. But in other cases they emerge retrospectively many years after the contenders have passed away and the case apparently was closed. It may be that new data or historical sources come to the light of day, or that scientists re-examine the case and argue that X rather than Y should be credited with the discovery. As we shall see below, the discoveries of aluminium and lutetium are examples.

Another and more recently discussed case concerns element 75, rhenium, which is credited work by Ida Tacke (later Noddack), Walter Noddack and Otto Berg in 1925. However, many years earlier the Japanese chemist Masataka Ogawa believed to have found evidence for the element, which he called nipponium. By 1925 nipponium was long forgotten, but as late as 2004 it was argued that Ogawa had indeed discovered the element.[21] To the extent that one can speak of a priority conflict in this rather unconvincing attempt of rehabilitation, it was constructed much *post festum* (see also Section 4).

4. AN OVERVIEW OF ELEMENT DISCOVERIES

It is generally agreed that phosphorus is the first element with a known discovery history and discoverer. The earlier elements known to ancient cultures, such as sulphur, gold, silver and tin, were not discovered in any real sense (Figure 1).

When the Hamburg merchant and alchemist Hennig Brand in or about 1669 produced a white, waxy and luminous substance by distilling male urine and heating the remaining paste, he serendipitously discovered phosphorus in the form P_4 (Figure 2).[22] But he did not, strictly speaking, discover the chemical element phosphorus as neither he nor his contemporaries conceived the substance as an elementary body. Nor did Brand communicate his discovery publicly, in the form of a publication. Only in 1678 did the German chemist Johann Kunckel publish an account of the new substance and how to prepare it. Still a century after Brand's discovery phosphorus was thought to be a composite body, namely "a kind of sulphur composed of a particular acid united with phlogiston … [and which] resembles vitriolic sulphur also in this point that its phlogiston may be burnt, even with rapidity, without any decomposition of its acid."[23]

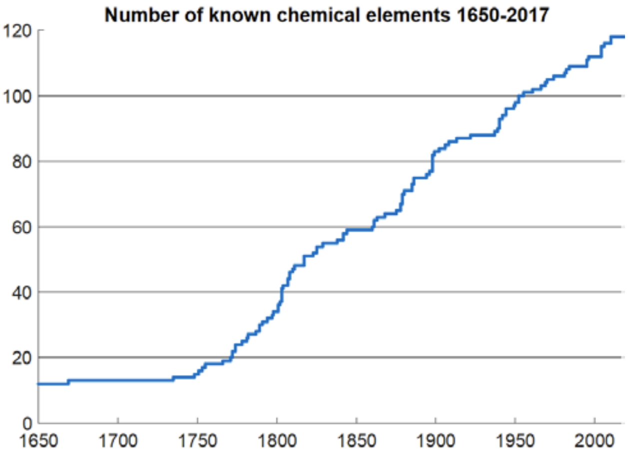

Figure 1. Discoveries of chemical elements since 1650. Source: https://commons.wikimedia.org/wiki/File:Known-elements-1650-present.png

Figure 2. Detail from Joseph Wright of Derby's painting of 1771 showing an alchemist discovering phosphorus. Source: https://resobscura.blogspot.com/2017/06/urine-phosphorus-and-philosophers-stone.html

TABLEAU DES SUBSTANCES SIMPLES.

	Noms nouveaux.	Noms anciens correſpondans.
Subſtances ſimples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.	Lumière	Lumière.
	Calorique	Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
	Oxygène	Air déphlogiſtiqué. Air empiréal. Air vital. Baſe de l'air vital.
	Azote	Gaz phlogiſtiqué. Mofete. Baſe de la mofete.
	Hydrogène	Gaz inflammable. Baſe du gaz inflammable.
Subſtances ſimples non métalliques oxidables & acidifiables.	Soufre	Soufre.
	Phoſphore	Phoſphore.
	Carbone	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique	Inconnu.
	Radical boracique.	Inconnu.
Subſtances ſimples métalliques oxidables & acidifiables.	Antimoine	Antimoine.
	Argent	Argent.
	Arſenic	Arſenic.
	Biſmuth	Biſmuth.
	Cobolt	Cobolt.
	Cuivre	Cuivre.
	Etain	Etain.
	Fer	Fer.
	Manganèſe	Manganèſe.
	Mercure	Mercure.
	Molybdène	Molybdène.
	Nickel	Nickel.
	Or	Or.
	Platine	Platine.
	Plomb	Plomb.
	Tungſtène	Tungſtène.
	Zinc	Zinc.
Subſtances ſimples ſalifiables terreuſes.	Chaux	Terre calcaire, chaux.
	Magnéſie	Magnéſie, baſe du ſel d'Epſom.
	Baryte	Barote, terre peſante.
	Alumine	Argile, terre de l'alun, baſe de l'alun.
	Silice	Terre ſiliceuſe, terre vitrifiable.

Figure 3. Lavoisier's table of "simple substances" in his *Traité Élémentaire de Chimie* from 1789.

Although Brand's work of 1669 does not live up to current philosophical, non-anachronistic ideas of what constitute an element discovery, somehow it seems artificial to deprive him of the credit of having discovered phosphorus. There was at the time a kind of priority controversy even though it did not concern phosphorus as an element but only as a new and exciting substance. Within a decade or two Brand faded into obscurity, his priority defended only by Leibniz. By the turn of the century priority had effectively been conferred to either Kunckel or his compatriot Johan Daniel Krafft.

The point is that according to the early chemists phosphorus was not elemental. A concept of chemical elements roughly similar to the modern one only arose in the 1780s, perhaps first stated by the German chemist Johann Gmelin.[24] More famously and in greater detail it was stated by Antoine Lavoisier in his seminal treatise *Traité Élementaire de Chimie* published in 1789. According to Lavoisier, phosphorus was an element or "simple substance," meaning that it could not be decomposed – or had not yet been decomposed – into still simpler bodies (Figure 3).

The later history of element discoveries may conveniently be classified in four chronological phases, the first of which is associated with John Dalton's atomic theory. The immediate importance of Dalton's *New System of Chemical Philosophy* was not so much the atomic hypothesis as the idea to associate the relative weights of atoms with a measurable quantity, the atomic weight. As far as the concept of element was concerned, Dalton followed Lavoisier's operational formula: "By elementary principles or simple bodies we mean such as have not been decomposed, but are found to enter into combination with other bodies."[25] With Jöns Jacob Berzelius' staunch support of Dalton's theory the establishment of still more precise atomic weights became a matter of prime concern. In 1826 Berzelius published his final table of atomic weights. To him and many of his contemporaries the identification of new elements relied on determinations of their atomic weights. Often credited as the discoverer of five new elements (cerium, selenium, silicon, zirconium, and thorium), Berzelius was eminently successful and his successes depended to a large extent on his analytical skills in determining the elements' atomic weights.[26]

Dmitri Mendeleev's classification of elements in 1869, which I take to be the beginning of phase two, rested crucially on the postulate that an element was defined by its atomic weight. In his Faraday lecture of 1889 the Russian chemist pointed out that before the periodic system "there was no special reason to expect the discovery of new elements." It was only the gaps in the sequence of atomic weights as organised in the periodic system that "enabled us to perceive undiscovered elements at a distance which formerly was inaccessible to chemical vision, and long ere they were discovered."[27]

With the acceptance of the periodic system or table it came to define the possibility of new elements: If X has no place in the table, it cannot possibly be an element. The dogma was challenged with the discovery of argon and helium in the 1890s, but in this case order was reinstated by adding a new group of inert gases to the system. Despite the authority of Mendeleev's system, or the corresponding one of Lothar Meyer, chemists continued to suggest new elements. They sometimes hid them in the poorly understood group of rare earths and at other times they were just unconcerned with whether they fitted into the system or not. Random examples are nebulium, etherion and carolinium.[28] Characteristically these discovery claims were rarely taken seriously.

In the third phase, starting with the introduction of isotopy and the atomic number Z in about 1913 it turned out that the atomic weight was not after all the defining property of an element.[29] Yet the periodic system survived the redefinition of an element and the change of the elements' ordinal number from the atomic weight to the atomic number. The latter quantity, as given by the charge of the atomic nucleus, could be measured by means of the method of X-ray spectroscopy pioneered by Henry Moseley. However, it took until 1923 before the new definition of an element was sanctioned by IUPAC, the International Union of Pure and Applied Chemistry. Whereas the periodic system did not originally restrict the number of possible elements, with the introduction of the atomic number the existence of elements lighter than hydrogen was ruled out. What had formerly been possible, if unlikely, now became impossible. On the other hand, the new understanding of the periodic system did not preclude new elements heavier than uranium. In principle there might be any number of them.

The fourth and last phase in the history of element discoveries may be said to have started in 1937 with the manufacture and hence discovery of the first artificial element, soon to be followed by many transuranic elements. Technetium, the approved name of element 43, was discovered by the physicist Emilio Segré and the mineralogist Carlo Perrier by analysing a molybdenum target irradiated with deuterons and neutrons. There had earlier been several unconfirmed claims of having detected element 43 in nature, noticeably by the Noddack-Tacke-Berg team which in 1925 claimed to have found small amounts of the element. This evolved into a priority controversy between "masurium" and technetium which much later was re-opened by scientists in favour of the masurium claim.[30] The much delayed attempts to change the discovery history of element 43 were ignored by IUPAC and the large majority of chemists.

5. THE THIRD-MOST COMMON ELEMENT

Given that aluminium makes up 8.1% of the Earth's crust, it is remarkable that its discovery dates back less than 150 years. In the case of element 13 there was no major priority controversy, but there are other features in the history of the element that makes it instructive from a discovery perspective.[31] It is generally agreed that the German chemist Andreas Sigismund Marggraf was the first to realise, in 1754, that there is a separate "earth" (alumina) in alum different from the one in limestone.[32] The still unknown earth appeared as "argile" in Lavoisier's table of 1789, with the author suggesting that it might be a metallic element saturated with oxygen. Attempts to isolate the metal in alumina made by Humphry Davy and later by Berzelius failed, although Berzelius was able to determine its atomic weight to 27.4. The element was known to exist and Davy had even coined a name for it, alumium or what later became aluminium, but it had not yet been discovered.

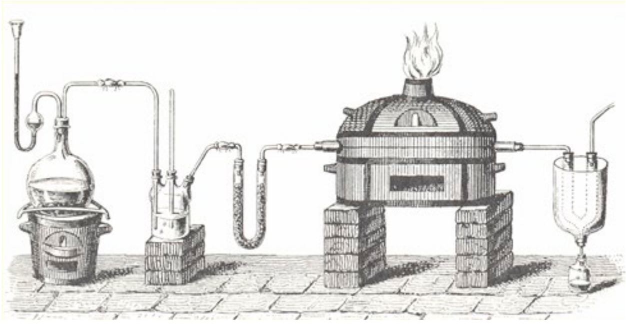

Figure 4. The first step in Ørsted's isolation of aluminium, the synthesis of $AlCl_3$. In modern nomenclature the process is $Al_2 O_3+3C +3Cl_2 \rightarrow 3CO+2AlCl_3$. Reproduced from a Danish textbook of 1853 (H. Westergård, *Uorganisk Kemi*).

The main steps in the element's discovery process are well known and need only to be briefly recapitulated. In early 1825 H. C. Ørsted, the discoverer of electromagnetism, reported to the Royal Danish Academy of Science a new method in which he transformed alumina (Al_2O_3) to anhydrous aluminium chloride and subsequently reduced it by means of potassium amalgam (Figure 4). The result was what Ørsted described as "a lump of metal resembling tin in colour and lustre."[33] The brief Danish report was abstracted in Schweigger's *Journal für Physik und Chemie* and Poggendorff's *Annalen der Physik und Chemie*, and in 1827 it appeared in a German translation in Berzelius' *Jahresbericht über die Fortschritte der physischen Wissenschaften*.[34] Nonetheless, it failed to attract interest. Ørsted, who did not find the method and the new element to be very important, never returned to the subject. In September 1827 young Friedrich Wöhler visited Ørsted, who told him about the metal and encouraged him to take a closer look at it. Back in Germany Wöhler was unable to confirm that Ørsted's method yielded aluminium, but by using pure potassium as the reducing agent he produced the metal in the form of a grey powder. Wöhler came to believe that what Ørsted had thought was a lump of aluminium was instead a kind of alloy of aluminium and potassium.

In his discovery paper of 1827 Wöhler gave full credit to Ørsted for his discovery of aluminium chloride, carefully pointing out that he had no intention to exploit Ørsted's pioneering work of 1825 or being disloyal. He mentioned that the Danish scientist "has indirectly encouraged me to try to attain to further results myself." Ørsted seems not to have cared about priority, and there was no rivalry between him and Wöhler. In 1845 Wöhler was able to obtain aluminium in a compact metallic if still impure form and to determine, for the first time, the metal's principal properties. If Ørsted's work of 1825 was the first birth of aluminium, and Wöhler's of 1827 and 1845 marked the second birth, the third birth dates from 1854 when Henri Saint-Claire Deville found a new method to produce the metal in pure form. It was only with Deville's work that aluminium became a useful metal and not a mere chemical curiosity.

Deville never claimed to have discovered aluminium, an honour he fully ascribed to Wöhler, and yet in France he was widely and in part for national reasons considered the true discoverer.[35] As to Ørsted's role in the discovery process, Deville simply ignored it. In his influential book *De l'Aluminium* from 1859, the first comprehensive work on the history and use of the new metal, there is no mention of Ørsted. For most of a century Wöhler was recognised as the one and only discoverer of aluminium, whereas Ørsted's earlier synthesis was generally considered to be wrong or incomplete, perhaps an anticipation of aluminium but not an isolation of the metal.

However, on the occasion of the centenary of the discovery of electromagnetism Danish chemists reconsidered Ørsted's method and reconstructed the old experiments to establish whether or not aluminium had been obtained back in 1825. The result of this attempt to rewrite history was that in all likelihood Ørsted had isolated impure aluminium two years before Wöhler, a conclusion in which there clearly was an element of national pride. It is about time, wrote the distinguished chemist Niels Bjerrum, "to reinstate Ørsted as the first who obtained aluminium."[36] Contrary to the earlier mentioned case of element 75 (Section 3), in this case the attempt of rehabilitation succeeded to some extent. According to Harry Holmes, an American chemist, "It is now in order for the world to atone for the injustice by giving the Dane credit for the discovery."[37] Not all chemists and historians agree, but today it is not uncommon to name Ørsted as the discoverer of aluminium or to share the credit between him and Wöhler.

So, when was aluminium discovered and to whom should priority be allocated? As indicated in Section 2, the question is misguided as it presupposes an answer in terms of a definite year and a definite discoverer. A summary of the discovery process may provide the only appropriate answer: In 1754 Marggraf recognised a special "earth" in alum which subsequently became known as an element and prepared by Ørsted in 1825 in an impure form; two years later Wöhler produced aluminium as metallic powder and in 1845 he determined its density and some other properties; finally, in 1854 Deville created pure aluminium and laid the base for its industrial use.

6. LUTETIUM, A CONTROVERSIAL ELEMENT

Contrary to the case of aluminium, the discovery of the rare earth element 71, lutetium, involved a series of convoluted priority controversies concerning scientific as well as external issues. Although disputes about fact entered the controversy, it was basically about priority. For a long time the number of rare earths and their position in the periodic system was a matter of confusion and dispute, a situation which was only settled in the mid-1920s. The uncertainty resulted in several premature or wrong discovery claims of which "celtium" as a candidate for element 72 has received much attention by historians of science. As it turned out in 1923, element 72 (hafnium) is not a rare earth but a homologue to titanium and zirconium.[38] The case of element 71 is closely connected with the celtium-hafnium controversy but started earlier, at a time when a chemical element was still defined by its atomic weight. The controversy over this element took place in two separate phases, originally around 1908 and with a second round in 1923. It provides one more example of how later research may throw new light on the history of the discovery of elements.

The ytterbium earth isolated by Jean C. G. Marignac in 1878 was generally accepted as a chemical element for more than two decades, but in 1907 two chemists, Georges Urbain in France and Carl Auer von Welsbach in Austria, independently concluded that ytterbium contained a hitherto unknown element. Urbain reported his finding to the Paris Academy of Science on 4 November 1907, whereas Auer presented his full report to the Vienna Academy six weeks later (but had stated his claim in preliminary communications of 1905 and 1906; Figure 5).

While Urbain named the new element lutecium (Lu), and proposed neo-ytterbium (Ny) for the more dominant element corresponding to Marignac's ytterbium, Auer suggested the names cassiopeium (Cp) and aldebaranium (Ad). Both chemists claimed priority and immediately engaged in a heated controversy.[39] For example, at one stage Auer accused his French rival of foul play, to which Urbain indignantly responded: "[Auer] goes as far as accusing me of simply plagiarizing him. … It is disgraceful of Mr. Auer v. Welsbach to

Figure 5. Carl Auer von Welsbach. Source: https://commons.wikimedia.org/wiki/File:Carl_Auer_von_Welsbach_1910.jpg

make such accusations against his colleagues."[40]

Without going into further details, in 1909 the International Committee on Atomic Weights decided in favour of Urbain's priority, primarily because he was the first to publish an atomic weight for what now became lutecium and since 1949, lutetium. Several years later Auer unexpectedly got a second chance.

In the wake of the celtium-hafnium dispute scientists at Niels Bohr's institute in Copenhagen investigated anew Auer's cassiopeium by means of optical spectroscopy and compared the result with Urbain's spectrum of celtium from 1911. From this they concluded not only that celtium anno 1911 was nothing but element 71, but also that Urbain's original sample of lutetium contained much less of the element than Auer's cassiopeium. Consequently the Copenhagen scientists initiated a campaign to reinstate the Austrian chemist as the discoverer of element 71. The campaign succeeded in so far that the German Atomic Weight Commission gave full credit to Auer in 1923, but IUPAC maintained the name lutetium, or rather lutecium, and Urbain's priority.

Contrary to what is often stated in the chemical literature, Urbain's claim of having discovered lutetium in 1907 rested on a somewhat shaky foundation. Element 71 was undoubtedly discovered this year, but it might be just as reasonable to credit Auer with the discovery and relegate Urbain as an independent co-discoverer. The International Committee's decision to honour Urbain was based on incomplete information and an interpretation of available data favourable to Urbain's claim.[41] A contributing reason may have been that in 1909 Urbain served as chairman of the International Committee, the other members being Wilhelm Ostwald, Frank W. Clarke and Thomas Thorpe. Finally, the American chemist Charles James is sometimes mentioned as an independent discoverer or co-discoverer of lutetium, but since James did not publish his discovery and never pushed his own claim, this is unjustified.[42] He could have discovered the element, but did not.

7. NOBELIUM, ELEMENT 102

The manufacture of many of the transuranic elements, and especially those with atomic numbers between 100 and 113, has given rise to controversies regarding identification, name and priority. A noteworthy example is element 102, nobelium, which was first claimed discovered in 1957 but only received official recognition by IUPAC 35 years later.[43] The controversy, which was primarily concerned with whether priority belonged to teams of American or Russian scientists, has certain features in common with the earlier controversy over element 72. As the latter controversy was coloured by the international political climate in the early 1920s, so the controversy over element 102 included external factors reflecting the political atmosphere of the Cold War era.

But it started with a third group of contenders, namely an international team working at the Nobel Institute of Physics in Stockholm and consisting of four Swedes, two Britons and one American. In 1957 the team announced that it had detected element 102 by bombarding a sample of curium ($Z = 96$) with ions of carbon-13. As regards the name of the element the Stockholm scientists suggested to call it nobelium in honour of Alfred

Nobel. The discovery claim created much attention in Swedish and British news media, not least because it was the first transuranic element discovered in Europe. At the time nuclear syntheses of heavy elements was a monopoly of two research groups, one associated with the University of California at Berkeley, and the other with the Dubna nuclear research facility in Russia. None of the groups accepted the news from Stockholm and they were unable to reproduce the claimed results.

Even though the Swedish-led discovery claim turned out to be unfounded, this was only the beginning of a much longer priority controversy involving American and Russian scientists as competitors. The discovery story of nobelium has been called "the most convoluted and misunderstood of all [the discovery stories of] the transfermiums."[44] In short, the Berkeley team led by Albert Ghiorso first claimed to have produced the element in 1958, but the Dubna team vehemently denied the claim and argued that, "Element 102 was discovered at Dubna in studies carried out during 1963-1966. Those papers contain unambiguous and complete evidence for the synthesis of its nuclei."[45] Ghiorso and his collaborators (including the Nobel laureate Glenn Seaborg) responded by criticizing the Russian results and maintaining the validity of their own work.

Somewhat strangely, element 102 is still named nobelium and thus refers to a discovery claim that was known to be wrong or at least highly insufficient. Although neither the Americans nor the Russians accepted the claim, none of them suggested a different name. Nobelium had quickly entered textbooks and periodic tables, and in 1961 IUPAC approved the name and symbol without evaluating the validity of the Stockholm experiments. For a while the Russians used the name "joliotium," a reference to the French nuclear physicist Frédéric Joliot (or Joliot-Curie), but the name never caught on.[46] It is not irrelevant to mention that Joliot was a devoted communist and staunch supporter of the Soviet Union.

To take care of the many priority disputes IUPAC and IUPAP (International Union of Pure and Applied Physics) established in 1985 a joint Transfermium Working Group (TWG) consisting of nuclear physicists and chemists. After a review of all relevant papers on element 102, in a report of 1992 the TWG concluded in favour of the Dubna team whereas it found that the Berkeley experiments did not qualify as a discovery. The decision caused strong reactions from the Americans who not only charged that the TWG panel was incompetent but also that it was biased in favour of the Dubna claim. But IUPAC accepted the TWG report, meaning that the Russian nuclear physicist Georgii Flerov (or Georgy Flyorov) and his team were approved as discoverers of element 102 (Figure 6). This was not quite the end of it, though, for Ghiorso and Seaborg restated their case in "an appeal to the historians of science to reread the cited literature and perhaps, belatedly, to reassign credit." If they could not get full credit they would accept "in the spirit of glasnost" to share it with the Russians.[47] But the appeal was ineffective. The controversy terminated by a mixture of resolution and closure.

Figure 6. Russian stamp of 2013 dedicated to G. Flerov after whom element 114, flerovium, is named. Flerov was also head of the research team credited with the discovery of nobelium. Source: https://commons.wikimedia.org/wiki/File:RUSMARKA-1660.jpg

The TWG panel was acutely aware that an assignment of priority for having discovered an element cannot be separated from a definition of what constitutes a discovery. The chosen and agreed-upon definition was simply that the discovery of a chemical element is an experiment which convincingly demonstrates "the existence of a nuclide with an atomic number Z not identified before." The TWG panel further reflected on the historical importance of element discoveries:

> *The centuries-old history of the definition and discovery of chemical elements has a deep scientific and general fascination. ... The problem is open although of final scope, unlike the number of continents upon the surface of the earth where we know with certainty that none still awaits discovery. These considerations give to the discovery of new elements an importance, an allure and a romance that does not attach to the discovery of, say, a new comet or a new beetle where many more such discoveries are to be anticipated in the future.*[48]

The TWG comment related to the synthetic elements produced at the end of the twentieth century, but it could as well have been written by chemists at the time of Mendeleev.

8. CONCLUSION

Although there are today formal criteria for the discovery of a new element, and for assigning priority to the discovery, these are not applicable to many discoveries in the past. The relevant criteria depend on the historical period and so do the accepted rules for priority. It seems hardly possible to come up with a fixed definition of element discovery which makes sense over the approximately 250 years during which chemists have searched for new elements. The search has often given rise to priority controversies, a phenomenon one can find throughout history and independent of whether or not the discovery was guided by theoretical expectations. To understand these and other controversies related to the discovery of new elements, one needs to adopt the norms and rules of the period in question and not those of a later time. In this essay I have also pointed out that accepted discovery histories may retrospectively be questioned and revised. At least in principle it is possible that a future list of element discoveries will differ significantly from the one accepted today.

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Carl Auer von Welsbach (1858-1929) - A Famous Austrian Chemist Whose Services Have Been Forgotten for Modern Physics

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Abstract. Carl Auer von Welsbach (1858-1929) was a chemist and entrepreneur famous beyond the borders of Austria, with good contacts to well-known chemists and physicists in Europe. This is evidenced by his extensive correspondence and the shipment of his rare earth preparations to known researchers. In 1895 he discovered the elements neodymium and praseodymium and in 1905 the elements ytterbium and lutetium. In his time he was considered a specialist for the rare earth elements (REE). He received his doctorate from Robert Bunsen in Heidelberg (1880-1882). Spectral analysis was his domain. His ability to neatly separate the chemically very similar SE elements from the minerals (e.g. monazite sand) to the then-known and further developed principle of "fractional crystallization" also made relatively accurate investigations of the magnetic properties of these elements possible. In particular, the chemists and physicists were interested in the question of whether or not the series of REE elements is complete with lutetium. The famous quantum physicist Niels Bohr had made a statement with his atomic model that lutetium must be the last element of this sequence in the periodic table of the elements and predicted the magnetic properties. They were confirmed by the experiments with the Auer von Welsbach preparations - in particular of lutetium - by the physicist Stefan Meyer (1842-1949) in Vienna. In 1925 the physicist and theoretician Friedrich Hund (1886-1997) from Göttingen then succeeded to set up a first quantum mechanical model (Hund's rule), which achieved good agreement with the experimental results from Vienna. This was an advance in early quantum mechanics, which is also due to the highly pure SE preparations of the chemist Carl Auer von Welsbach.

Keywords. Carl Auer Welsbach, Rare earth Elements, magnetic properties, Niels Bohr, Friedrich Hund, quantum mechanics.

1. INTRODUCTION. CARL AUER VON WELSBACH – THE MOST IMPORTANT STAGES OF HIS LIFE AS A RESEARCH SCIENTIST

Carl Auer von Welsbach was born on September 1st 1858 in Wels (Austria) and later especially known for the invention of the incandescent gas mantle. His father Alois Welsbach was already famous as chief of the imperial court printing house and well-known beyond Austrian borders.

Auer von Welsbach was born into a wealthy family. This meant that even though he lost his father at a young age, after completion of his military service year (Lieutenant Patent 1878) he was still able to attend the Technical University of Vienna to study mathematics, chemistry, and physics. There he became acquainted with Adolf Lieben (1836 – 1914), a professor of chemistry, who, as a member of the Imperial Academy of Sciences and later as a member of the Radium Commission, supported Auer von Welsbach´s research projects.

Initially Auer von Welsbach switched to the University of Heidelburg. This University, where famous chemists and physicists such as Robert Wilhelm Bunsen (1811 – 1899) and Gustav Robert Kirchhoff (1824 – 1887) taught, was a Mecca for many young scientists at the time. Even the famous physicist and physiologist Hermann Helmholtz (1821 – 1894) was working there from 1858. Under the guidance of Bunsen, Auer von Welsbach soon occupied himself with the technique of chemical spectral analysis, which Bunsen and Kirchhoff had developed, in order to research rare earth metals. These were little known, sparingly researched and were of complex formulation. Here, he distinguished himself quickly in experimental chemistry and physics, completing his doctorate (without any written work) with "in insignis cum laude", and had acquired trust and recognition from Bunsen.[1]

In 1882, Auer von Welsbach returned to Vienna and worked as an unpaid assistant to Professor Adolf Lieben in the basement of the University of Vienna's Institute of Chemistry. In 1885, with the help of spectral analysis, he succeeded in proving that the rare earth element didymium in fact consisted of two elements, namely of neodymium and praseodymium.[2]

Then followed an almost unparalleled period of discoveries as a chemist and technician and success as an entrepreneur, namely through the development of the thorium und cerium incandescent gas mantle (patented 1891) and the development of the first metal-filament lightbulb with osmium as the base material (patented 1898) and the marketing of this innovation from 1902 (Auer Os-light, later Osram). The residual material from the production of the illuminants, namely the cerium oxide, was reused as a raw material in his firm in Treibach-Althofen (Carinthia, Austria). The product, flint (Auer Metal/ferrocerium), has been (and is still today) produced and sold by the billions.

In 1905 he was once again successful in his laboratory at Welsbach castle (near Althofen) but now as a private scholar, who slowly withdrew from his economic activities. He separated the rare earth element ytterbium into the elements aldebaranium (today ytterbium) and cassiopeium (today lutetium).[3] 20 years later the physical properties of cassopeium were to play an important role in the further development and confirmation of quantum mechanics.

With the beginning of the first decade of the 20th century, Auer von Welsbach devoted himself to the new phenomenon of radioactivity. In his firm in Atzgersdorf, Vienna, the first radium preparations in Austria were produced from the residues of a pitchblende ore outside of Jáchymov, Czech Republic. He personally examined these residues ("hydrates") at Welsbach castle, separated ionium, polonium and actinium preparations, and provided them to the University of Vienna's Institute of Physics and the Institute of Radium Research in Vienna, which opened in 1910, for further research.[4,5] At the same time, the examination of rare earth metals proceeded and he provided their preparations to scientists, many of them later Nobel Prize laureates, all over Europe. With this, he had supported the classification of the rare earth metals in the periodic table of elements and nuclear and quantum physics in the critical early stages. These activities, which were naturally hindered during the First World War, can be seen in figures 1 – 3.

Measured by his research activities, Auer von Welsbach published relatively little. He was more devoted to his experiments than the documentation and explanation of his research outcomes. Perhaps that can be attributed to the influence of Robert Bunsen in Heidelburg. He was an experimental chemist, experimental physicist and technician. If you look closely however, you can determine that he indeed followed developments in the fields of chemistry and physics, and consciously wanted

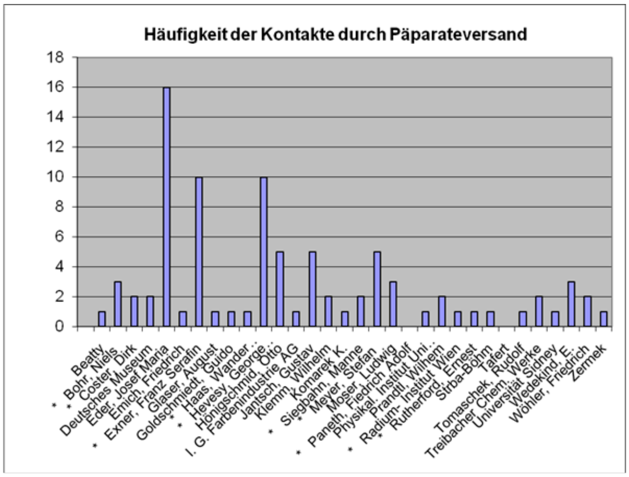


Figure 1. Frequency of contact through Eversand Compound. Source[13] : Gerd Löffler, *Carl Auer von Welsbach und sein Beitrag zur frühen Radioaktivitätsforschung und Quantentheorie*, ISBN 978-3-200-04400-5**, 2015**, p. 125.

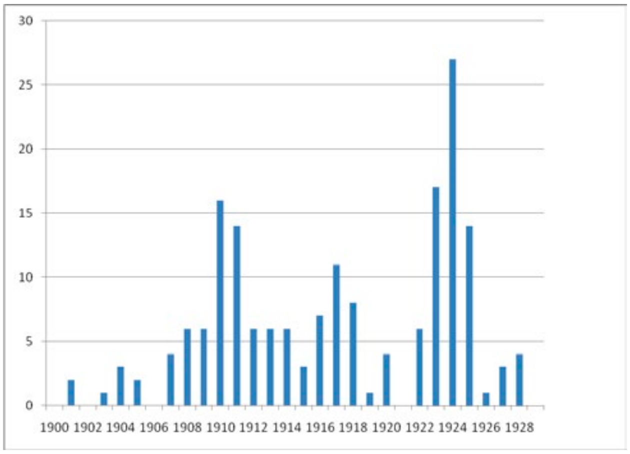


Figure 2. Auer von Welsbach – correspondence with chemists and physicists in Europe. Source[14] : Gerd Löffler, *Carl Auer von Welsbach und sein Beitrag zur frühen Radioaktivitätsforschung und Quantentheorie*, ISBN 978-3-200-04400-5**, 2015**, p. 127,

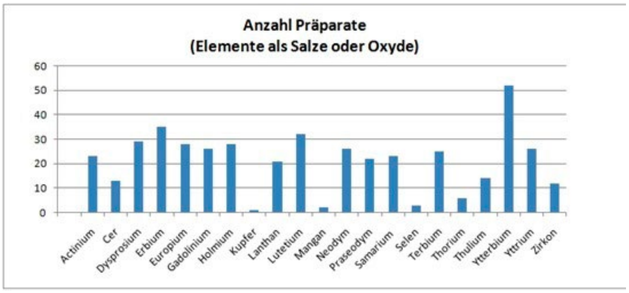


Figure 3. An overview of the compounds of the rare earth metals, which Carl Auer von Welsbach made available to other researchers. Number of compounds (element as a salt or oxide). Source[15]: Gerd Löffler, *Carl Auer von Welsbach und sein Beitrag zur frühen Radioaktivitätsforschung und Quantentheorie*, ISBN 978-3-200-04400-5, **2015**, p. 126.

to assist these developments and their representatives, such as Ernest Rutherford and Niels Bohr for example. He strove to preserve science institutes with considerable donations where the need after the First World War was greatest, such as the Radium Institute of Vienna.[6]

In 1926, he published the results of his search for the rare earth element No. 61 (Atomic number 61).[7] With the experimental methods at the time, there was nothing that could be detected. Von Welsbach was to be proved right. This gap in the periodic table of elements was able to be filled only in 1945 by producing 61 (promethium) using the nuclear reactor at Oak Ridge, USA. It is evident that a stable element (isotope) does not exist.[8]

Auer von Welsbach was distinguished in his lifetime with many honors. He was recognized not only in Austria, but also throughout Germany for his many achievements, such as, for example, with the "Siemens-Ring" (1921) which was unofficially designated as the German version of the Nobel Prize. He enjoyed an exceptionally high reputation with the Gesellschaft deutscher Chemiker (GDCh), who also hailed him and his accomplishments as a researcher and as a businessman on the 150th anniversary of his birthday in 2008.[9,10] Auer von Welsbach was a member of various academies in Europe, e.g. from 1911[11] he was a full member of the Kaiserliche Akademie der Wissenschaften in Austria, and from 1913[12] – appointed by Max Planck – he was a corresponding member of the Preußische Akademie der Wissenschaften in Germany.

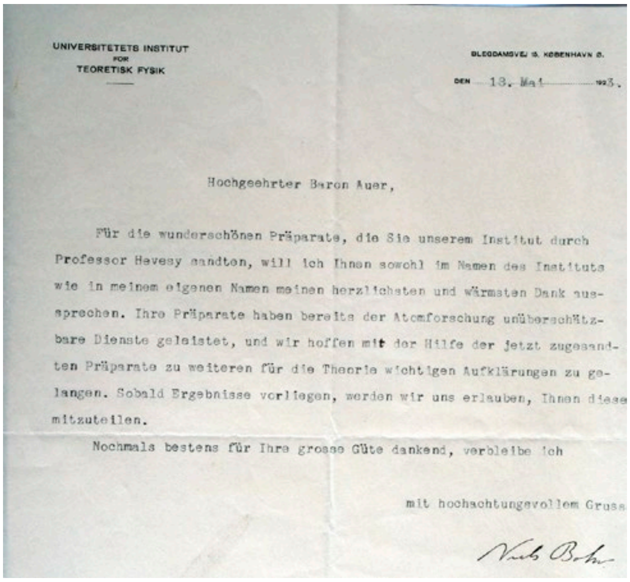
Carl Auer von Welsbach passed away in Welsbach castle, near Althofen, on 4th August 1929, and was buried in Vienna.

2. COLLABORATION WITH AND SUPPORT OF NIELS BOHR'S WORK

It is little known that Auer von Welsbach carried out pioneering work in the field of early quantum theory and made a considerable contribution as an experimental chemist to the slowly developing quantum theory of Max Planck from 1900, and then from 1910 to 1913 to that of Niels Bohr, culminating in an initial high point. He made numerous preparations of the rare earth elements for the physicists and chemists in Europe at that time in his laboratory in Carinthia in particular, in order to test the new theory in Copenhagen and Cambridge. The gratitude expressed by Niels Bohr to Auer von Welsbach in 1923 (see Fig. 4) was made at a time when George von Hevesy and Dirk Coster had discovered the long sought-after element hafnium in a zirconium mineral at the end of 1922, following previous extensive X-ray spectroscopic investigations, as well as the Welsbach preparations. This rare document underlines the connection between the Carinthian physicist and early quantum theory at that time.

2.1 Carl Auer von Welsbach's incandescent gas mantle and Max Planck's radiation formula. Forgotten details from the beginnings of quantum theory

Chemists and physicists, who do not or have not concerned themselves in particular with quantum physics, are mostly unaware why Carl Auer von Welsbach was so closely linked in the early phases of quantum theory with researchers in this field. Fig. 1 gives a short insight when names such as Bohr, Rutherford, Hevesy,



UNIVERSITETETS INSTITUT
FOR
TEORETISK FYSIK

BLEGDAMSVEJ 15. KØBENHAVN Ø.

DEN 13. Mai 1923.

Hochgeehrter Baron Auer,

Für die wunderschönen Präparate, die Sie unserem Institut durch Professor Hevesy sandten, will ich Ihnen sowohl im Namen des Instituts wie in meinem eigenen Namen meinen herzlichsten und wärmsten Dank aussprechen. Ihre Präparate haben bereits der Atomforschung unüberschätzbare Dienste geleistet, und wir hoffen mit der Hilfe der jetzt zugesandten Präparate zu weiteren für die Theorie wichtigen Aufklärungen zu gelangen. Sobald Ergebnisse vorliegen, werden wir uns erlauben, Ihnen diese mitzuteilen.

Nochmals bestens für Ihre grosse Güte dankend, verbleibe ich

mit hochachtungsvollem Gruss

Niels Bohr

Figure 4. Niels Bohr to Carl Auer von Welsbach (05/13/1923). Source: Archives Auer-von-Welsbach Research Institute, File: Correspondence; Location: Auer-von-Welsbach Museum, Althofen (Carinthia).

Coster, Aston, and Siegbahn arise as recipients of von Welsbach preparations. Who remembers today that even the “father” of Japanese nuclear physics, Yoshio Nishina (1869-1951), investigated rare earth element preparations from Carl Auer von Welsbach by X-ray spectroscopy during his studies in Copenhagen with Niels Bohr from 1923 onwards?[16,17]

The discoveries of the Planck radiation formula in 1900 and of the photoelectric effect (Einstein, 1905) can be considered turning points in our concept of the world of physics at that time. The rare earth elements and their final classification in the periodic system of the elements was a “real test” for the further development of nuclear and quantum physics at the beginning of the 20th century. If it had not been for the achievements of the chemists, who had specialized in the discovery and isolation of these “rare” metals – including in particular Carl Auer von Welsbach – quantum physics would not have been able to take the well-known dramatic developments in the first two decades of the last century. As one example for many other documents, this assessment arises from the letter from Niels Bohr to Carl Auer von Welsbach dated May 13, 1923 (see Fig. 4).

2.1.1 The interest of quantum physicists in the Auer light

The step taken by the natural sciences in the field of quantum physics was not very straightforward. It started in retrospect with the radiation laws of the physicist Gustav Kirchhoff governing the radiating properties of solid bodies. Together with Robert W. Bunsen, Kirchhoff established Heidelberg‘s reputation as a research center, where the scientific career of Carl Auer von Welsbach also began. In 1860, Kirchhoff recognized that the ratio of the emissivity to the absorption capacity for all types of radiation, independent of the material properties of the body and for a certain wavelength, only depends on the temperature of the body. In 1875, Kirchhoff was appointed professor of theoretical physics in Berlin, which later became the center for quantum physics. Kirchhoff’s radiation law, with which theoretical physics introduced the term “black body,” as an ideal state, which a body approaches with increasing temperature,[18] was the starting point for further considerations and experiments of physicists to describe the energy emitted by a body with a comprehensive law, which was finally presented on December 14, 1900 as the radiation formula at a convention of the German Physical Society by Max Planck. Kirchhoff himself sensed the fundamental significance of his findings and/or his radiation law and knew in which direction further research would have to be carried out in order to find a generally valid radiation law. In 1860, he wrote in this respect: “It is a task of great importance to find this function.[19] Not until we have solved this problem, will we be able to reap all the fruits of our labors.”[20]

The time span of about 40 years alone exemplifies the efforts, struggles and aberrations which had been experienced in order to come to a conclusive result. Starting with Kirchhoff, several physicists, such as Wilhelm Wien (1864-1928), Friedrich Paschen (1865), Otto Lummer (1860-1925) and Heinrich Rubens (1865-1922), were involved. Max Planck was also not immune to making errors until he decided “in an act of desperation”[21] to introduce two natural constants: namely, the Boltzmann constant k[22] and the action quantum h, which had already been described in 1900, into the previously unsatisfactory drafts for a radiation formula and as such open the door to quantum physics. The main problem was to bring experiment and theory into agreement with one another in the infrared range. If, however, Kirchhoff had not introduced the “black body” and its physical properties (see above) in 1860, most certainly years, if not decades would have passed before this era of physics would have come up with the breakthrough insight created a completely new world view from 1900 onwards.

Producing a body which came closest to the “black body” postulated by Kirchhoff, was by no means trivial. There were many failed attempts in this respect. In particular, Wilhelm Wien and Otto Lummer attempted to find a solution at the Physical-Technical Imperial Institute in Berlin. The same applied from an experimental point of view to the development of a photometer, which could measure the wavelengths of radiating bodies with sufficient accuracy. Thermally insulated (heated) platinum tubing was finally used as a black body and as of 1889 a newly developed photometer was used, the so-called "Lummer-Brodhun cube".[23] As a radiating body emits electromagnetic waves in the ultraviolet to the ultra-red range, it was also necessary to filter out the wavelengths from this spectrum with sufficient precision and intensity. In the development of this technology, the physicist Heinrich Rubens distinguished himself in particular with the residual radiation method. The aim was to clarify the discrepancies between theory and experiment in the ultra-red range. The method developed by Rubens was particularly suitable for this purpose. In the experiments, light sources and temperatures were necessary which could provide an ultra-red range with sufficient intensity. For this purpose, Rubens used the Auer light, i.e. the incandescent gas mantle.[24,25] The Auer light is an excellent source of radiation in that only a small part of the emitted energy is in the visible range. Most of the energy is emitted in the ultraviolet and in particular in the infrared and the ultra-red range – which in this case was of great interest. Fig. 5 shows the principle of selective electromagnetic radiation for a certain wavelength starting from an emitter. Fig. 6 shows why the Auer incandescent mantle possesses suitable radiation capacity especially in the ultra-red range. The residual radiation method is based on the fact that some crystals have a selective reflectivity, such as e.g. rock salt, fluorspar and quartz. By positioning several plates of these crystals behind one another (multiple reflectivity), stray rays are suppressed and only electromagnetic waves of a certain wavelength are forwarded with a high degree of reflectivity (to a thermocouple). With an Auer light, one can thus create very precise radiation with a wavelength of λ=43 μm with sufficient intensity. Optical grids were not suitable for this purpose.[26] In order to underscore the advantage of the Auer light using the residual radiation method, Heinrich Rubens is quoted as follows (extract): "As I explained earlier, one already obtains very pure residual rays after three-fold reflection of the radiation emitted by the Auer burner in a strength which amounts to 1.7 % of the entire radiation. A perfect black body at 1800 degrees abs. would result in less than 1 per mille of residual radiation under the same circumstances."[27]

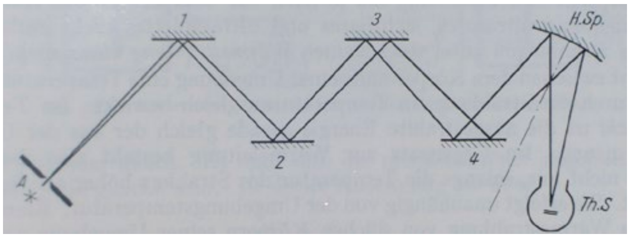


Figure 5. The residual radiation method according to Heinrich Rubens. A: Emitters, e.g. Auer incandescent mantle, H.SP: Concave mirror, Th.S: Thermal column, crystal plates 1, 2, 3, 4. Source: Gerthsen, Christian; Kneser, H. O.: "Physics", Textbook, (Berlin 1969), 371.

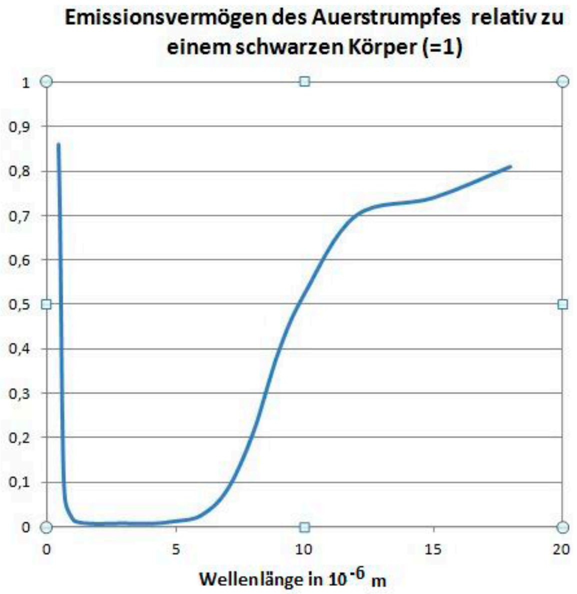


Figure 6. The emissivity of the Auer incandescent mantle relative to a black body (=1). Wellenlänge = wavelength 10^{-6} m. Source: Rubens, Heinrich: "The emission spectrum of the Auer incandescent mantle", in: Proceedings of the German Physical Society 7 (1905), Table, 349.

The significance of the "radiation physicists" in Berlin, in particular Heinrich Rubens, and the experimental physics advanced by them cannot be praised highly enough for the acceptance of quantum physics, which gave rise to a completely new way of looking at processes on an atomic scale.

2.2 Quantum theory and magnetism of the rare earth elements

A short introduction to the subject of "magnetism"

It is general knowledge today that the earth possesses a magnetic field and that anyone can navigate themselves through the earth's magnetic field with the help of a compass using the direction given by the magnetic needle. In the same manner, it is general knowledge that a magnetic field can be created using simple means with a current flowing through a coil, whereby the coil likewise behaves as a magnetic needle in the earth's magnetic field if it is freely suspended. It is also known for objects of everyday life, e.g. in electronic products (televisions, computers), from food processors to cars, as well as in large manufacturing components, such as machines in all branches of industry, not least of all in power generating plants such as those utilizing atomic, thermal, water and wind energy, that all of the above use magnets and/or metals and metal alloys with magnetic properties.

There are four types of magnetism which can be differentiated: diamagnetism, paramagnetism, ferromagnetism and ferrimagnetism,[28] depending on the different physical properties of the metal compounds which occur in nature, or artificially manufactured metal oxides and metal alloys. For a long time, the causes of the different magnetic behavior of substances, i.e. the elements and their compounds, was not known. The technical applications were far ahead of an understanding of the actual physics.[29] Up until today, magnetism is a special field of solid state physics and the subject of further developments in quantum mechanics.

At this point in time, ferromagnetism, which is a characteristic of the substances iron, cobalt, nickel as well as the rare earth element gadolinium, and in which a magnetic force can also be determined without any external influence (without an additional external magnetic field), will not be further discussed here, as early quantum theory could not provide any conclusive explanation for this. The same applies for ferrimagnetism.[30] The situation is different with the diamagnetism of the elements, characterized by diamagnetic substances which are crowded out of an existing external magnetic field ($\mu < 0$; $\kappa < 1$).[31] Paramagnetic substances are drawn into an existing magnetic field ($\mu > 0$; $\kappa > 1$). Experimentally, in the first case, there is attenuation of the existing magnetic field and in the second case it is intensified. Since the causes of this were not being pursued at that time (i.e. quantum physics was not a topic of interest), the differing behavior of diamagnetic and paramagnetic substances was described as "Lenz's principle",[32] whereby it should be mentioned that both element types cannot be differentiated in their magnetic behavior if no external magnetic field is present. However, there is a further characteristic difference: diamagnetism is independent of temperature, whereas paramagnetism decreases with increasing temperature (Curie's Law). Further, it should be remembered that some paramagnetic substances (compounds) have a characteristic color.

Besides the elements of the iron group, the rare earth elements can also be included with those in the periodic system that are characterized by their special magnetic behavior (see above), with which Carl Auer von Welsbach had worked on so intensively and/or was decisively involved in their preparation in a pure state.

The understanding of magnetism only changed slowly and stepwise when the French physicist Paul Langevin (1872-1946) assumed from an atomic model in 1905 that an electron gas is a prerequisite for non-magnetic substances, whereby the quotient of the charge of the electrons to their mass is more than one thousand-fold greater than that of the compensating positive particles. Both particle types ensure external electrical neutrality. According to the classical theory, the electrons move in a circular motion (Larmor frequency) around an external magnetic field. These circular motions produce a magnetic moment. From this, the magnetic susceptibility for diamagnetism can be derived, as it still applies in principle today. It became apparent that the assumption of Langevin in this form was not tenable, as the properties of an electron gas residing around a positive charge had not been completely described. Such a model assumed by Langevin creates an opposite dipolar moment by the (spherically shaped) surface of the electron gas, so that the entire magnetic moment is zero. Niels Bohr referred to this in his dissertation in the year 1911.[33] Further steps in the development of nuclear and quantum physics were needed (Bohr-Rutherford, Bohr-Sommerfield atomic model) as well as the step to quantum mechanics by Werner Heisenberg, Max Born, amongst others, in the mid 1920's. However, Langevin still deserves credit for his attempts and his conclusion that the magnetic behavior of the elements can be attributed in principle to that of the electrons.

2.3 The long road to a first quantum physical model for the magnetic behavior of the REE

Despite the progress that quantum theory had made, thanks to the famous theorists such as Bohr, Sommerfield and Heisenberg, until the middle of the 1920's the abnormal Zeeman effect (splitting of the spectral lines in a strong magnetic field into more than 3 terms),[34] the Paschen-Back effect (multiple splitting of the spectral lines in a strong electrical field)[35] and the complicated spectra of the rare earth elements had not yet been disentangled. It was thus appropriate to understand the magnetic properties of these elements, starting with the previous findings about the numbers of occupied electrons according to the different main quantum numbers (= "electron shells") of the lighter elements and the empirically obtained magnetization numbers (or magnetic susceptibility).[36] The physicist Friedrich Hund (1886-1997) in Göttingen, a student of the theorist Max Born (1882-1970), was particularly specialized in this field. Hund published the results of his work in 1925 (see below).[37]

It was a long road which had to be taken until this point in time was finally reached:

Bohr had already ascertained in his dissertation in 1910,[38] that the magnetic properties of the elements known then could not be explained using classical theory (with free electrons or those bound to atoms). According to classical theory (Langevin's theory of paramagnetism), it could be derived that all elements must have paramagnetic properties. In reality, however, the situation was and still is very different: most elements are diamagnetic.[39] The supporters of quantum theory were thus challenged again, and further development of quantum theory was urgently needed. This process concerned researchers, both opponents and advocates of quantum theory, for many years to come.

This discrepancy was addressed by Niels Bohr in several stages. In 1913, he went one step further by establishing a fundamental postulate. His solution to the further development of quantum theory was to assert the consistency of the angular momentum of an electron in an orbit, also in the presence of an external magnetic field. It can be shown using perturbation theory (in principle a mathematical process) that under this assumption one individual electron (of an atom) performs work against the external field,[40] i.e. the diamagnetic substances are crowded out of the (external) magnetic field. Physics only allows this explanation for the occurrence of diamagnetism, however, if the external magnetic field is vertical to the circular electron level. In other words, a theoretical model was only imaginable for one special case. Bohr's quantum theory had reached its limits.[41] Progress in quantum physics was needed. This work was essentially carried out by Sommerfeld and subsequently by Max Born (1882-1970)[42] and his students Werner Heisenberg, Pascal Jordan, Friedrich Hund (scientist for theoretical physics in Göttingen) as well as by the Austrian Wolfgang Pauli.[43,44] From 1925 onwards, the step from quantum theory to quantum mechanics had been fulfilled. Besides Copenhagen, Göttingen became a center for theoretical physics.[45] The Stern-Gerlach experiment and that of Samuel Goudsmit and George Eugene Uhlenbeck were correctly interpreted in the course of this development. A difficult process from theory and experiment now led to the belief that a half-integral angular momentum (= ½ h/2π) and thus a magnetic moment had to be attributed to an electron. This was in no way to be taken as a matter of course, as up until then electrons and protons were still considered to be the building blocks of the atomic nucleus (Thomson's atomic model).

2.4 Comparison of the magnetic properties of RRE: theory versus experiment

As already mentioned, Carl Auer von Welsbach discovered the rare earth element cassiopeium (called lutetium today) with the atomic number 71. In addition to other preparations, Auer von Welsbach also sent this preparation to the Institute for Radium Research in Vienna, where the head - Stefan Meyer - was working on the measurement of the magnetic properties of different elements, amongst other things.[46] On 2/29/1924, Meyer wrote to Auer von Welsbach:[47]

> *Institute for Radium Research" Vienna, 2/29/1924*
> *IX., Boltzmanngasse 3.*
> *Dear Doctor!*
> *As I already wrote to you, your pure* $Cp_2\ (SO_4)_3 \times 8\ H_2O$ *is diamagnetic, which is of great interest. Likewise,* HfO_2 *is diamagnetic.*[48]
> *With kindest regards and greetings,*
> *Yours faithfully,*
> *Stefan Meyer*

A few days later, on 3/6/1924, Carl Auer von Welsbach replied:

> *It will greatly please Bohr to hear that his prediction about the diamagnetism of Cp has been confirmed.*[49]

The letter from Auer von Welsbach to Bohr is one of the few direct pieces of evidence amongst the documents still remaining which shows that Auer von Welsbach was aware of the significance of the explanation of magnetism by quantum theory. Following this, Stefan Meyer published one year later the magnetization numbers of the other rare earth elements starting with atomic number 57 (lanthanum) up to atomic number 71 (cassiopeium = lutetium).

Meyer compared the measurements with the results of the famous Spanish physicist Blas Cabrera (1878-1945), who can also be included in this small circle of specialists in this area. The results concurred well, if one takes into account the state of measurement technology available at that time (see Fig. 7).

Remarks: Regarding the magnetization numbers (Weiss's magnetons)[51] of the rare earth elements (lanthanum La to cassiopeium Cp), see the following footnotes.[52,53]

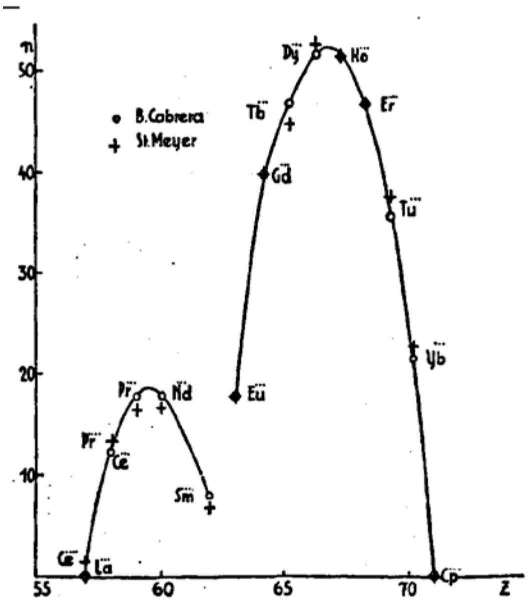


Fig. 7 The magnetization numbers (Weiss's magnetons) of the rare earth elements (lanthanum ^{57}La to cassiopeium ^{71}Cp). n: Weiss's magnetons; Z = atomic number (= number of protons). Source[50]: Stefan Meyer, Magnetization numbers of the rare earths, *PhysikalischeZeitschrift*, **1925**, 26, p. 53.

Stefan Meyer (1925) wrote in the introduction:

> *Since the discovery of the unusual magnetic properties (1899[1]) of the rare earths, I have always had the opportunity to measure their magnetization numbers thanks to the kindness of C. Auer-Welsbach and have repeatedly reported about this.[2]*
>
> *1) Vienna. Ber, (IIa), 108, 861, 1899 2) Vienna. Ber. (IIa), 109, 403, 1900; 110, 541, 1901; 111, 38, 1902; 117, 995, 190 8)*

Meyer continues: "At the beginning of 1924, I informed the interested parties, especially the Bohr Institute in Copenhagen, that both cassiopeium (71) as well as hafnium (72) are diamagnetic, and that in the first instance this information referred to Cp preparations from 1915 and 1924."[54] Niels Bohr had already recognized the significance of the Welsbach preparations in 1923, when he classified them as "inestimable" for atomic research (see the letter from Bohr to Auer von Welsbach dated 05/13/1923, Fig. 4).

Experimentally obtained data on the magnetic behavior of the rare earth metals were now available and could be considered essentially verified according to the state of measurement technology at that time. However, the theoretical explanation was still missing.

In 1925, the physicist Friedrich Hund succeeded in essentially explaining theoretically the experimental data which had been collected up until then about the magnetic behavior of the above-mentioned metals on the basis of the work of the afore-mentioned physicists in Göttingen, the assumptions of Niels Bohr about the successive occupation of the subjacent electron shells (today described as the 4f-electrons),[55] furthermore taking the Pauli principle and especially the preliminary work of Heisenberg into consideration.[56,57] Hund described his theoretical model in an abridged form, as follows: "Shortly thereafter, he [Hund] was able to explain the magnetic behavior of the rare earths by giving the basic state of their trivalent ions using the rule that from the possible multiplets with the deepest energetic configuration, the multiplets with the highest multiplicity lie deepest and that which is the deepest is the one with the highest angular momentum."[58]

Hund established the Bohr magneton numbers (for the trivalent ions of the rare earth elements lanthanum and subsequently) and then converted these into Weiss's magneton numbers.[59] In this way, he could compare his theoretically established values with the data determined experimentally by Blas Cabrera and Stefan Meyer. The comparison with the data from Stefan Meyer is shown in Fig. 8.[60]

The level of agreement between theory and experimental results was astoundingly good considering the experimental techniques used by Stefan Meyer and the state of quantum theory at that time. In particular, the occurrence of two maxima by Hund could be comprehended using one of the theories based on quantum physics. Both lanthanum and lutetium ions are clearly diamagnetic.

There is, however, a noticeable deviation between theory and experiment for the europium ion. Stefan Meyer explained that the europium preparation used must have still contained 5-6 % gadolinium, in other words it was slightly impure. He states that for this reason, Weiss's magneton number would have to be 15.5 instead of 18.5.[61] According to this, the difference between theory and experiment would then be reduced, although for the europium ion it would still be significant.[62] The comments from Meyer, however, also show that through the advances made in measurement techniques the investigations of magnetic properties were suitable to identify the rare earth elements in substances and/or to establish their degree of impurity.

The actual objective to disentangle the spectral lines of the rare earth elements came one step closer by an understanding of their magnetic properties, namely by quantum theoretical specifications for the permissible energy states of an atom and/or these elements. In

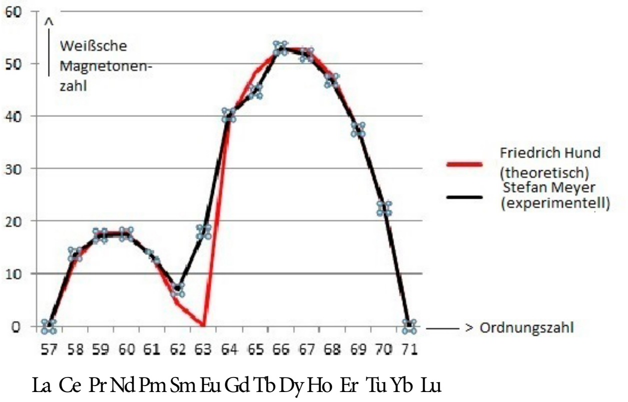


Fig. 8 Magnetic properties of the rare earth elements (trivalent ions of ^{57}lanthanum to ^{71}lutetium). Source[63]: Friedrich Hund, Atomtheoretische Deutung des Magnetismus der Seltenen Erden (= Theoretical atomic signification of magnetism of the rare earths), *Zeitschrift für Physik*, **1925**, 33, Table 1, p. 857.

this respect, the quality and purity of the preparations of these elements (mostly sulfates) which were also supplied by Carl Auer von Welsbach played an important role. However, it must be brought to mind here that the arc and spark spectra, e.g. of dysprosium and yttrium compounds exhibited more than 3,000 and/or more than 2,000 lines, respectively.[64] However, the spectra of the rare earth elements were not fully explained during the lifetime of Carl Auer von Welsbach. Further advances were linked to continued developments in quantum mechanics and achieved after his death in the 1930's.[65]

Today, rare earth elements are used in numerous industrial products (in the form of complex metal compounds) due to their magnetic properties, in particular in the electronics industry. This is referred to as an inherent "magnetic technology". This rapid development was unimaginable at that time up to the end of the 1920's. However, it shows the true significance of basic research work which was carried out almost 100 years ago.

3. THE DETERMINATION OF THE ATOMIC WEIGHTS OF YTTERBIUM AND LUTETIUM

The two elements ytterbium and lutetium conclude the lanthanide series. These findings and the properties of these two elements still have an important significance for chemists and physicists today. The discovery and the following chemical-physical investigations commencing with ytterbium by Jean Charles de Marignac (1817-1894)[66] in a mineral obtained from the area around the Swedish town of Ytterby near Stockholm (1878) and finally the separation of this element by Auer von Welsbach commencing 1905-1914 – almost at the same time as the French chemist Georges Urbain – into ytterbium as it is known today (called aldebaranium at that time) and lutetium (called cassiopeium at that time) has given today's table of the elements its definitive structure through modern chemistry and physics.

Auer von Welsbach had already worked on ytterbium relatively early on, as can be seen from the records of his most important employee, Ludwig Haitinger (1860-1945).[67] Here it is briefly described how he separated the original ytterbium from the elements scandium and erbium contained in the starting mineral. Auer was also aware of the weak basicity of ytterbium before 1893. He also knew that the oxalate of this supposed element (a white powder) was almost insoluble in water and dilute hydrochloric acid. Besides the knowledge of the spectrum, these findings served him later on in his further work to determine the atomic weight of the actual elements, namely ytterbium and lutetium. The procedure used for the separation of ytterbium (old) into ytterbium (aldebaranium) and lutetium (cassiopeium), starting from half a ton of crude ytteroxalate in 1906[68] is described in detail in the Sitzungsberichte der Kaiserliche Akademie der Wissenschaften.

The "birth" of the new element, in this case the discovery of the element lutetium, can best be described by the discoverer in his own words, and therefore his description of this moment and/or the time at the beginning of 1905 should be reproduced verbatim, similarly his description of the first atomic weight determinations in 1906 should be quoted. These were repeated in

Table 1. (to Fig. 8).

Atomic number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Mg. number Cabrera	0.0	12.5	17.8	17.8	13.4	4.2	0.0	39.4	48.3	52.8	52.8	47.7	37.6	22.5	0.0
Mg. number Meyer	0.0	13.8	17.3	17.5	13.4	7.0	18.0	40.2	44.8	53.0	51.9	46.7	37.5	22.5	0.0

Mg. number = Weiss's magneton number

the years to follow. Several records from 1912 about the determination of the atomic weights of ytterbium (aldebaranium) and lutetium can be found in handwritten documents, which are archived in the Carl Auer von Welsbach Museum (see Fig. 9, Fig. 10 and the literature references below).

The earliest announcement of this discovery of the composition of the old ytterbium from two elements results from the notification of these findings by Auer von Welsbach with the Imperial Academy of Sciences in Vienna in 1905. However, this did not yet include the atomic weights and spectra of the two elements. For this reason, however, we know that mainly the spectral findings at this point in time supported these results.[69] In 1906 and 1907, he then described how he proceeded exactly and his results (spectra, atomic weights of the newly discovered elements, in this respect see also below).

In 1906, readers were informed in a separate treatise via the journal 'Justus Liebig´s Annalen der Chemie' about the exciting situation in his laboratory at the time of the discovery.[70] Here he wrote:

> *During the investigation of ytterbium ammonium oxalate, I noticed some strange phenomena which suggested that ytterbium is not a uniform body. I first compared the different fractions (remark of the author: fractionated crystallization) amongst themselves and also using pure ytterbium from earlier presentations, but could not find any indications for the correctness of my assumption despite careful comparison. Nevertheless, I continued the fractionation. After a longer period of time, I obtained a preparation which demonstrated quite distinct changes in intensity, which in the case of weak arcing showed up by all means in some of the characteristic lines in the red of ytterbium in comparison to other ytterbium preparations. When this separation process was continued, these changes became even more striking. Individual lines in the red started to become paler, others became more pronounced with all the more radiance. Now the change in the intensity of the lines became noticeable also in the remaining parts of the spectrum.*
>
> *When I then compared the ytterbium fractions which were farthest apart later on, after protracted continuation of the separation process, the distinct differences of the two spectra came to light. With the continuation of the separation process, I realized that the purest preparations did not have any common lines any longer even with strong arcing in the optical part of the spectrum.*
>
> *I now photographed the spectra which had been produced with the help of a concave grid under fully identical experimental conditions in the range λ = 4500-2600 (Å).*[71] *The glass-clear, very high-contrasting negatives gave, when compared directly, an extremely interesting picture. Almost all lines were very precise upon moderate enlargement …*

Following a short description of the spectra, he continued

> *Thanks to these explanations which were most certainly needed, the exact scientific proof of the successful separation of ytterbium into two bodies had been provided.*

Auer von Welsbach then established that he "had already informed anyone who had asked in the year 1906", and that he had informed them about the approximate wavelengths and the approximate atomic weights. He had determined the atomic weights for Ad= 172.52 g/mol (ytterbium) and Cp= 174.28 g/mol (lutetium).

The separation method he used was fractional crystallization (Appendix). This method was also suitable, amongst other things, as the rare earth elements all crystallize isomorphically. His particular contribution to the further development was that he used the different solubility of ammonium binoxalate of the rare earths in ammonium oxalate (intentionally mixed with some ammonia so that no turbidity occurred)[72] during fractionation and was thus able to follow in many hundreds of steps the slow separation by continuous analysis of his (arc) spectra,[73] until no change in the spectra of the elements ytterbium (new) and lutetium could be observed.

In the years that followed up until 1914, very exact spectra and atomic weights which had been determined by further experiments were published. The publications not only appeared in the communications of the Imperial Academy of Sciences but also partly in other scientific journals.[74]

The rare earth elements which are discussed here were certainly available to him in 1903 through the basic maceration of the raw material monazite (using sodium hydroxide)[75] as oxides and/or as salts, even though he did not expressly mention this. Monazite was the starting material for the extraction of thorium, which was on the one hand the main constituent of the incandescent mantles of his gas lights which were sold and used on a worldwide basis. During their production, different mixtures of the rare earths, amongst other things, accumulated copiously as a "waste product". The French chemist Marginac (who had previously also discovered gadolinium and was very well known) succeeded in extracting the old ytterbium from these mixtures in 1878, as already mentioned above.

In 1907, Auer von Welsbach published a comprehensive paper and determined thereby the atomic weights of ytterbium (aldebaranium) and lutetium (cassiopeium) as 172.90 and 174.23 on the basis O=16 according to the Bunsen method. In the same publication, he also published the corresponding spectra.[76]

In 1912, Auer von Welsbach made a further attempt to determine the atomic weight of the elements ytterbium (new) and lutetium, which he had extracted from the old ytterbium in 1905, apparently in order to improve the accuracy of his procedure and thus the result. The route that he took is to be looked at more closely here:

After conclusion of the fractional crystallization, which extended as far as the 320th series, he still had various ytterbium and lutetium preparations from 1903 in the form of solid substances (oxalates, oxides) and (not further fractionated) lyes. In a renewed spectroscopic examination, he noticed that some spectra of these preparations still showed slight traces of calcium (Ca), sodium (Na), zinc (Zn) manganese (Mn) and thorium (Th) as well as several traces of silicic acids (SiO_2). For the determination of the atomic weights, Auer von Welsbach concentrated on the Cp (lutetium) preparations which were still slightly impure with silicic acid amounting to 18.2 grams and which originated from the end fractions from the 147th – 319th series. The elimination of K and Na succeeded by the skillful addition of nitric acid and hydrogen sulfide. Finally, a few steps later, a Cp-nitrate solution was produced which was precipitated with ammonia. A part of the hydrate was dissolved in nitric acid, the other part was smelted. The oxide Cp_2O_3 (Lu_2O_3) was obtained. The K and Na traces had been eliminated in this Cp preparation.[77]

In order to remove the traces of silicic acid, the purification process had to be extended and continued with other substances. The Cp oxide obtained in the first step was dissolved again in nitric acid. The solution was concentrated and heated until the evolution of nitric oxide. The smelt was partially dissolved in water. In addition to the turbidity of the water, a flaky precipitate occurred in a small amount, which did not dissolve after the renewed addition of nitric acid or water, and no turbidity of the liquids could be observed. It could be proven that the SiO_2 traces (and also thorium traces) had been at least partly removed with the precipitate. Finally, Auer von Welsbach used oxalic acid to which nitric acid had been added twice in a row while heating the precipitate to incandescence, with precipitation of the respective mother liquor. By "vigorous" heating to incandescence of the last oxalate precipitate in a platinum crucible, he obtained Cp oxide as a white powder. "Contrary to expectations", however, the silicic acid had not entirely disappeared. At this time, Auer von Welsbach had a platinum crucible, which he had used for "more than 30 years", but the impurities in the platinum itself could not be completely excluded. By weighing the crucible before and after heating to incandescence, he could exclude such an effect. The accuracy of his weighing activities must have amounted to approx. $^{+}$- 0.001 grams.

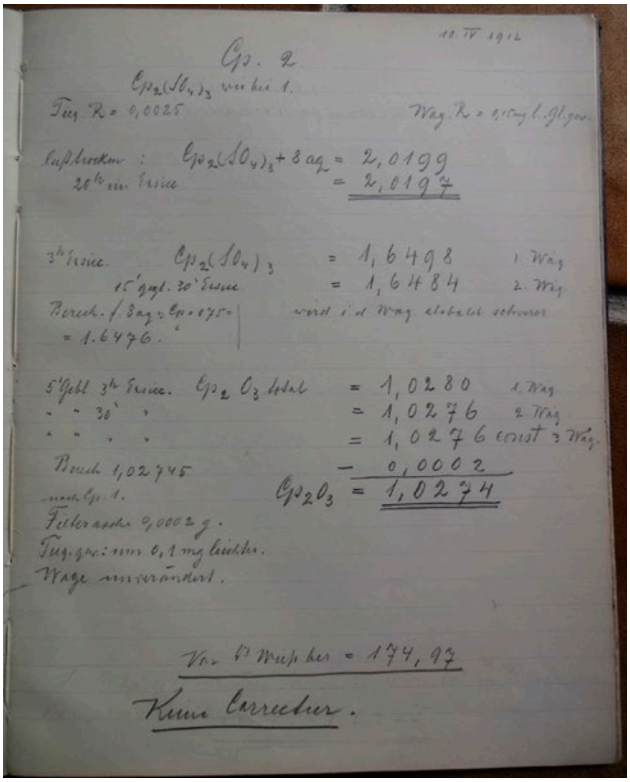
The Cp oxides were now dissolved in nitric acid. This clear solution was mixed with sulfuric acid in a slight overage and slowly concentrated. "Crystal clear" and "nice-looking" sulfate crystals were formed. These were then dissolved in a little water so that a completely clear solution was obtained. In the last step, oxalic acid "free of ash residues" was added to this solution. The Cp oxalate was precipitated, was washed and finally heated to incandescence. The result was Cp_2O_3 (Lu_2O_3) as an oxide which had been purified several times from the traces of other elements.

Auer von Welsbach had now produced lutetium (Cp) in different compound forms starting from a defined amount, namely as a defined amount of hydroxide, sulfate and as oxide. The last two compounds alone, whose exact amounts he determined gravimetrically, would have sufficed in order to determine the atomic weight of lutetium (Lu) by a simple calculation. In a similar manner, he continued experimentally with the original ytterbium (new) that he had produced in 1905. In 1912/1913 he repeated these experiments a total of three times with essentially the same results. The details of the atomic weight refer to the atomic weight for oxygen O= 16. On average, these experiments resulted in 173.00 for ytterbium and 175.00 for lutetium.[78]

The handwritten laboratory records used for the determination of the Lu atomic weight from the year 1912 are still mostly available and are archived in the Auer von Welsbach Museum. These are to be considered according to the sources given as an obvious preliminary result of the final results, which were published in June 1913 in the monthly edition of the Chemie Mitteilungen (Chemical Communications)[79]. It is apparent here, amongst other things, that Auer von Welsbach had gradually come closer to the final result through his corrections, using as an example the element lutetium, (cassiopeium = Cp), (see Fig. 9 and Fig. 10)

Compared to the current values used today for Yb= 173.045(10), Lu= 174.9668, this is to be considered an outstanding result considering the technology available to chemists at that time in 1910.[80]

One of the highlights of the exhibits in the Auer of Welsbach Museum is that there is still a sealed test tube with a lutetium preparation (Cp_2O_3) originally produced by Auer (see Fig. 11)



10. IV 1912

Cp. 2

$Cp_2(SO_4)_3$ wie bei 1.

Tieg. R = 0,0025 Wag. R = 0,15 mg [illegible]

Lufttrocken: $Cp_2(SO_4)_3 + 8 aq$ = 2,0199
20h im Exsicc. = 2,0197

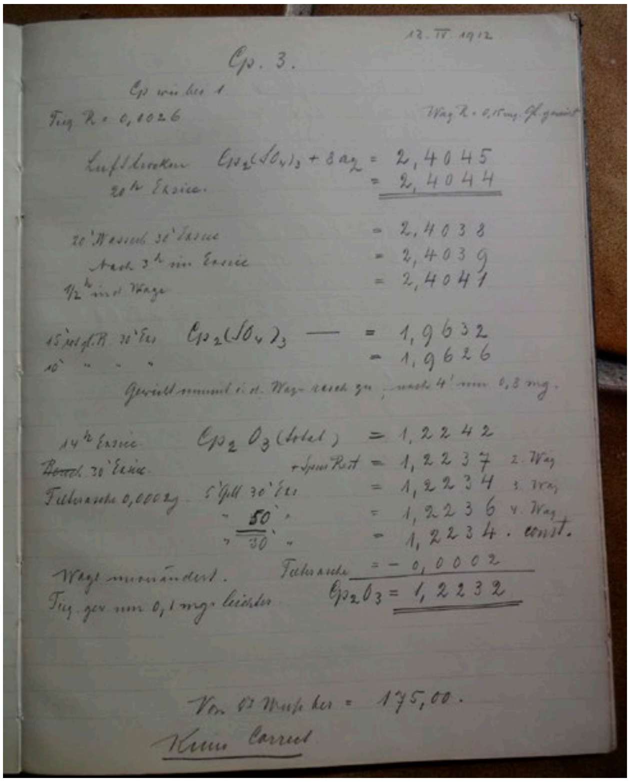
3h Exsicc. $Cp_2(SO_4)_3$ = 1,6498 1. Wag.
15' gegl. 30' Exsicc. = 1,6484 2. Wag.
Berech. f. 8 aq u. Cp = 175 = 1.6476. | wird i. d. Wag. [illegible] schwerer

5' Gebl. 3h Exsicc. Cp_2O_3 total = 1,0280 1. Wag.
" " 30' " = 1,0276 2. Wag.
" " " " = 1,0276 const 3. Wag.
Berech 1,02745 − 0,0002
nach Cp. 1. Cp_2O_3 = 1,0274
Filterasche 0,0002 g.
Tieg. gew. um 0,1 mg leichter.
Wage unverändert.

Von [illegible] = 174,97

Keine Correctur.

Figure 9. Lutetium (Cp), atomic weight determination, second to last step 1912.



12. IV. 1912

Cp. 3.

Cp wie bei 1.

Tieg. R = 0,1026 Wag. R = 0,15 mg [illegible]

Lufttrocken $Cp_2(SO_4)_3 + 8 aq$ = 2,4045
20h Exsicc. = 2,4044

20' [illegible] 30' Exsicc. = 2,4038
Nach 3h im Exsicc. = 2,4039
1/2h in d. Wage = 2,4041

15' [illegible] 30' Exs. $Cp_2(SO_4)_3$ — = 1,9632
10' " " " = 1,9626
Gewicht nimmt i. d. Wag. rasch zu; nach 4' um 0,8 mg.

14h Exsicc. Cp_2O_3 (total) = 1,2242
~~Berech.~~ 30' Exsicc. + [illegible] Rest = 1,2237 2. Wag
Filterasche 0,0002 g 5' Gl. 30' Exs. = 1,2234 3. Wag
" 50' " = 1,2236 4. Wag
" 30' " = 1,2234. const.
Wage unverändert. Filterasche = − 0,0002
Tieg. gew. um 0,1 mg leichter Cp_2O_3 = 1,2232

Von [illegible] = 175,00.

Keine Correct.

Figure 10. Lutetium (Cp), atomic weight determination 1912 (last step).

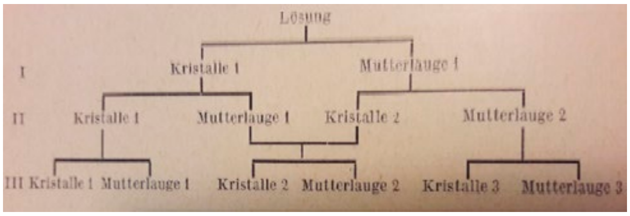
Figure 11. Test tube with a lutetium preparation (Cp_2O_3) originally produced by Carl Auer von Welsbach.

APPENDIX: FRACTIONAL CRYSTALLIZATION

The principal procedure used in the separation of substance mixtures by "fractional crystallization": A method to separate the rare earth elements and mixtures of radioactive substances.

Multicomponent mixtures, dissolved at an increased temperature until saturation, e.g. in distilled water, nitric acid or in other solvents, can be separated into individual components, i.e. for example, into oxides or salts of the individual elements of the mixtures of these substances, in which this heated solution is cooled down (e.g. by allowing it to stand). As the components of this mixture of substances as a rule possess differences in solubility, depending on the temperature, these element compounds crystallize at different points in time. If the crystallization process is interrupted at the right time and the alkaline solution (mother liquor) is removed, one obtains the first fraction (top fraction) of an element – e.g. as a salt – which has become more concentrated and is relatively free of the other components of the original mixture. This precipitate is then redissolved and the procedure is repeated. The respective mother liquors are evaporated again and then cooled down as in the first step. Through the skillful combination of crystallization, dissolution and evaporation, the most hardly soluble element becomes increasingly concentrated and as such separates from the original mixture of substances. The sequence of this procedure can be seen schematically in Fig. 12.

The greater the number of crystallization steps, the purer the presentation of the individual components will



← sparingly soluble easily soluble →

[Lösung = solution; Kristalle = crystals; Mutterlauge = mother liquor]

Figure 12. Schematic sequence used in fractional crystallization.[81]

become (as salts of the element). The least soluble elements crystallize at the beginning, and the most easily soluble components at the end.[82]

The rare earth metals almost always occur in nature as similar mixtures of such substances. Chemists then speak about a "socialization" of the elements, which however is only observed with the rare earth metals. Auer von Welsbach developed this separation method - which had originally already been used by Dimitri Iwanowitsch Mendelejew (1834 – 1907) - to perfection when investigating the rare earth metals and the elements of this series that he discovered. However, for this purpose many thousands of crystallization steps were necessary in each single case.

Auer von Welsbach's procedure for the separation of didymium into neodymium and praseodymium in 1905 using a double nitrate salt of ammonium (1885) was briefly described by Hevesy[83]. The separation of ytterbium in 1905 was performed by Auer von Welsbach using the double oxalate of ammonium by the same method. The different separation experiments to concentrate actinium during his research into radioactivity also took place using fractional crystallization.[84]

In principle, the method of fractional crystallization was used, e.g. by Madame Curie in the discovery (isolation) of radium and by Otto Hahn in the discovery of nuclear fission (the separation of radium from barium chloride and identification of the rare earth metals as nuclear fragments). These elaborate procedures for the separation of mixtures of substances have been extensively replaced today by chromatographic and ion exchange processes. The true complexity of the method used by Auer von Welsbach at that time (from around 1895 onwards) is to be seen in the light of more recent research, e.g. in the paper by Rosmanith[85].

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13. Gerd Löffler, *Carl Auer von Welsbach und sein Beitrag zur frühen Radioaktivitätsforschung und Quantentheorie*, ISBN 978-3-200-04400-5**, 2015**, p. 125.
14. ibid p. 127.
15. ibid p. 126.
16. Letter from Georg Hevesy to Carl Auer von Welsbach dated **10/19/1923**, Archives Auer-von-Welsbach

Research Institute, File: Correspondence; Location: Auer-von-Welsbach Museum, Althofen (Carinthia).

17. Yoshio, Nishina, On the L-absorption Spectra of the Elements from Sn(50) to W(74) and their Relation to the Atomic Constitution, *Philosophical Magazine and Journal*, **1925**, 49, 522 f.
18. In practice, hollow spheres and cylinders from fireproof materials with circular openings of a few millimeters were used. These objects were kept at a constant temperature. The (electromagnetic) radiation coming from the opening was then analyzed in relation to the temperature. One analytic method (German: Reststrahlenmethode "residual rays method") is shown in schematic form in Fig. 5.
19. The increasing industrialization of the economy was another driving force to gain a clear understanding of the processes of heat and light generation. For example, in 1860, there was no safe, i.e. continuingly glowing, illuminant yet. The gas mantle that was developed by Carl Auer von Welsbach was not patented until 1885 and was only introduced on the market in series production as a safe light source around 1891. Source: See online http://www.althofen.at/welsbach.htm (03/04/2019).
20. Wilfried, Hauser, *Strahlungsphysiker ebnen in Berlin den Weg zur Quantentheorie – Vienna, Paschen, Lummer, Rubens*, in: Wilhelm Treue; Gerhard Hildebrandt, *Berlinische Lebensbilder "Naturwissenschaftler"*, Berlin, **1987**, p. 92.
21. Armin Hermann, *Max Planck. Vorträge und Erinnerungen*, see online: http://www.zeit.de/1984/08/vortraege-und-erinnerungen (**24/03/2019**).
22. Max Planck finally decided, after some hesitation, to build on the work of Austrian physicist Ludwig Boltzmann in the area of thermodynamics for the development of his radiation formula. Boltzmann was seen to be a proponent of "atomism."
23. See online https://physicsmuseum.uq.edu.au/lummer-brodhun-photometer (**23.04.2014**)
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25. Heinrich Rubens; Friedrich Kurlbaum, Anwendung der Methode der Reststrahlen zur Prüfung des Strahlungsgesetzes, *Annalen der Physik*, **1901**, 4, 649-666.
26. Meschede, **2006**, p. 588.
27. Heinrich Rubens, Über das Emissionsverhalten des Auerbrenners", *Annalen der Physik* **1905**, 14, 734.
28. Horst, Stöcker, *Taschenbuch der Physik*, Frankfurt/Main, **2010,** pp. 441-447.
29. Carl Auer von Welsbach built his first hydroelectric power plant in 1898 for generating electricity for the production of osmium lamps and the production of rare earth elements in his factory in Althofen-Treibach. For his construction of power plants in Carinthia, see Roland Adunka, Carl Auer von Welsbach. Entdecker – Erfinder – Firmengründer, **2015**, 64-67.
30. Ferrimagnetism is the characteristic of crystals that have partial grids with opposing magnetization. They only compensate each other in part and are therefore only slightly ferromagnetic. Source: Horst Stöcker, *Taschenbuch der Physik*, **2010**, pp. 956 f.
31. $\mu = \kappa - 1$ applies, whereby μ indicates magnetic susceptibility and κ indicates magnetic permeability – which is the relationship of magnetic flux density B (in the material) to the outer magnetic field strength H. The magnetic susceptibility μ is identical or rather proportional to the rate of magnetization used by many researchers.
32. Fachredaktion für Naturwissenschaften und Technik des Bibliografischen Instituts (Ed.), *Meyers Physik-Lexikon*, **1973**, p. 525.
33. Dieter Wagner, Das Rätsel des Magnetismus**,** *Physik Journal***, 2005**, 4/3, 23 f.
34. The normal Zeeman Effect (division of a spectral line into 3 sections) has already been explained by means of the classical electrodynamics and early quantum theory, as the spin of electrons was not known at this time.
35. Both the physicists Friedrich Paschen (1865-197) and Ernst Back (1851-1959) discovered the Paschen-Back effect in 1921.
36. $M = \chi$ x H_0 : → $\chi = M/H_0$ magnetic susceptibility, M= magnetic moment, H_0 = outer magnetic field
37. Friedrich, Hund, Atomtheoretische Deutung des Magnetismus der seltenen Erden, *Zeitschrift für Physik* (**1925**), 33, 855-859.
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45. Werner Heisenberg, Über quantentheoretische Umdeutungen kinematischer und mechanischer Beziehungen, *Zeitschrift für Physik*, **1925**, 33, pp. 879-893 and Max Born; Pascal Jordan, Zur Quan-

tenmechanik, *Zeitschrift für Physik*, **1925**, 34, 858-888. Max Born; Werner Heisenberg; Pascal Jordan, Zur Quantenmechanik. II., *Zeitschrift für Physik*, **1926,** 35, pp. 557-615. In 1933 Heisenberg, along with Erwin Schrödinger and Paul Dirac, received the Nobel Prize for Physics for the formulation and presentation of the "new" quantum mechanics.

46. The physicists Stefan Meyer and Egon v. Schweidler in Vienna were experimentally perfectly equipped for this. In 1899/1900, at around the same time as the French H. Becquerel and German chemist F. Giesel, they proved through the deflection of magnetic and electric fields, that radium rays (β-rays) behaved as though they were negatively charged (electrons). Through an attempt at deflecting the polynomial rays it was determined that they were twofold positively charge helium atoms, which were identified as α- rays.
47. Letter from Stefan Meyer to Carl Auer von Welsbach dated **02/29/1924**, Archives Auer-von-Welsbach Research Institute, File: Correspondence; Location: Auer-von-Welsbach Museum, Althofen (Carinthia).
48. Cp is the abbreviation for the rare earth element cassiopeium, called lutetium (Lu) today. Hf is the abbreviation for the element hafnium, which will be dealt with later.
49. Letter from Carl Auer von Welsbach to Stefan Meyer dated **03/06/1924**, Archives Auer-von-Welsbach Research Institute, File: Correspondence; Location: Auer-von-Welsbach Museum, Althofen (Carinthia).
50. Stefan Meyer, Magnetization numbers of the rare earths, *Physikalische Zeitschrift*, **1925**, 26, p. 53.
51. The French physicist Pierre-Ernest Weiß (1865-1940) had studied metals and their compounds (e.g. iron, cobalt, nickel, magnetite) intensively even before the beginnings of Bohr's quantum theory. See: "Über die rationalen Verhältnisse der magnetischen Momente der Moleküle und das Magneton", in: Physikalische Zeitschrift 12 (1911), 935-952. They demonstrated a strong magnetic attraction without an outer field, thus were ferromagnetic. His investigations led to the conclusion that in such bodies, small microscopic dipoles must exist, which are also equally aligned in very small areas (max. 1mm diameter). These areas are called Weiß'sche Bereiche (magnetic domains). Through external influences, for example through a magnetic field, a multitude of these dipoles can be aligned in different areas. In doing so we get to magnets used in electronics, dynamos and other propulsion machinery. The correct explanation for this characteristic was provided not till modern quantum mechanics. Rare earth elements play an important role in producing magnets of this kind. Above the so-called ferromagnetic Curie-temperature, which is a material constant, the magnets slowly lose their characteristics and become paramagnetic. Source:
52. Horst Stöcker, **2010**, p.445, p. 661.
53. Stefan Meyer measured the anhydrous sulfates of rare earth elements. In this compound the elements were trivalent, which is the preferred valency. Source: see Holleman; Wiberg, *Lehrbuch der anorganischen Chemie*, **2007**, p. 1939. (Nomenclature by Stefan Meyer e.g. for the lanthanum cation: La). The sulfate anions provide no contribution to magnetization. The cations La and Cp are diamagnetic. According to Stefan Meyer the remaining cations are paramagnetic. For the element with the atomic number 61 (promethium) no rate of magnetism could be determined, because this element in its extreme rarity was impossible to determine. See also Carl Auer von Welsbach, Über einige Versuche zur Auffindung des Elements Nr. 61, *Chemiker-Zeitung*,**1926**,118, p. 990. Here magnetic susceptibility means the specification of magnetization (on the ordinate in Fig. 7), the value of the so-called Weiß magnetons. Stefan Meyer chose this measuring unit in order to be able to compare his results with those of Cabrera.
54. Blas Cabrera had also received rare earth compounds from Carl Auer von Welsbach via the institute for radium research in Vienna. This emerges from a letter from Stefan Meyer to Auer von Welsbach from 1924. Cabrera paid the institute 300 pesetas for this compound. Stefan Meyer thanked Auer von Welsbach. Source: Letter from Stefan Meyer to Auer von Welsbach dated **07/25/1924**. Archives Auer-von-Welsbach Research Institute, File: Correspondence; Location: Auer-von-Welsbach Museum, Althofen (Carinthia).
55. Stefan Meyer, Magnetisierungszahlen der seltenen Erden, *Physikalische Zeitschrift*, **1925**, 26, 51 f.
56. The head of the radium institute in Vienna, Stefan Meyer, who had been working mostly with preparations from Carl Auer von Welsbach during his research on magnetic behaviors of rare earth elements since 1899, pointed out that he had already in 1915 expressed the assumption that the magnetism of these elements could not be explained solely by the valence electrons (in the outer shell of the atom) but that electrons in the inner shells had to play a role. Source: Meyer, **1925**, 52.
57. Werner, Heisenberg, Zur Quantentheorie der Multiplettstruktur und der anormalen Zeemaneffekte, Zeitschrift für Physik**,** **1925**, 32, 841-860.
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59. Friedrich Hund, *Geschichte der Quantentheorie*, **1975**, p,117. These selection rules became referred to as Hund's rules. They are explained as follows: When adhering to the Pauli principal in an atom L equals the sum of all orbital angular momentum, S equals the sum of all electron spins and J=L+S, it can be concluded that:
    1. the basic state takes the maximum possible total spin S -à Smax, d. h., it possesses the maximum possible total symmetry
    2. the basic state also possesses, along with rule 1, the maximal possible orbital angular momentum, L -à Lmax
    3. The total angular momentum J takes on the lowest horizontal state of worth:
    J = IL – SI with less than half full shell
    J = IL + SI with more than half full shell
    Cf. Dieter Meschede, *Gerthsen Physik*, **2005**, p, 853. These rules can be deduced from quantum mechanics. A basic principle is that every atom takes the lowest possible energy state. Rule number three makes it also plausible, that in Fig. 7 two characteristic curbed lines occur.
60. Hund, **1925**, p. 857 f.
61. Ibid., p, 858.
62. Meyer, **1925**, p.478 f.
63. In this respect, it should be noted that in 1925 it was not yet usual to determine measuring errors in an experiment in either systematic and statistical errors and publish them accordingly. In the present case besides contamination, other systematic errors could have had occurred.
64. Friedrich Hund, Atomtheoretische Deutung des Magnetismus der Seltenen Erden (= Theoretical atomic significance of magnetism of the rare earths), *Zeitschrift für Physik*, **1925**, 33, Table 1, p. 857.
65. Roughly cited from Georg Hevesy, *Die seltenen Erden vom Standpunkte des Atombaues*", **1927**, p. 80 f.
66. Vleck assessed the presented explanation for the magnetic behavior of the rare earth elements by Friedrich Hund in 1925 (s. o.) in his Nobel Prize speech in 1977 as follows "In 1925 Hund (…) wrote a paper on the magnetic susceptibilities of rare earth compounds which was the crowning achievement of empiricism of the old quantum theory.". See: J.H. Vleck, Quantum Mechanics. The Key to understand Magnetism, *Sience*, **1978,** 201,4341, p.115.
67. Ludwig Haitinger, *Handbuch der Anorganischen Chemie*, **1893**, III, p. 53.
68. Ibid.
69. Auer von Welsbach, Carl, Über die Elemente der Yttergruppe, (erster Teil), *Proceedings of the Imperial Academy of Sciences*, *Sect. II b*, **1906,** 115, pp. 737-747.
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71. Commemorative publication *Adolf Lieben and Liebig´s Annalen der Chemi,***1906,** 351, pp. 464-465., also cited in: Carl Auer von Welsbach, Zur Zerlegung des Ytterbiums, *Chemie-Heft* ,**1909**, 9, p. 49.
72. Auer von Welsbach does not give a unit of measurement. Since his spectral analytical research was conducted in the visible area, only Å = 10^{-10} m is a possible unit of measurement.
73. Carl Auer von Welsbach, Über die Elemente der Yttergruppe, (1. Teil), *Proceedings of the Imperial Academy of Sciences, Sect. II b*, **1906,** 115, pp. 737-747.
74. Auer von Welsbach published the spectroscopical technology that was further developed by him in 1922: Carl Auer von Welsbach, Spektroskopische Methoden der analytischen Chemie, *Proceedings of the Imperial Academy of Sciences, Sect. II b*, **1922,** 131, pp. 387-408.
75. Carl Auer von Welsbach, Über die Elemente der Yttergruppe, (1. Teil), *Proceedings of the Imperial Academy of Sciences, Vol. CXV, Sect. II b*, **1906** 115, pp. 737-447. Carl Auer von Welsbach, Die Zerlegung des Ytterbiums in seine Elemente, *Proceedings of the Imperial Academy of Sciences, Vol. CXVI, Sect. II b*, **1907**, pp. 1425-1469. Carl Auer von Welsbach, Zur Zerlegung des Ytterbiums, *Proceedings of the Imperial Academy of Sciences, Sect. II b, Supplement*, **1909**, 118, pp. 307-312. Carl Auer Auer von Welsbach, *Zeitschrift für anorganische Chemie*, **1911**, 86, pp. 58-70.
76. See online: https://commons.wikimedia.org/wiki/File:Monazit_Behandlung_basischer_Aufschluss.svg (02/04/2019)
77. Carl Auer von Welsbach, Die Zerlegung des Ytterbiums in seine Elemente, *Proceedings of the Imperial Academy of Sciences, Sect. II b*, **1907**, 116, pp. 1425-1469.
78. Auer von Welsbach was always in close contact with experts F. Exner, J.M. Eder and E. Valenta in Vienna, making his preparations available to them for further spectral analytical research. See e.g. J.M. Eder; E. Valenta, *Wellenlängenmessungen im sichtbaren Bereich der Bogenspektren der von Auer von Welsbach entdeckten Elemente Aldebaranium und Cassiopeium, Zeitschrift der Anorganischen und Allgemeinen Chemie*, **1910**, 67, pp. 102-106.
79. *Chemical Monthly*, **1913**, 84, 1713-1728.

80. There are hints in literature that point to the results also having been published in July 1913 in the proceedings of the Imperial Academy of Sciences Sect. II b, **1913**, 22. This seems likely as Carl Auer von Welsbach generally published his publications in the Academy first. However, these proceedings cannot be found today in the library of the Austrian Academy in Vienna.
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83. See Online: http://www.chemieunterricht.de/dc2/lanthan/trennung.htm (11/11/2018)
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A Book Collector's View of the Periodic Table: Key Documents before Mendeleev's Contributions of 1869

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Abstract. The present article identifies and discusses some of the books and scientific articles that played important roles in the development of the periodic law, before Mendeleev published his Periodic System in 1869. For each book, information is given about the edition in which the discovery was made, and for each scientific article, information is given about the form in which it was issued, such as whether offprints were printed in addition to the journal appearance. Some observations of interest to book collectors are included, such as assessments of the availability of these documents on the rare book market. This paper may also be of use to those who wish to learn about (or to teach) the history of the periodic law from the original documents that first announced important advances toward its creation.

Keywords. Periodic table, Mendeleev, chemical elements, rare books, offprints, bibliography.

INTRODUCTION

One of the most important unifying principles in all of science is the periodic law of the chemical elements. The history of the conception and development of the system and its associated periodic table is both rich and fascinating, and the books, monographs, and journal publications that led to its creation and improvement have been the subject of much study and commentary.[1-5]

The purpose of the present article is to identify and discuss, from a book collector's perspective, some of publications that played important roles in the development of the periodic law. In the current paper, I will focus on those contributions that were made before Mendeleev published his breakthrough ideas beginning in 1869. Most of these documents appear only infrequently on the rare book market but can be acquired by the patient collector. This paper may also be of use to those who wish to learn about (or to teach) the history of the periodic law from the original documents that first announced important advances toward its creation.

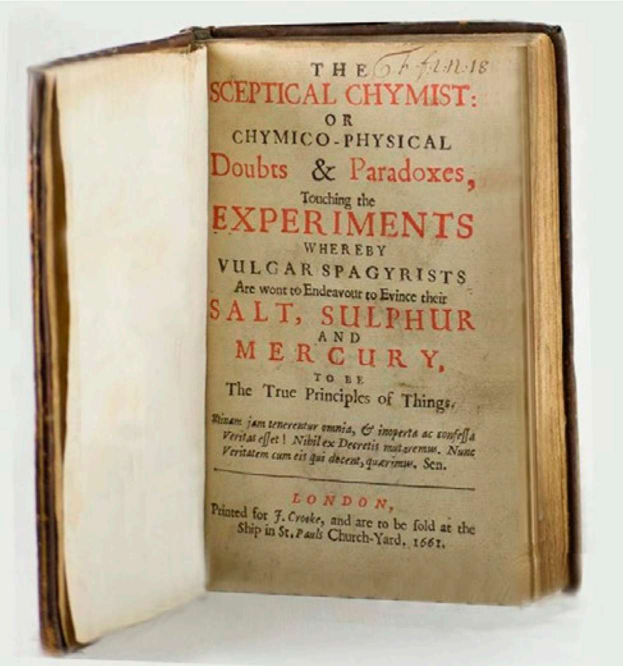
BOYLE'S DEFINITION OF AN ELEMENT (1661).

The book *The Sceptical Chymist: or Chymico-Physical Doubts and Paradoxes*[6] by the Anglo-Irish natural philosopher Robert Boyle (1627-1691) is an appropriate place to start because it contains early speculations about the basic particles of matter. In this book (Fig. 1), Boyle presented his theory that matter consists of a hierarchical arrangement of particles, and defined elements as "certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved."

Of the books mentioned in the current paper, the *Sceptical Chymist* is one of the rarest. In a census carried out in 1960, only 27 copies of the first (1661) edition could be located, and 5 others previously known to be in private collections could not be traced.[7] My own efforts to update the census suggests that perhaps 65 copies exist, of which perhaps six are privately held. These are very small numbers even for a seventeenth century book.

Some variants of the first edition of the *Sceptical Chymist* are known. The leaf bearing pages 243 and 244 is found in two states: about 20% of the known copies have the leaf in its original state (in which a part of a sentence is inadvertently printed twice) and most of the rest contain a replacement leaf that corrected the error. In addition, about 20% of the known copies lack the four-page list of errata that usually appears at the end of the text. Copies without the errata more likely to have the original leaf, and copies with the errata are more likely to have replacement leaf. These correlations suggest that the addition of both the replacement leaf and the errata occurred sometime after the book was printed, but before all the copies had been bound and sold.

The second English edition of the *Sceptical Chymist* (Oxford, 1680) is nearly twice as long as the first edition because it contains much new material, under the subtitle *Experiments and Notes about the Producibleness of Chymical Principles*. Several Latin editions of the *Sceptical Chymist* were also printed. All of these later editions are also scarce, although not as rare as the first English edition, which is today almost impossible to collect.


THE
SCEPTICAL CHYMIST:
OR
CHYMICO-PHYSICAL
Doubts & Paradoxes,
Touching the
EXPERIMENTS
WHEREBY
VULGAR SPAGYRISTS
Are wont to Endeavour to Evince their
SALT, SULPHUR
AND
MERCURY,
TO BE
The True Principles of Things.

Utinam jam tenerentur omnia, & inoperta ac confeſſa Veritas eſſet! Nihil ex Decretis mutaremus. Nunc Veritatem cum eis qui docent, quærimus. Sen.

LONDON,
Printed for *J. Crooke*, and are to be ſold at the
Ship in St. *Pauls* Church-Yard, 1661.

Figure 1. One of the two title pages in the first edition of Boyle's *Sceptical Chymist*, 1661. Only about 65 copies of this book are known, perhaps six of which are owned privately, the rest being in institutional libraries

LAVOISIER'S TABLE OF SIMPLE SUBSTANCES (1787 AND 1789)

In 1787, the French chemist Antoine Laurent Lavoisier (1743-1794), along with three compatriots, Louis-Bernard Guyton de Morveau (1737-1816), Claude Louis Berthollet (1748-1822), and Antoine François de Fourcroy (1755-1809), published an important book, *Méthode de Nomenclature Chimique*,[8] which grew out of a paper that had been written by Guyton de Morveau in 1782.[9] This book introduced a new system of chemical nomenclature, still used today, in which names are based on the chemical content; for example, the substance the alchemists called "pompholix" is referred to instead as zinc oxide.

In the context of the development of the periodic table, the *Méthode* is notable for being one of the first to give a list of chemical elements, which the authors defined as substances that cannot be further decomposed. In Table II, the book gives a list that contains fifty-one "simple substances". Of these, twenty-one were elements as we recognize them today (N, H, C, S, P, Au, Pt, Ag, Hg, Sn, Cu, Pb, Fe, Zn, Mn, Ni, Bi, Sb, As, Mo, W), seven were elements that they suspected were combined with oxygen (K, Na, Ba, Ca, Mg, Al, and Si), and three others were radicals that had not yet been isolated from their acids (Cl, B, and F). The remaining substances were the radicals of various organic acids, along with ether and alcohol.

Interestingly, two states of the first edition of the *Méthode* have been identified: in one, pages 257-272 are misnumbered 241-256; in the other, only half of these pages are misnumbered. These states were once considered to be different issues of the first edition, meaning that they were printed and sold by the publisher at different times.[10] It is more likely, however, that all of the first edition copies stem from the same print run, and that some of the page numbers were corrected partway through the printing but before the books were bound. Today, the two states of the *Méthode* are of equal value. The second edition, which was a page-for-page reprinting dated the same year, can be recognized because it bears a different figure on the title page (a vase of flowers instead of a cherub supervising a distillation) and it lacks the printer's colophon on p. 314.

Two years after the appearance of the *Méthode*, Lavoisier published his landmark textbook *Traité Élémentaire de Chimie, présenté dans un ordre nouveau et d'après les découvertes modernes…* [*Elementary Treatise on Chemistry, Presented According to a New Order and After the Modern Discoveries…*].[11] In this book, Lavoisier overthrew the phlogiston theory, emphasized the concept of the conservation of mass, and proved that the increase in the weight of calcined metals was due to something taken from the air, which had first been given the name "oxygen" in the *Méthode*. The *Traité* also contains a "Tableau des substances simples," which looks much more like a modern list of chemical elements: it repeats the list of simple substances given in the *Méthode*, but omits the organic radicals, ether, and alcohol. Lavoisier's list also includes light and heat among these substances; interestingly, he omitted the "fixed alkalies" potash and soda from this list because he believed them to be compounds of unknown composition.

The first edition of the *Traité Élémentaire de Chimie* is a relatively common book, and copies are regularly available for purchase. Most copies of the first edition consist of 653 pages, but before the publication of the full text of the first edition, Lavoisier had a small number of copies of the book bound in one volume of only 558 pages.[10] This version lacks the "Tables à l'Usage des Chimistes," the "Table des Matières," and the approbation of the Académie des Sciences (dated 4 February 1789), which had not yet been printed. Although the 558-page version has been referred to as a first edition, and the regular 653 page version as a second edition,[12] they are more properly described as the first and second issues of the first edition.[13]

The first issue is most easily identified by the absence of the words "Tome Premier" on the half-title and title page; ten copies of the first issue are currently known. Four of these are bound in calf, three of which are in institutional libraries: the National Library of France (BNF, rebound), the Mazarine Library in Paris, and Cornell University (Lavoisier's personal copy). The fourth known copy in calf was sold at auction in Paris in 2010.

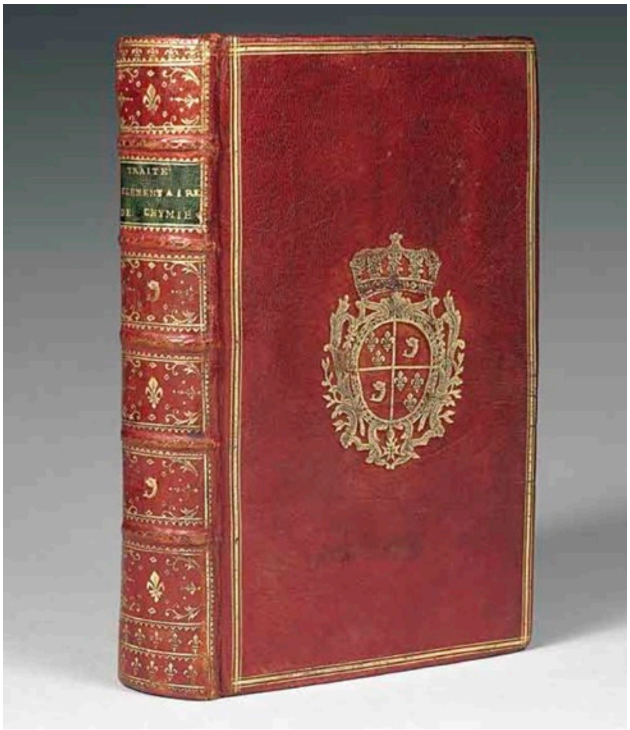


Figure 2. One of ten known 558-page first issues of Lavoisier's *Traité Élémentaire de Chimie*, 1789, in a presentation binding for the dauphin Louis-Joseph-François-Xavier de France, the eldest son of Louis XVI and Marie Antoinette, who died in June 1789 at the age of eight.

The six other known copies were given to the Royal Family and were sumptuously bound in red morocco bearing the arms of the recipient in the center of each of the boards (Fig. 2). Five of these are in institutional libraries: that of Louis XVI at the Library of Versailles, that of Marie Antoinette at the BNF, that of Louis Stanislas Xavier de Bourbon, Count of Provence (later Louis XVIII) at the Sainte Geneviève Library, that of Charles Philippe of France, Count of Artois (later Charles X) at the Library of the Arsenal, and that of Marie-Thérèse de Savoie, Countess of Artois at the Institute of France. One other copy bound in red morocco was given to the eldest son of Louis XVI and Marie Antoinette, the dauphin Louis-Joseph-François-Xavier de France, who died in June 1789 at the age of eight; this copy sold at auction in Paris in 2005.

Several later editions of the *Traité Élémentaire* were published during Lavoisier's lifetime, and the book also appeared in English, Spanish, German, Italian, and Dutch translations

DALTON'S ATOMIC WEIGHTS (1805 AND 1808).

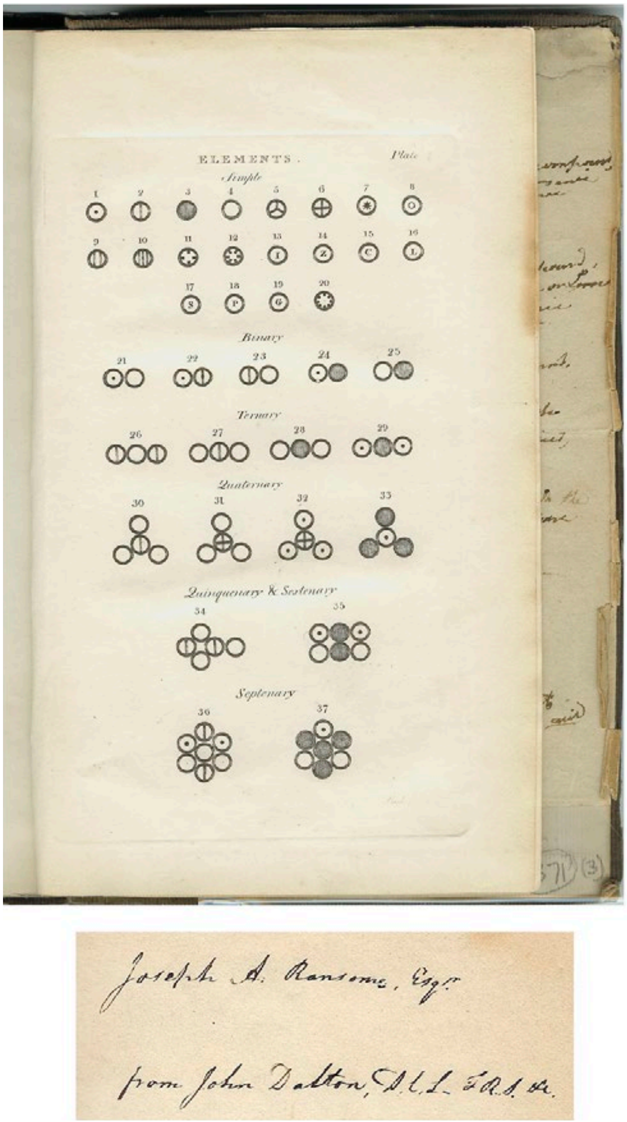
The English chemist John Dalton (1766-1844) is well known for his atomic theory of matter, in which he proposed that all atoms of a given element are identical in mass and properties. Dalton's atomic theory is important for several reasons: one is that it made it possible for the first time to devise chemical formulas for pure substances, and another is that it provided the first way to list the elements in an order that (eventually) would be used to uncover periodic relationships.

Dalton first proposed the idea that atoms of an element had a characteristic weight in a journal article he published in 1805 entitled "The Absorption of Gases by Water and Other Liquids."[14] Dalton was led to this hypothesis during his research that showed that different gases were differently soluble in water: gases with low densities and only one kind of atom (such as hydrogen) were less soluble than gases with larger densities and more than one kind of atom (such as carbon dioxide). He proposed that the amount of gas that dissolves in water at a given gas pressure "depends upon the weight and number of the ultimate particles of the several gases, those whose particles are lightest and single being least absorbable and the others more, according as they increase in weight and complexity."

Without any further discussion, Dalton appended a table to his article, in which he listed his measurements of "the relative weights of the ultimate particles of gaseous and other bodies." His list is (mostly) in order of increasing weight, beginning with hydrogen (which he assigned a relative weight of 1) and continuing with 20 other substances, the one with the largest relative weight being sulfuric acid. Some of Dalton's numbers are molecular weights and some are atomic weights; among the latter are proposed values for H, N, C, O, P, and S, although none of the values matches modern atomic weights because Dalton made mostly incorrect assumptions about combining ratios.

Although most early scientific discoveries were first announced in books, from the 18th century onward it became increasingly common for new ideas to be presented as papers in scientific journals. Authors began requesting separate copies of their papers for them to distribute to scientific colleagues. Such authors' separates are known as "reprints" among practicing scientists but are called "offprints" in the book trade.[15] As far as I know, however, no offprints of Dalton's 1805 article in the *Manchester Memoirs* exist; this document can be collected only as the journal issue or bound volume.

Dalton gave more information about his atomic ideas in his magnum opus, *New System of Chemical Philosophy*, published in three volumes between 1808 and 1827.[16] The first of the three volumes was devoted almost entirely to a discussion of heat and the forces between chemical substances. Only in the last four pages of the first volume did Dalton turn to his atomic theory; he wrote, "Now it is one great object of this work, to shew the importance and advantage of ascertaining *the relative weights of the ultimate particles, both of simple and compound bodies*…" (italics in original). In one of the figures that appears after the end of the text (Fig. 3),



Joseph A. Ransome, Esqr

from John Dalton, D.C.L. F.R.S. &c.

Figure 3. Dalton's table of elements and compounds from the first volume of his *New System of Chemical Philosophy* (top). This copy also contains experimental notes in Dalton's handwriting (partially visible at right) as well as Dalton's handwritten inscription presenting this copy to his personal physician, Joseph A. Ransome (bottom).

Dalton gave for the first time a table of the then-known elements arranged in order of increasing atomic weight; remarkably, the atomic weights themselves appear only in the caption to this figure!

Complete sets of all three volumes of Dalton's *New System* are hard to find on the collector's market, in part because few people who bought the first two volumes were persistent enough (and still alive) to purchase the third volume, which appeared nearly 20 years later.

AMPÈRE'S ATTEMPT TO CLASSIFY ELEMENTS (1816)

One of the earliest attempts to classify elements according to their chemical properties was devised by the French physicist André-Marie Ampère (1775-1836). In 1816, Ampère published a journal article, "Essai d'une classification naturelle pour les corps simples [Essay on a Natural Classification of the Elements],"[17] in which he classified the elements according to their relative affinity for oxygen and the nature of the compounds they form with it. Ampère's system of classifying elements according to their chemical reactivity resembles the approach of Étienne François Geoffroy (1672-1731), who published the first table of relative chemical affinities in 1718.[18] Like Mendeleev's periodic table, Ampère's system was intended to be an instrument of chemical research, and in fact it was still being used in the 1860s.[19]

Ampère commissioned offprints of his 1816 journal article, which are identifiable by the repagination of the two parts as pages 1-44 and 1-35. These offprints are quite scarce, however, with perhaps five or so copies still extant. Far more common is the 1816 journal volume of the *Annales de chimie et de physique* in which Ampère's paper appears.

DOBEREINER'S TRIADS (1817 AND 1829)

In 1817, the German chemist Johann Wolfgang Döbereiner (1780-1849) took one of the first steps towards the creation of the periodic table. In a letter sent in 1817 to *Annalen der Physik*, Dobereiner's colleague Ferdinand Wurzer (1765–1844) briefly reported Döbereiner's observation that the equivalent weight of strontia was almost exactly the arithmetic mean of those for lime and baria.[20] By 1829, Döbereiner had extended his initial observation by finding similar trends in certain properties of selected groups of elements.[21] For example, lithium, sodium, and potassium were well known to have very similar chemical properties, and Döbereiner pointed out the fact that the average of the equivalent weights of lithium and potassium was close to that of sodium.

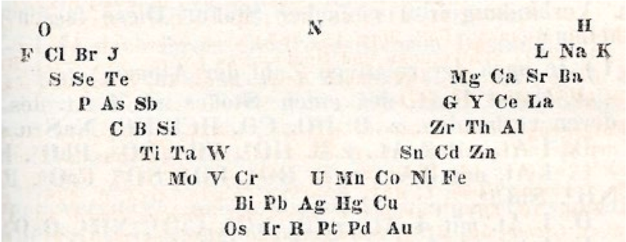


Figure 4. Gmelin's "Körpernetze" from his *Handbuch der theoretischen Chemie* (1843).

Döbereiner found other triplets of chemically similar elements whose equivalent weights obeyed the same rule: one was calcium, strontium, and barium, another was sulfur, selenium, and tellurium, and a third was chlorine, bromine, and iodine. Moreover, for some of these triads the gas or solid densities of the elements and "the intensity of chemical affinity" followed a similar pattern. These sets of elements became known as Döbereiner's Triads.

Offprints of Döbereiner's 1829 paper seem not to exist (there is no evidence that any were printed) but one can find copies of the paper in the form of its appearance in the journal *Annalen der Physik und Chemie.*

GMELIN'S NETWORK OF ELEMENTS (1843)

In 1819, the German chemist Leopold Gmelin (1788-1853) published the first edition of his *Handbuch der theoretischen Chemie* [*Handbook of theoretical chemistry*]. The second and third editions had similar titles and arrangements, but the fourth edition was intended to cover all types of chemistry, and Gmelin chose a new title, *Handbuch der Chemie*.[22] It is in this fourth edition that Gmelin's remarkable forerunner to the periodic table first appears: his "Körpernetze" or network of elements.

In volume 1 of his *Handbuch*, Gmelin presents a system, based on Döbereiner's triads, which established relationships between 55 chemical elements by arranging triads (or sometimes groups of four, five, or six elements) into an overall V-shape (Fig. 4). Gmelin states that, within the V, the triads are stacked vertically by electronegativity, with the most electronegative triad (F, Cl, Br, I) occupies the upper left of the V, the most electropositive (Li, Na, K) the upper right, and those with intermediate electronegativities (mostly what we now call the transition elements) are placed at the bottom. Within each triad, the elements are ordered from left to right by increasing atomic weight. Oxygen, nitrogen, and hydrogen are not placed into any of the triads, but instead are given privileged positions above the V.

Gmelin's Körpernetze arranged most of the then-known main group elements in the same fashion (albeit rotated and slanted) as seen in a modern periodic table, despite the handicap of using "pre-Cannizzaro" equivalent weights. Although some of the elements are not arranged "correctly," Gmelin's Körpernetze is still a remarkable achievement.[3]

Original multivolume sets of the fourth edition of Gmelin's *Handbuch* are fairly readily available for purchase. The eight volumes were issued in nine parts (volume 7 being divided into two parts). Volume 1 is dated 1843 and the following volumes were issued in subsequent years; volume 8 appeared in 1866. Two supplementary volumes were issued in 1868.

NUMERICAL REGULARITIES IN THE ATOMIC WEIGHTS COMMON TO DIFFERENT GROUPS OF ELEMENTS (1850-1860)

In the 20 years after Gmelin published his Körpernetze, several chemists tried to find mathematical regularities among the atomic weights of the elements. Some of these, such as Josiah Parsons Cooke (1827-1894), discussed only regularities that occur within individual groups.[23] The first to propose that there might be regularities that pertain to more than one group of related elements was the German chemist Max von Pettenkofer (1818-1901), in his 1850 article "Ueber die regelmässigen Abstände der Aequivalentzahlen der sogenannten einfachen Radicale [On the regular spacings of the equivalent numbers of the so-called simple radicals]."[24]

After quoting the passages in Gmelin's *Handbuch* that discuss Döbereiner's triads, Pettenkofer made the observation that the differences in equivalent weights in the alkali metal, alkaline earth, and nitrogen groups (and a few other pairs of elements) are either 8 or a multiple of 8. He then commented, "The recurrence of differences between the cited equivalent numbers of such bodies that belong to a natural group, and which are nearly divisible by 8, is too frequent to be thought to be a mere coincidence in the size of the divisor." Pettenkofer went on to suggest that there the regularities in the equivalent weights of the elements might be analogous to those seen for the organic groups methyl, ethyl, butyryl (i.e., butyl), and amyl, for which the differences in equivalent weights were 14, 28, and 14.

In 1853, in an article entitled "On the Relations between the Atomic Weights of Analogous Elements,"[25] the English chemist John H. Gladstone (1827-1902) tried to fit the equivalent weights of several related groups of elements, as given in Gmelin's 1843 network, to formulas of the kind $a + nx$, where n is an integer. Gladstone noted (as Pettenkofer had, but without citing his paper) that similar formulas had recently been found to apply to series of organic compounds such as the methyl-ethyl-amyl series. He went on to comment that there was a regularity that persisted across several groups of elements: the increment x in his formula was 24 for both the Ca-Sr-Ba and S-Se-Te series, and also for the Zn-Cd pair. Gladstone speculated (again, like Pettenkofer) that these and similar regularities were unlikely to be due to chance, and suggested that they might reflect some regular aspect of the inner constitution of the elemental bodies.

In 1858, in his three-part paper "Mémoire sur les équivalents des corps simples [Memoire on the equivalents of simple bodies],"[26] the French chemist Jean Baptiste André Dumas (1800-1884) carried out an analysis of the equivalent weights of the elements in terms of algebraic formulas similar to those introduced by Gladstone (although Dumas cited Cooke's later paper[23] of 1854 as the source of the idea). In particular, Dumas fitted the weights to formulas of the type $a + nd + md' + d''$. For some groups, however, fewer than four terms sufficed: the magnesium (i.e., alkaline earth) and oxygen groups, for example, required only the first two terms.

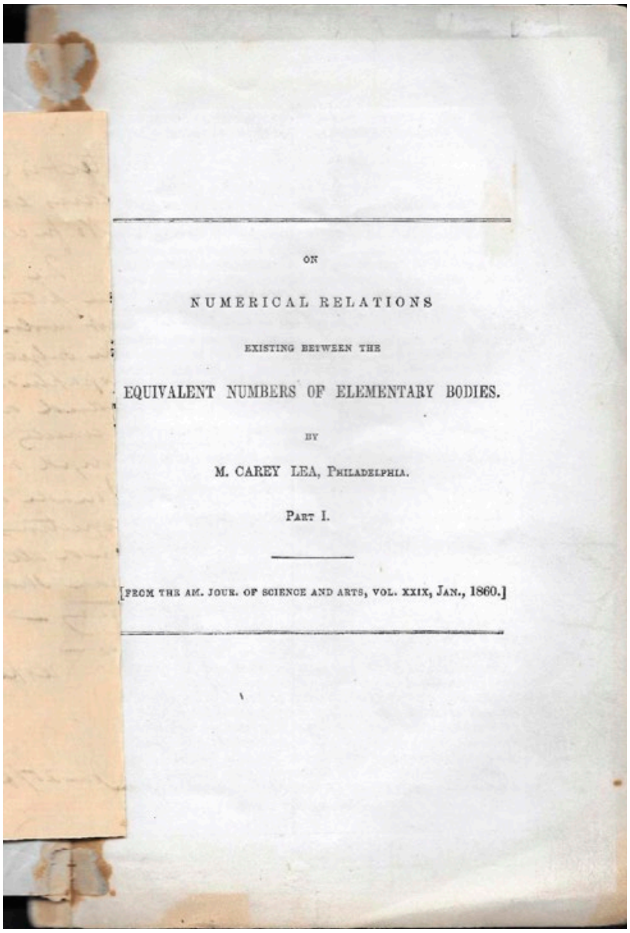
Dumas noted that the elements in the magnesium and oxygen groups could be paired up in such a way (oxygen with magnesium, sulfur with calcium, etc.) that the difference in equivalent weight within each pair was exactly 4; here, Dumas's weights for all these elements are half the modern values. He went on to point out that a similar relationship could be constructed for the halogens and pnictogens,[27] except here the difference in equivalent weight between pairs was 5. Dumas illustrated these relationships in a way that, in hindsight, clearly expresses the intergroup relationships of elements in the same period. For example, for the halogen and pnictogen elements, he wrote the atomic weights one below the other in two parallel rows:

Azote 14	Phosphore 31	Arsenic 75	Antimoine 122
Fluor 19	Chlor 35.5	Brome 80	Iode 127

In 1859, the German chemist Adolph Strecker (1822-1871) published a small book entitled *Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente* [*Theories and Experiments on the Determina-*

tion of Atomic Weights of the Elements].[28] Strecker's discussion of the numerical relationships among atomic weights occupies the last 10 pages of his book. Much of this section consists of a critical analysis of Dumas's 1857 paper on this topic. But on page 145 Strecker wrote, "If one doubles the atomic weight of the elements in the [carbon group], then the differences of each pair of atomic weights are all 22*n* except between carbon and silicon, where it is 16, i.e., approximately the same number that also is seen for nitrogen, fluorine, lithium and oxygen (if one doubles its atomic weight)." Strecker's statement is the first in the chemical literature that suggests the possibility of modifying the then-current atomic weights so as to create more regular numerical interrelationships with elements from other groups. This idea was to lie fallow until Mendeleev resurrected it with great effect, most notably in 1870, when he multiplied cerium's atomic weight of 92 by 1.5 so as place it in its proper location between barium and tantalum.

Mendeleev, who had brought Strecker's book with him when he returned from his study abroad in 1859-1861, credits the book with stimulating his interest in atomic weight relationships, an interest that led to his creation of his Periodic System. Years later, Mendeleev wrote, "A. Strecker, in his work *Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente* (Braunschweig, 1859), after summarising the data relating to the subject, and pointing out the remarkable series of equivalents Cr = 26.2, Mn = 27.6, Fe = 28, Ni = 29, Co = 30, Cu = 31.7, Zn = 32.5 remarks that: 'It is hardly probable that all the above-mentioned relations between the atomic weights (or equivalents) of chemically analogous elements are merely accidental. We must, however, leave to the future the discovery of the *law* of the relations which appears in these figures.'"[29] Mendeleev's great achievement was to do exactly that.



ON

NUMERICAL RELATIONS

EXISTING BETWEEN THE

EQUIVALENT NUMBERS OF ELEMENTARY BODIES.

BY

M. CAREY LEA, Philadelphia.

Part I.

[FROM THE AM. JOUR. OF SCIENCE AND ARTS, VOL. XXIX, Jan., 1860.]

Figure 5. One of two known copies of the offprint of Carey Lea's 1860 paper "On Numerical Relations Existing between the Equivalent Numbers of Elementary Bodies," This particular copy was sent by Lea to the American chemist Franklin Bache (1792-1864), great-grandson of Benjamin Franklin.

Another notable contribution in this area was made by the American chemist Mathew Carey Lea (1823-1897). In his 1860 paper "On Numerical Relations Existing between the Equivalent Numbers of Elementary Bodies,"[30] (Fig. 5), Lea makes several remarkable observations: (1) the equivalent weights of elements with similar chemical properties often differ by 44 or 45; Lea, however, fancifully finds additional pairs of elements related in this way by extending the algebra to negative equivalent weights, (2) the phenomenon of isomorphism is used to correct the equivalent weights of some elements, such as doubling copper's atomic weight to 63.4 (the modern value), thus foreshadowing Mendeleev, (3) the numerical regularities of equivalent weights are used to make some of the first predictions of the existence of undiscovered elements; Lea predicts that an element of equivalent weight 164 should be intermediate between antimony and bismuth in the nitrogen group (although incorrect, Mendeleev later made the same prediction), (5) the stoichiometries of recently discovered organometallic compounds, especially those of mercury and phosphorus, are employed to verify valence assignments and atomic weights, much as Edward Frankland (1825-1899) had done a few years earlier, and (6) correlations are sought between the equivalent weights and the atomic volumes of elements in the same group, thus foreshadowing Lothar Meyer's (and Mendeleev's) work ten years later.

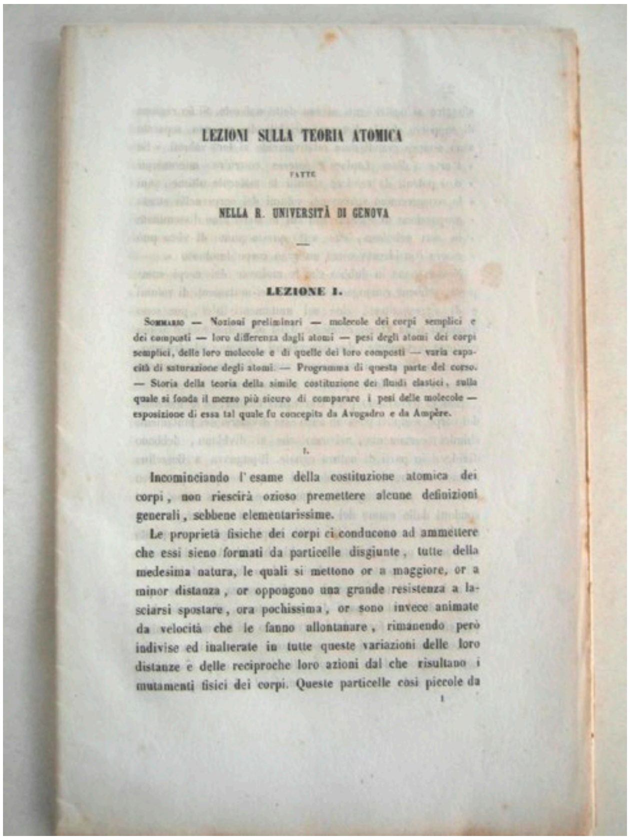
The four papers by Pettenkofer, Gladstone, Dumas, and Lea are available to the collector as the journal article, with Pettenkofer's being the hardest to find. Offprints are known only for the Dumas and Lea papers, which can be identified by the renumbering of the pages beginning with page 1, and by the addition of a separate title page. Both are scarce: slightly more than a dozen copies of the offprint of Dumas's paper are documented, and only two copies of the Lea offprint can be traced. Copies of Strecker's book are also scarce, and many years often separate the appearance of copies for sale.

CANNIZZARO'S PROPOSAL OF A SINGLE SET OF ATOMIC WEIGHTS (1858)

Before about 1860, all those who tried to find more universal relationships among the atomic weights of the elements (as opposed to relationships within individual triads) were handicapped by using equivalent weights that were sometimes true atomic weights and sometimes not; often, the equivalent weights in use in the 1850s and before differed from true atomic weights by a factor of two (and sometimes by other numbers such as 3 or 4 or 3/2). With such sets of equivalent weights, the construction of a periodic system that includes all (or even most) of the elements is essentially impossible.

In 1858, the Italian chemist Stanislao Cannizzaro (1826-1910) wrote two articles that played a decisive role in the formulation of modern atomic-molecular theory and the development of the periodic table. These two papers, which explained how he taught the atomic theory to his students at the University of Genoa, covered both the fundamental concepts of the theory and how it could be used to determine which of the several existing (and incompatible) systems of atomic weights was physically most correct. Cannizzaro's ideas were not new, but instead he emphasized the value of combining the ideas of Amedeo Avogadro (1776-1856) and André-Marie Ampère that equal volumes of gases contain equal numbers of particles, of Pierre Louis Dulong (1785-1838) and Alexis Thérèse Petit (1791-1820) on the constancy of the product of specific heat and equivalent weight (although Cannizzaro does not mention their names), and the definitions of Charles Gerhardt (1816-1856) and Marc Antoine Auguste Gaudin (1804-1880) for the terms "atom" and "molecule."

One of these papers, "Sunto di un Corso di Filosofia Chimica [Sketch of a Course on Chemical Philosophy],"[31] is well known to chemical historians: it was written in March 1858 and appeared in the May 1858 issue of the journal *Il Nuovo Cimento*. The other paper, "Lezioni sulla teoria atomica fatte nella R. Università di Genova [Lessons on Atomic Theory Given in the Royal University of Genoa],"[32] (Fig. 6), is almost unknown, but it is in fact the earlier of the two: it was published in the combined 15 March and 30 March 1858 issue of a Genovese periodical, *La Liguria Medica*. As the earlier paper, it therefore is the form in which Cannizzaro first introduced his ideas to the larger scientific community.



LEZIONI SULLA TEORIA ATOMICA

FATTE

NELLA R. UNIVERSITÀ DI GENOVA

LEZIONE I.

Sommario — Nozioni preliminari — molecole dei corpi semplici e dei composti — loro differenza dagli atomi — pesi degli atomi dei corpi semplici, delle loro molecole e di quelle dei loro composti — varia capacità di saturazione degli atomi. — Programma di questa parte del corso. — Storia della teoria della simile costituzione dei fluidi elastici, sulla quale si fonda il mezzo più sicuro di comparare i pesi delle molecole — esposizione di essa tal quale fu concepita da Avogadro e da Ampère.

I.

Incominciando l'esame della costituzione atomica dei corpi, non riescirà ozioso premettere alcune definizioni generali, sebbene elementarissime.

Le proprietà fisiche dei corpi ci conducono ad ammettere che essi sieno formati da particelle disgiunte, tutte della medesima natura, le quali si mettono or a maggiore, or a minor distanza, or oppongono una grande resistenza a lasciarsi spostare, ora pochissima, or sono invece animate da velocità che le fanno allontanare, rimanendo però indivise ed inalterate in tutte queste variazioni delle loro distanze e delle reciproche loro azioni dal che risultano i mutamenti fisici dei corpi. Queste particelle così piccole da

1

Figure 6. One of five or six known copies of the offprint of Cannizzaro's 1858 paper "Lezioni sulla teoria atomica.

Cannizzaro's description of the atomic theory in his *Lezioni* article could be used essentially unchanged in modern textbooks: "Examining the facts, we discover that there is limit to the division of the molecules of every simple body; … half a hydrogen molecule is the smallest quantity of this body that ever enters whole in the molecules of its compounds. We give to this smallest quantity the name of atom...." In addition to making the distinction between atoms and molecules fully clear, Cannizzaro called attention in this paper to Avogadro's and Ampère's hypothesis and showed how one could use it to determine relative molecular (and atomic) weights from vapor densities.

Cannizzaro's later *Sunto* paper became far better known because copies of it were distributed at the 1860 Karlsruhe Congress, which was attended by many leaders and future leaders in the chemical profession. Among those present were Dmitri Mendeleev and Lothar Meyer, both of whom were impressed by Cannizzaro's arguments and became converts to his views; both later cited Cannizzaro's work as a key enabler of their independent development of the periodic table in 1869. Mendeleev wrote, "The decisive moment in the development of my theory of the periodic law was in 1860, at the conference of chemists in Karlsruhe, in which I took part, and at which I heard the ideas of the Italian chemist S. Cannizzaro. I regard him as my immediate predecessor, because it was the atomic weights which he found, which gave me the necessary reference material for my work"[33] and Lothar Meyer commented, "I read [Cannizzaro's paper] again and again and was amazed at the clarity which that short treatise shed on the most important points of contention. Scales fell from my eyes, doubts vanished, and the feeling of the most serene certainty took their place."[34]

Offprints of Cannizzaro's *Lezioni* paper in *La Liguria Medica* exist but only about five or six are extant; these offprints are distinguishable from the periodical appearance by the repagination and renumbered signatures, by the absence of Cannizzaro's name in the reset title on the first page, and by the statement on the last page that the text was extracted from issues 5 and 6 of *La Liguria Medica*. The journal appearance is almost as scarce.

Cannizzaro's *Sunto* paper appeared in several different forms in the 19th century, including (i) the journal appearance in *Il Nuovo Cimento*; (ii) an offprint from *Il Nuovo Cimento*, which was distributed to the attendees at the Karlsruhe conference in 1860. This 62 page pamphlet was printed in Pisa and also contained the text of Cannizzaro's note on the condensation of vapor, which had appeared in the same issue of *Il Nuovo Cimento*; (iii) an 1880 separate edition, in which the *Sunto* paper was reprinted along with his "Nota sulle condensazioni di vapore," and with his 1858 *Lezione* paper from *La Liguria Medica*. This 80 page pamphlet was printed in Rome, possibly in commemoration of the 20th anniversary of the presentation of Cannizzaro's ideas at the Karlsruhe conference; (iv) the 1896 book *Scritti intorno alla teoria molecolare ed atomica*, which reprints the *Sunto*, the *Nota*, and the *Lezione* papers, along with several other papers by Cannizzaro on related topics. This 387 page text was printed in Palermo to commemorate Cannizzaro's 70th birthday. Two versions of this book are known, one with a frontispiece portrait of Cannizzaro, and one without. The first three of these forms of Cannizzaro's paper are rare: the journal appearance can be found in libraries but is almost unknown in the book market, and fewer than 10 copies of the offprint and the 1880 separate are extant. Only the 1896 book appears regularly for sale.

BÉGUYER DE CHANCOURTOIS'S TELLURIC SCREW (1862-1863)

The *Vis Tellurique*, or Telluric Screw, formulated in 1862 by the French geologist Alexandre-Émile Béguyer de Chancourtois (1820-1886), was an important precursor to the periodic table. In it, Béguyer de Chancourtois positioned the known chemical elements in order of increasing atomic weight on a slanted line wrapped around a cylinder, with 16 mass units per cylinder turn. When he did so, closely related elements lined up vertically. This regularity led him to state that "the properties of the elements are the properties of numbers." He was the first to recognize that the properties of the elements, considered as an entire group and not just within individual triads, are periodic functions of their atomic weights.

Béguyer de Chancourtois's ideas were originally published in several parts[35] in the *Comptes Rendus* in 1862 and 1863 but he was frustrated – and the impact of his ideas was blunted – because the journal refused to include a figure showing his helix. As a result, Béguyer de Chancourtois commissioned a combined offprint of his articles under the title *Vis Tellurique. Classement naturel des corps simples ou radicaux obtenu au moyen d'un système de classification hélicoïdal et numérique.* [*The Telluric Screw. Natural Grouping of Simple Bodies or Radicals by means of a Helical and Numeric System of Classification*].[36] The combined offprint was distributed with a privately-commissioned printing of the diagram of his helix; it is perhaps not too surprising that the journal did not print the diagram – printed in red, green, and black – because it is 1.45 meters long (Fig. 7).

The offprint of *Vis Tellurique* evidently was issued in at least two editions. The first edition, dating from 1862, was issued in paper wrappers and there is no mention of plates on the title page. A later (second) edition, probably dating from 1863, was issued in printed boards; the subtitle on the title page calls for two plates, the first being described as "Tableau chromolithographié des caractères des corps [chromolithographed table of the characters of bodies]" and the second as "une seconde planche muette, du développement du cylindre disposée pour l'étude et l'extension du système [a second wordless illustration of the development of the cylinder arranged for the study and extension of the system]." The chromolithographed diagram of his telluric helix is always designated as "Première Esquisse" but there are at least three printings, the first dated 7 Avril 1862 and the third dated 16 Mars 1863. I do not know of a copy of the second printing.

As far as I am aware, only four copies of the offprint of *Vis Tellurique* have been offered for sale in the last

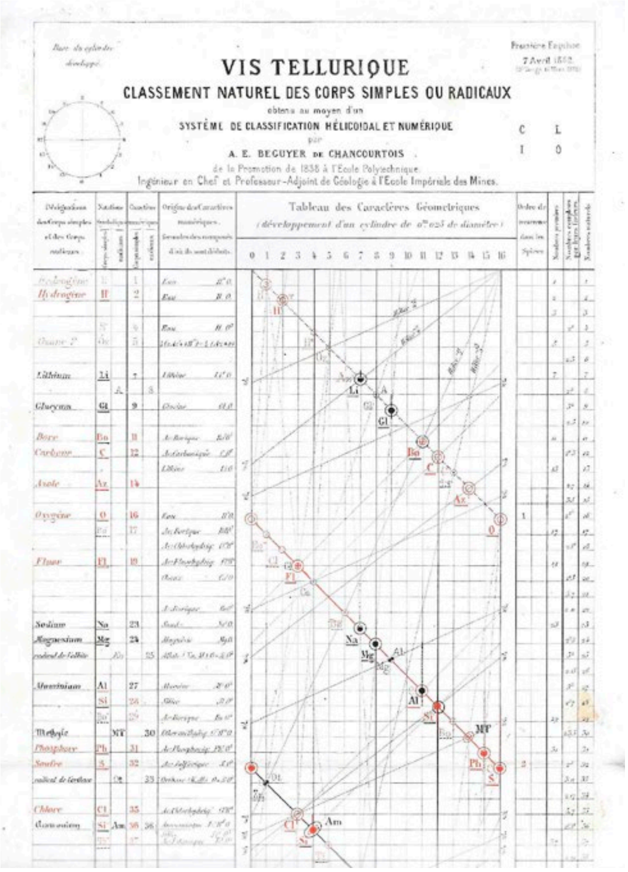


Figure 7. One of about a dozen known copies of the table accompanying the offprint of Béguyer de Chancourtois's 1862 paper *Vis Tellurique*. This figure shows only the upper 25 cm of the 145 cm long chart. This particular copy of the chart is the one that was owned by the Italian chemist Stanislao Cannizzaro

50+ years, and only about 10 copies of the offprint are documented in institutional libraries. The journal issues of the *Comptes Rendus* containing Béguyer de Chancourtois's articles are more readily available, but these lack the all-important diagram.

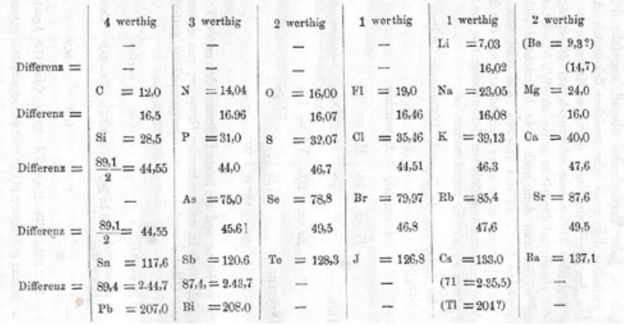
MEYER'S FIRST PERIODIC TABLE (1864)

A significant advance is seen in the first edition of the book by the German chemist Julius Lothar Meyer (1830-1895), *Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik*. [*The Modern Theories of Chemistry and their Meaning for Chemical Statics*],[37] written beginning in 1862 and published in 1864. Near the end of his book, Meyer included a tabular arrangement of 28 elements, ordered by increasing atomic weight (except for the Te/I inversion). This table (Fig. 8) depicted the periodic relationships of the elements far more effectively than did Béguyer de Chancourtois's Telluric Screw.

Meyer's table, which arranged the then-known main group elements into six families, contained three important features, although none of these was explicitly discussed in the text: first, the table clearly shows that the valencies of the elements are correlated with atomic weight: the valency decreases from 4 to 3 to 2 to 1 when moving from the carbon group elements (which are at the left of his table) through the pnictogens and chalcogens to the halogens, and then the valency increases from 1 to 2 upon continuing from the alkali metals to the alkaline earths (which are at the right side). Thus, Meyer's table implies that there are regular relationships between different groups of elements. A second important feature that is not explicitly discussed in his accompanying text is that the table includes gaps to denote presumably unknown elements.

Third, the table also contains information about the differences in the atomic weights between elements in the same group but different periods. The differences seen between elements in the first and second row, and between the second and third row, are all about 16, whereas the difference seen for elements in the third and fourth row, and fourth and fifth row, are all between 44 and 49. One of the gaps in the table is below silicon (atomic weight of 28.5) and above tin (117.6), corresponding to the then-unknown element germanium. Meyer's table implies (but does not state) that the atomic weight of this missing element should be about 44.55 larger than that of silicon, and about 44.55 smaller than that of tin.

In addition to the table of main group elements, Meyer presented two additional tables on the following page, the first showing intergroup relationships between six "early" transition metals, and the second showing intergroup relationships among sixteen "late" transition metals (speaking anachronistically). As for the main



	4 werthig	3 werthig	2 werthig	1 werthig	1 werthig	2 werthig
	—	—	—	—	Li = 7,03	(Be = 9,3?)
Differenz =	—	—	—	—	16,02	(14,7)
	C = 12,0	N = 14,04	O = 16,00	Fl = 19,0	Na = 23,05	Mg = 24,0
Differenz =	16,5	16,96	16,07	16,46	16,08	16,0
	Si = 28,5	P = 31,0	S = 32,07	Cl = 35,46	K = 39,13	Ca = 40,0
Differenz =	$\frac{89,1}{2}$ = 44,55	44,0	46,7	44,51	46,3	47,6
	—	As = 75,0	Se = 78,8	Br = 79,97	Rb = 85,4	Sr = 87,6
Differenz =	$\frac{89,1}{2}$ = 44,55	45,6!	49,5	46,8	47,6	49,5
	Sn = 117,6	Sb = 120,6	Te = 128,3	J = 126,8	Cs = 133,0	Ba = 137,1
Differenz =	89,4 = 2.44,7	87,4 = 2.43,7	—	—	(71 = 2.35,5)	—
	Pb = 207,0	Bi = 208,0	—	—	(Tl = 204?)	—

Figure 8. Mayer's periodic table from his 1864 book *Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik.*

group elements, the tables illustrate trends in the valencies (oxidation states) across the groups. Meyer's transition metal triads are somewhat jumbled with respect to the modern placings, but he accurately put Zn, Cd, and Hg into one triad, and Cu, Ag, and Au into another, thus becoming the first to incorporate these triads into a general classification scheme of the elements.

Meyer's book was issued in a very small edition and, as a result, it has long been a rarity in the rare book market. Many well-known private collections of science or chemistry books did not include a copy. My investigations suggest that fewer than a half dozen copies have been sold at auction or by rare book dealers in the last 70 years.

NEWLANDS'S LAW OF OCTAVES (1864-1866)

In July 1864 the chemist John Alexander Reina Newlands (1837-1898), born in London but the son of a Scottish father and an Italian mother, devised a table of 37 of the then-known elements, arranged (mostly) by increasing atomic weight and grouped into ten families. This paper, "Relations between Equivalents," was one of a series of papers on his ideas about the relationships of the chemical elements that Newlands submitted to the journal *Chemical News*.[38]

In Newland's 1864 table, the main group elements are arranged exactly as in the modern table except that he is uncertain of the place of lithium, and (not too surprisingly given the stabilities of their lower oxidation states) thallium and lead are placed in the alkali metal and alkaline earth groups, respectively. Eight transition elements are included in the table, and several of them are not placed as one would today: osmium is in the oxygen group, gold is in the boron group, zinc and cadmium are grouped with magnesium, and Mo-V-W and Pd-Pt are placed in their own groups.

Newlands's 1864 table leaves gaps in several places, such as those later to be occupied by gallium and germanium. Although he does not discuss these gaps explicitly, he states "So frequently are relations to be met with among the equivalents of allied elements, that we may almost predict that the next equivalent determined, that of indium, for instance [which had been recently discovered], will be found to bear a simple relation to those of the group to which it will be assigned."

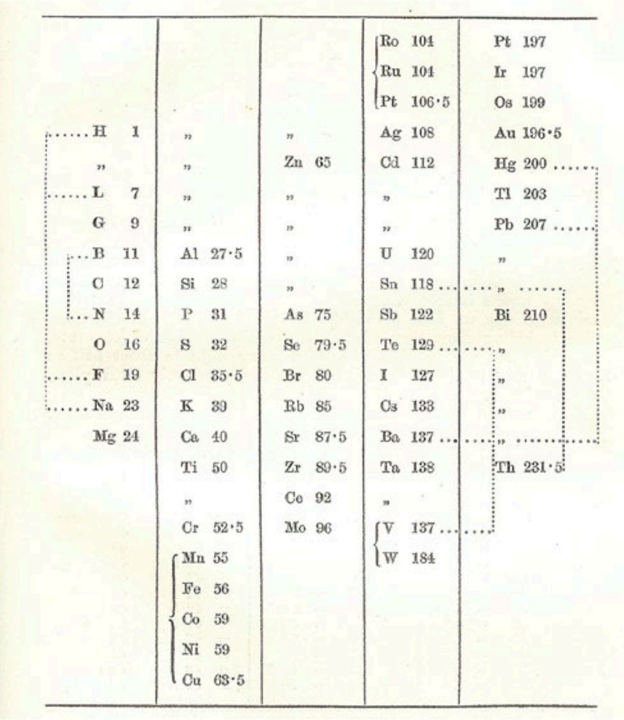
In 1865, Newlands published a follow-up paper, "On the Law of Octaves," and in 1866 he gave a talk at a meeting of the Chemical Society that was also abstracted in *Chemical News*.[38] In the 1865 paper, he wrote "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear in the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves of music.… This peculiar relationship I propose to provisionally call 'The Law of Octaves.'" Here, "the numbers of the analogous elements" are not atomic weights but rather the ordinal number that the element has in his sequence, i.e., akin to (but not) an atomic number.

In his effort to find more regularity in the properties and interrelationships of the elements than he had been able to find in 1864, Newlands forced the elements into seven families, eliminated the gaps from his previous table, and sometimes placed two elements in a single place; the net result is a distinct backward step. In the discussion after Newlands's 1866 talk, John H. Gladstone – whose own contributions to this area are mentioned above – objected to the new table (quite appropriately, as later events showed) because it assumed that no elements remained to be discovered.

Offprints of articles from *Chemical News* from this period do exist, but are unknown for Newland's papers and it is probable that they were never printed. Newlands's original papers in *Chemical News* are readily available as the bound volumes for those years, however, often as library discards. In 1884, fifteen years after Mendeleev announced his Periodic System, Newlands issued a collected reprinting of his articles from the *Chemical News* as the book *On the Discovery of the Periodic Law, and on Relations among the Atomic Weights*.[39] Normally, presentation copies of books, i.e., those bearing a signed inscription from the author, are prized because so few exist, but Newlands sent signed copies to a very large number of chemists and institutions. Today, signed copies are frequently seen on the rare book market; unsigned copies are actually not as common.

ODLING'S TABLE OF THE ELEMENTS (1864)

In October 1864, the English chemist William Odling (1829-1921) published a remarkable paper "On the Proportional Numbers of the Elements,"[40] which contained an important precursor to the periodic table. In this paper, Odling succeeded in arranging 57 elements into a table that looks very much like Mendeleev's first periodic table of 1869 (Fig. 9). Odling stated in his article, "Upon arranging the atomic weights or



			Ro 104	Pt 197
			Ru 104	Ir 197
			Pt 106·5	Os 199
H 1	”	”	Ag 108	Au 196·5
”	”	Zn 65	Cd 112	Hg 200
L 7	”	”	”	Tl 203
G 9	”	”	”	Pb 207
B 11	Al 27·5	”	U 120	”
C 12	Si 28	”	Sn 118	”
N 14	P 31	As 75	Sb 122	Bi 210
O 16	S 32	Se 79·5	Te 129	”
F 19	Cl 35·5	Br 80	I 127	”
Na 23	K 39	Rb 85	Cs 133	”
Mg 24	Ca 40	Sr 87·5	Ba 137	”
	Ti 50	Zr 89·5	Ta 138	Th 231·5
	”	Ce 92	”	
	Cr 52·5	Mo 96	V 137	
	Mn 55		W 184	
	Fe 56			
	Co 59			
	Ni 59			
	Cu 63·5			

Figure 9. Odling's periodic table from his 1864 article "On the Proportional Numbers of the Elements."

proportional numbers of the sixty or so recognized elements in order of their several magnitudes, we observe a marked continuity in the resulting arithmetical series…. With what ease this purely arithmetical seriation may be made to accord with a horizontal arrangement of the elements according to their usually received groupings is shown in the following table, in the first three columns of which the numerical sequence is perfect, while in the other two the irregularities are but few and trivial."

Odling's table places the main group elements in the center, and the transition elements above and below them. Odling, like Meyer and Newlands, independently introduced the inversion of the elements tellurium (129) and iodine (127) in order to associate these elements with their chemical relatives. The main group elements are arranged in groups that correspond exactly to the modern groups of elements; the relationships among the transition elements were more difficult to untangle, as they were to be even for Mendeleev.

Odling noted that many pairs of chemically related elements have atomic weight differences that lie between 84.5 and 97 and that, of these pairs, about half are the first and third members of known triads. He added that, "the discovery of intermediate elements in the case of some or all of the other pairs is not altogether improbable." It cannot be said that these predictions are based on a periodic law; instead, they are predictions based on individual incomplete triads. Most of these predictions, however, didn't pan out because most of the pairs Odling cited had atomic weight differences that (as we now know) are affected by the interposition of the then-unrecognized lanthanide series of elements.

Odling incorporated a modified version of his table in the second (1865) edition of his book, *A Course of Practical Chemistry Arranged for the Use of Medical Students. A Course of Practical Chemistry Arranged for the Use of Medical Students.*[41] Starting on page 226 of that book, after the end of the text, are a series of appended tables. In the first of these, entitled "Atomic Weights and Symbols," 45 elements are arranged much as they are in the modern periodic table, with gaps for nine elements indicated by dashes. Three of the gaps stem from not placing copper, silver, and gold into a triad, and another from not placing chromium, molybdenum, and tungsten together; it is interesting to note that Odling had correctly placed silver and gold together, and chromium and molybdenum together, in his 1864 table. The remaining four gaps correspond to elements that had not yet been discovered: gallium, germanium, technetium, and indium. Unfortunately, Odling nowhere discusses this table in the text, nor does he comment on the gaps.

Mendeleev's first paper on his Periodic System[42] included a footnote stating that, after his paper had been submitted, he had been informed that a very similar table of elements had appeared in Odling's *Practical Chemistry*. Mendeleev emphasized that he had not been aware of Odling's table before this time.

No offprints of Odling's 1864 paper are recorded, but it is available as the bound journal volume. The 1865 edition of Odling's *Practical Chemistry* is remarkably scarce and rarely appears for sale; the other editions (1854, 1869, 1876) seem to be more common but none contains Odling's table.

HINRICHS'S PROGRAM OF ATOMECHANICS (1867)

The last of the contributions to the development of the periodic table that we will discuss in the present article were made by the chemist Gustavus Detlef Hinrichs (1836-1923); Hinrichs had been born in Holstein, then part of Denmark but now part of Germany, but had immigrated to the United States in 1861. In 1867, he privately published a lithographed reproduction of a 44 page hand-written treatise, entitled

Programme der Atomechanik, oder die Chemie eine Mechanik der Panatome [*Program of Atom mechanics, or Chemistry a Mechanics of Panatoms*].[43] He also wrote an abstract in French and a 4 page abstract in English, the latter submitted in August 1867 to the *American Journal of Mining*.[44]

Hinrichs, like many of those mentioned above, was passionately devoted to the challenge of finding deep meaning in the atomic weights of the elements (and other phenomena, such as the orbital radii of the moons of the outer planets and the wavelengths of the dark lines in the solar spectrum). He proposed that there was a unit of matter, which he called a panatom, which had an atomic weight equal to half of that of hydrogen. He further proposed that there were two kinds of atoms, which he called trigonoids and tetragonids; the former had inner structures consisting of stacks of trigonal/hexagonal arrays of panatoms, whereas the latter had inner structures consisting of stacks of square arrays of panatoms. His attempts to shoehorn the elements into these two classes are replete with ad hoc assumptions to account for the deviations of the atomic weights from the numbers that one would expect from such stacks.

After presenting this proposal for atomic structure in his *Programme der Atomechanik*, Hinrichs then proposed a spiral classification scheme for the elements in which those with larger atomic weights appear at larger distances from the center of the spiral (Fig. 10). His scheme captures some of the intergroup relationships that are present in the modern periodic table, but there are many oddities. Most notably, the nitrogen group elements are placed between the chalcogen and halogen groups. The transition elements are again mostly jumbled, although Hinrichs (like Lothar Meyer before him) grouped copper, silver, and gold together.

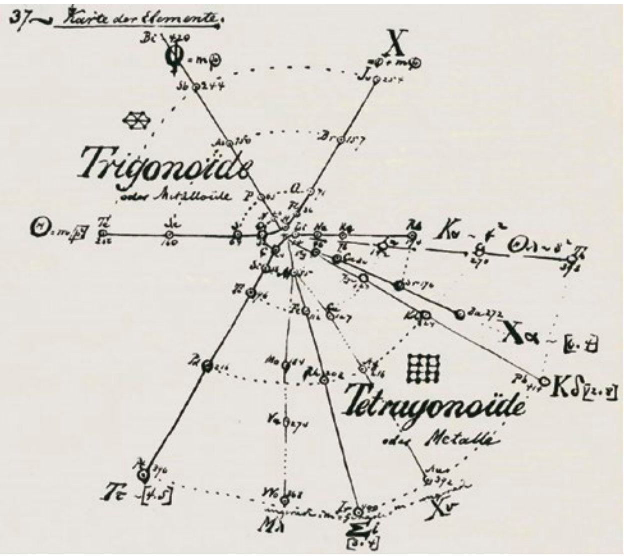


Figure 10. Hinrichs's spiral periodic table from his 1867 book *Programme der Atomechanik*. Image reproduced with permission of the University of Dresden.

Two years later, Hinrichs published a revision of his classification system in two papers, one presented in August 1869 to the 18th annual meeting of the American Association for the Advancement of Science, "On the Classification and the Atomic Weights of the so-called Chemical Elements, with reference to Stas' Determinations,"[45] and the other the same summer to the journal *The Pharmacist,* "Natural Classification of the Elements".[46] In these two papers, the nitrogen group is now in its modern place relative to (i.e., between) the oxygen and chlorine groups. But other oddities are introduced; for example, the transition elements are listed in reverse order of their atomic weights. Hinrichs's tables of 1869 contain numerous gaps, but he gives no indication that the gaps are significant.

Hinrichs's 1869 table is tabular instead of spiral: the elements within a period being listed in a vertical column, and elements within a group being arranged in rows from left to right. Of all the early attempts to arrange the elements in tabular form, only Odling's table of 1864 and Mendeleev's first table of 1869 are arranged in this way.

Hinrichs clearly recognized the periodic interrelationships that are brought out by his tables: "[I]n this table the elements of like properties, or their compounds of like properties, form groups bounded by *simple lines.* Thus a line drawn through C, As, Te, separates the elements having metallic lustre from those not having such lustre. The gaseous elements form a small group by themselves,… so also the … *heavy metals* (specific gravity above five).… Of great practical importance are the lines expressing certain properties of definite compounds [such as] solubilities … reactions in the wet way [and] blowpipe reactions…."

To my knowledge, no copies of Hinrichs's 1867 *Programme der Atomechanik* have been available for purchase on the rare book market in the last 50 years. The American Academy for the Advancement of Science printed a proceedings volume that contained the text of all the papers (including Hinrichs's) presented at their 1869 meeting; copies of this volume can occasionally be found for sale. Hinrichs also reprinted this paper (using the same setting of type) as paper no. 4 of his *Contributions to Molecular Science, or Atomechanics.*[47] I have not seen an original copy of this reprint available for sale in recent decades.

CONCLUDING REMARKS

With the contributions of Hinrichs, the stage was set for the entrance of Mendeleev into the story in 1869: in that year, Mendeleev circulated a privately-printed periodic table and also published it in both a journal article[42] and a textbook, *Osnovy Khimii*.[48] It is important to point out, however, that the discussion above lists only some of the principal documents that led more or less directly to the concept of the periodic law. Many other contributions, which either were important but peripheral or were later recognized as blind alleys, have been omitted for the sake of brevity. But this brevity necessarily paints a distorted picture of how this important and fascinating area of science actually developed.

Many of the books and papers mentioned above are quite rare: for some, fewer than a dozen copies exist, but others are more common and appear regularly for sale at auction or by rare book dealers. Acquiring all of these foundational documents in a collection devoted to the history of the periodic table, in the original editions, would be a challenging but enjoyable pursuit. Holding these documents in one's hands conveys a real sense of connection with the great scientists of the past. This sense is especially keen if the pamphlet or book bears a handwritten inscription from the author, such as the copy of Dalton's *New System* shown in Figure 3. Such special copies, known as presentation copies among collectors, are very hard to find and are considerably more interesting (and valuable) than ordinary copies. In addition, the documents often contain the signatures of one or more former owners. Although sometimes the previous owners are well known scientists, more often they are not. Tracking down their identities can be a challenging puzzle that calls upon skills and methods similar to those employed when tracing family genealogies.

As is true of all collecting hobbies, the hunt for and capture of suitable items to acquire is an endeavor of continual pleasure. The process affords opportunities to meet dealers and other collectors who share similar interests, and can result in long-lasting friendships. Rare book dealers are often scholars themselves who not infrequently add to our understanding of history. Without their unflagging passion to locate great books and find good homes for them, both private and public libraries would be much the poorer.

But even if forming a collection is not one's primary goal, these documents remain of great interest, and they can be viewed in person at major institutional libraries.[49] By consulting them in their original forms, much can be learned about key parts of the path that led to the creation of the periodic law and its iconic table, one of the triumphs of modern science.

ACKNOWLEDGMENTS

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A Brief History of Early Silica Glass: Impact on Science and Society

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Abstract. Silicon in the form of silica is the basis of common glass and its uses predate recorded history. The production of synthetic glass, however, is thought to date back to no earlier than 3000 BCE. This glass technology was not discovered fully fashioned, but grew slowly through continued development of both chemical composition and techniques for its production, manipulation, and material applications. This development had become fairly advanced by the Roman period, resulting in a wide variety of glass vessels and the initial use of glass windows. Following the fall of the Roman Empire, glass grew to new heights in Venice and Murano, where improvements in composition and production resulted in both more chemically stable and clearer forms. The quality of this new glass ushered in the development of lenses and eyeglasses, as well as the greater use of glass as a material for chemical apparatus, both of which changed society and the pursuit of science. Finally, glass in the North developed along different lines to ultimately result in a new form of glass that eventually replaced Venetian glass. This Bohemian glass became the glass of choice for chemical glassware and dominated the chemical laboratory until the final advent of borosilicate glass in the 1880s. A brief overview of the early history of silica glasses from their origins to the development of borosilicate glasses will be presented.

Keywords. Soda-lime glass, potash-lime glass, glassblowing, chemical glassware, eyeglasses, windows.

INTRODUCTION

Silicon is one of the most abundant elements of the periodic table, comprising the eighth most common element in the universe by mass and the second most abundant element in the Earth's crust after oxygen (ca. 28% by mass). In nature, silicon occurs almost exclusively in combination with oxygen. Silicon dioxide, SiO_2, occurs in a variety of forms in nature and is known as silica. One form of silica is α-quartz, a major constituent of common sand, sandstone, and granite, as well as the timekeeper in most watches. Silicon also occurs in many minerals as silicates (consisting of compounds in which SiO_4 units may be fused by sharing corners, edges, or faces) or aluminosilicates. For the discussion here, silica also plays a critical role as the major component of common glass.[1-4]

While quartz is a crystalline solid with a regular repeating lattice as shown in Fig. 1,[5,6] glass has no regular repetition in its macromolecular structure and exhibits a disordered structure similar to substances in the liquid state as illustrated in Fig. 2.[3,7] Due to the extent of disorder in amorphous structures, the glass state of a material is higher in energy than its crystalline state and thus glasses can suffer from devitrification (i.e. frosting and loss of transparency as a result of crystallization).[1] As a result, stable glasses are those that can form a highly disordered state that is of comparable energy to the corresponding crystalline state.[8]

Glass as a material shares the properties of both solids and liquids. As such, glass at room temperature is commonly described as either a supercooled liquid or an amorphous solid,[1-3,7-9] although these can both be viewed as oversimplifications.[9] Thus, a glass is a solid, but due to its highly disordered nature, it exhibits properties much like a liquid that is too viscous to flow at room temperature. This dichotomy has led to the commonly cited myth that glass is really a highly viscous liquid and thus observable flow can be detected in objects of a sufficient age. This belief originates from the observation that stained-glass windows of 12th century cathedrals are thicker at the bottom than the top.[2,10-14] It has been verified via theoretical calculations, however, that the compositions used in either medieval or contemporary windows would not exhibit measurable flow at room temperature within the time scales of humanity,[10,12,14] and physical measurements have confirmed that unless sufficient compressive stress is applied, glass does not flow below 400 °C.[11,13] In truth, the uneven nature of medieval windows is the result of the limited technological methods used in their manufacture, and because of the resulting variable thickness, the thicker edges of the panes were logically mounted at the bottom of the window.[10-12]

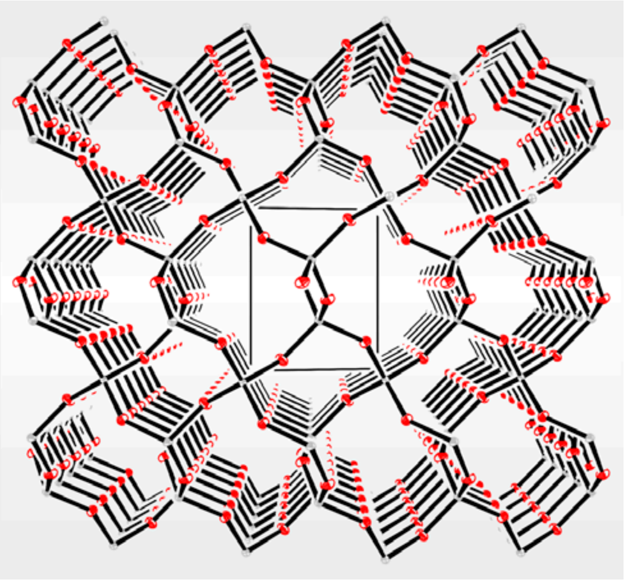

Figure 1. X-Ray structure of quartz viewed down the a-axis.

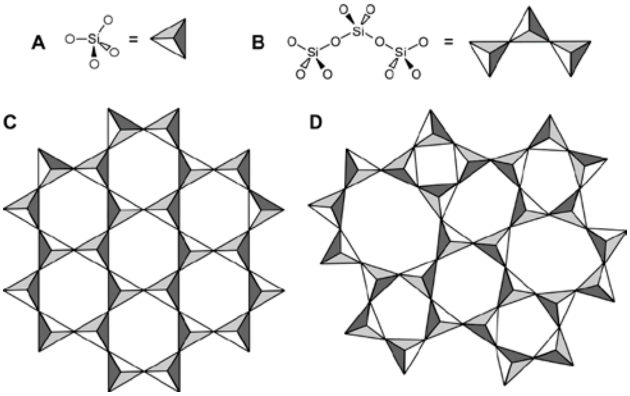

Figure 2. Simplified two-dimensional silicate structures: SiO_4 tetrahedron (A); oligomeric structure (B); crystalline structure (C); amorphous structure (D).

Glass is unlike any other early material and its production required some of the most advanced methods of any of the chemical technologies originating in antiquity. In terms of material properties, the closest modern analogues of silicate glasses are the organic plastics ubiquitous in modern society.[1] Molten glass could be poured into almost any shape and would retain that shape upon cooling. In addition, preformed pieces of glass could be thermally fused together to produce either air-tight seals or more complex structures. Furthermore, chemically stable glasses are relatively inert and can be produced in a wide range of color, opacity, or transparency. As such, this made glass a broadly versatile material for a vast range of applications.

COMPOSITION AND PRODUCTION OF EALRY SILICATE GLASSES

Although it is possible to produce a glass from silica alone, the temperature needed to melt silica (~1710 °C) is too high to have been achieved through methods available during the formative years of glass production.[6,15-19] Sometime during the 3rd millennium BCE,[18] however, it was discovered that the use of a flux (from the Latin *fluxus* - "flow"), such as soda (sodium carbonate, Na_2CO_3), could lower the fusion temperature of silica sources to below 1000 °C.[6,16-19] While this approach successfully reduced the temperature needed to produce molten glass, the sodium contained in the resulting glass is highly soluble and thus susceptible to attack by water. As a result, the glass produced via the application of soda as a flux is of low chemical stability.[1] In order to produce viable glass materials, a third component is thus required that acts as a stabilizer for the final glass product.[17,18] Such stabilizing species generally contribute less soluble cations, with calcium or magnesium compounds the most commonly applied. While potential sources of these ions could be lime, shells, or other mineral additives,[17,20,21] the critical nature of these stabilizing species was not initially recognized and it is believed that calcium was not intentionally added as a major constituent until the end of the 17th century.[20-22] As such, the calcium and magnesium content of all early glasses is thought to have been introduced via impurities in the silica or soda sources utilized.[1,2,21-23] The glasses produced through the addition of soda and calcium species to silica are typically referred to as soda-lime glass and it was these soda-lime formulations that made up the majority of all early glasses in the Western world.[1,2,16,19-24]

Early glass was produced from a silica source (such as beach sand) and a crude source of soda, with both components containing enough lime and/or magnesia to provide some chemical stability.[1,2,23] Heating this mixture would initiate fusion of the soda and other salt species, which would then start reacting with the sand to generate various sodium silicates and initial formation of liquid material. Lime and other basic species would then begin to react with the fusing mixture of silica and silicates to join the growing melt.[21,25] As the melt temperature increased, the viscosity of the mixture was reduced and any remaining silica would be incorporated into the melt.[25] Throughout the generation of the melt, gases would be liberated as the various carbonate, nitrate, and sulfate components were converted to their corresponding oxides,[15] resulting in violent agitation of the fusing mixture and significant bubbles in the final molten glass.[25,26]

In order to minimize the effect of these escaping gases, glass production was often carried out in two distinct stages. The silica-soda mixture would first be heated in shallow pans at a temperature to allow the reaction of the silica with soda and lime, but below that required to achieve homogenous fusion. The majority of the gaseous byproducts would thus be liberated in the process, after which the mixture would be cooled to give an intermediate product commonly referred to as a *frit*.[2,17,21,27] This frit would then be crushed to enhance more intimate mixing and then heated a second time at higher temperatures in order to achieve complete fusion.[17] Via this process, a final glass could be produced that was relatively free of bubbles.[27]

Table 1. Colorants commonly employed in early silica glasses.

Color	Transition or main group metal	Coloring oxides	References
White	calcium/antimony, or tin	$Ca_2Sb_2O_7$; SnO_2	2,7,16,18,28
Yellow	lead/antimony, or iron	$Pb_2Sb_2O_3$; Fe_2O_3	2,6,7,16,18,28
Red	copper and/or lead	Cu_2O; Cu[a]; Pb_3O_4	2,7,16,19,29
Purple	manganese	Mn_2O_3	2,6,7,16,19,28
Blue	cobalt or copper	CoO; CuO	2,6,7,15-19
Blue-green	iron	FeO	2,6,7,15-18
Green	chromium	Cr_2O_3	2,6,19,30

[a] Metallic copper nanoparticles can result in a ruby red color.

Although commonly known as soda-lime glass, the chemical composition of these materials was really more complex than suggested by this simple designation. Besides the three primary components (silica, flux, and stabilizer), glasses also contained colorants (Table 1) and/or decolorizing agents, as well as a variety of unintended impurities introduced along with the primary reagents. As a consequence, the composition and structure of the resulting glasses could be quite complex and extremely variable, resulting in a range of physical and chemical properties. Furthermore, the nature of a particular glass depends not only on its chemical composition, but also the manner and degree of heating, as well as the rate the hot glass is cooled (i.e. annealing of the glass).[15,26,27]

ORIGIN AND INTIAL DEVELOPMENT

The origin of synthetic glass is unknown and its discovery has been attributed to the Syrians, the Egyptians, and even the Chinese.[2,31-33] Of course, various legends have developed around the discovery of glassmaking,[2,32-35] the most famous of which was recorded by the 1st century Roman author Pliny the Elder.[32] Pliny's account gives the story of a ship moored along the Belus river in Phoenicia, whose merchants used blocks of soda to support their cooking pots. As the combination of the sand and soda were heated by the cooking fire, it was stated that streams of liquid glass poured forth. While attempts to reproduce this legend have shown that glass cannot be produced in this fashion,[2,33,35] this story continues to be repeated into the present. In contrast, scholars believe glass resulted as either a byproduct of metallurgy, where fluxes were first utilized to convert rock impurities into liquid slag during the smelting of metals, or via an evolutionary sequence in the development of silica-based ceramic materials.[1,2,16,18,31,35-38]

Regardless of the specific developmental path, glass as an independent material is not believed to predate 3000 BCE.[2,39-42] Reports have claimed the analysis of glass beads that date back to as early as 2600 BCE, but at least some of these dates are questionable.[7] Glass objects have been found in Syria that date to 2500 BCE, and by 2450 BCE, glass beads were believed to be plentiful in Mesopotamia.[23,43] Some glass objects were also produced in Egypt during the 3rd millennium BCE,[38,40] but the oldest Egyptian glass of undisputed age is believed to date to only ~2200 BCE.[43] As such, historians have revised the original belief that glass was an Egyptian discovery and current views place the most likely development of the earliest glass in the Mitannian or Hurrian regions of Mesopotamia.[39,44] Furthermore, there is little doubt that glass was made from an early period in both Babylonia and Assyria[45] and routine Mesopotamian glass production is thought to have started ca. 1550 BCE.[41] The first glass objects included beads, plaques, inlays and eventually small vessels,[23,39,40,46] although such glass vessels did not become prevalent until after the middle of the 2nd millennium BCE.[47]

It is generally thought that introduction of glass technology into Egypt occurred during the reign of Tuthmosis III (1479-1425 BCE) via glass objects and ingots being imported as tribute[37,38,40,41] and the import of Mesopotamian glassmakers around 1480 BCE.[37,38,41] As such, this ultimately resulted in the local Egyptian production of glass by the time of Amenophis III (ca. 1388 - ca. 1350 BCE)[40] with evidence supporting onsite glass production in the Egyptian city of Amarna around 1350 BCE. Glass objects exhibiting genuine Egyptian style were made soon after, supporting their manufacture within Egypt. Archaeological evidence further supports this through the identification of several glass workshops in Egypt.[41]

Glass manufacture soon became a major industry and was spread throughout the Mediterranean for the next 300 years.[4] Glass objects of this early period (1500 - ca. 800 BCE) are characterized as a typical soda-lime glass with a high magnesia (3-7%) and potash (1-4%) content,[2,16,24,28,38,40,44,45] which is thought to be representative of glass produced or used throughout the Mediterranean area.[24] These vitreous materials were commonly produced from a mixture of silica and a crude source of alkali. Both the silica and alkali could then act as sources of lime or magnesia to give the resulting glass some chemical stability.[23]

In terms of the specific raw materials used during this early period, crushed quartzite pebbles and sand are usually cited as the two most common sources of silica.[2,21,28] However, the analysis of glasses of this time period reveal very low alumina content (~1.3% or less)[37,38] which is inconsistent with the high alumina content found in the majority of analyzed sands. As such, it is generally believed that these early glasses utilized crushed quartzite pebbles as the source of silica, an interpretation supported by the fact that large angular quartz particles have been found to survive in frits analyzed from Amarna.[38] For the alkali source, the two primary sources for early glassmaking were natron, a naturally occurring mineral source of soda, and various types of plant ash.[7,16,21,27,28,48-52] While both sources were used during this initial period, glass throughout the Eastern Mediterranean, Egypt and Mesopotamia was characterized by high magnesia (3-7%) and potash (1-4%) content.[16,23,24,40] This increased magnesia and potash content has been linked by many authors with the nature of the alkali used in the glass, and as glasses made with natron usually contain less than 1% of either MgO or K_2O,[43,64] this has led to the common view that plant ash was the predominant alkali source during this period.[16,40] In addition to the necessary soda flux, the plant ash also provided calcium and magnesium as chemical stabilizers for the resulting glass.[37] However, sea shells and calcinated corals have been mentioned in Mesopotamian tablets as reagents for glass production, both of which could have acted as additional sources of calcium.[7,27]

Processing methods for the formation of glass objects were fairly rudimentary during this early time period, consisting of either core-molding or cast glass[2]. The first of these dates to ~1500 BCE and was the earliest known technique for the production of hollow glass vessels.[24,46,53,54] As is outlined in Fig. 3, this involved the shaping of a form or core onto the end of a wooden or metal rod,[16,54-56] after which it could then be heated to help set its shape (Fig. 3C), and then glass layers were built up around the central set core. The most commonly cited methods for adding the glass layers involved treating the core with an organic binder (egg white or honey) and then by rolling it in crushed glass (Fig. 3D);[16,56] winding hot strands of glass around the core (Fig. 3D');[40,55,56] or immersing the core in molten glass not much above the softening temperature (Fig. 3D").[7,40,43,54-56] The assembly would then be heated to generate a uniform layer of glass (Fig. 3E), cooled, and another layer applied. Via such a repetitive process, the glass walls would be built up iteratively until the desired thickness was achieved.[54,56] The exterior of the object

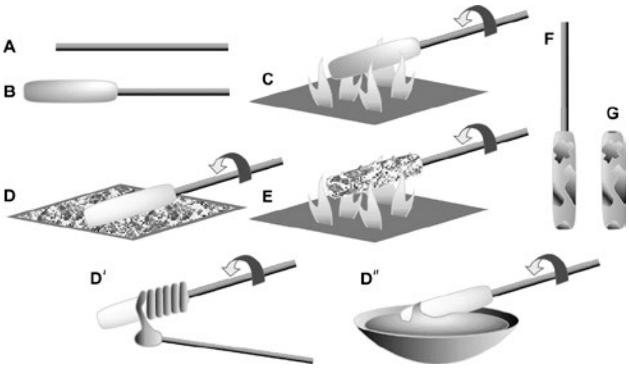

Figure 3. Production of core-molded vessels: (A) metal or wooden rod; (B) formation of core form; (C) firing the core; (D) glass application via rolling in crushed glass; (E) firing of applied layer; (F) completed object; (G) vessel after removal of rod/core. Alternate methods for glass application: (D') coiling strands of softened glass around the mold or (D") dipping the core in molten glass [adapted from reference 42 with permission from Springer Nature].

could then be worked and the object cooled (Fig. 3F), after which the rod was removed from the vessel so that the core material could be carefully dug from its center to give the final hollow vessel (Fig. 3G, Fig. 4).

The next significant advancement in glass forming was then made in ca. 1200 BCE, when the Egyptians learned to press softened or molten glass into open molds,[2,31,54] which allowed the production of simple shapes such as bowls, dishes, and cups not possible via the previous core molding methods. As outlined in Fig. 5, casting involved melting glass pieces into a mold which provided the simple, crude shape of the desired object.[55,57] After the glass had cooled, the mold could then be removed[57] and carved or polished to give the final product.[55]

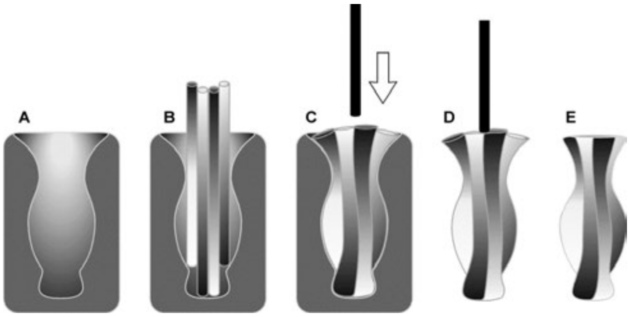

Figure 5. Fuse-casting of glass objects: (A) production of black mold; (B) glass pieces added, heated to fuse and fill mold; (C) metal rod inserted; (D) mold removed; (E) piece ground and polished to finish [adapted from reference 42 with permission from Springer Nature].

Figure 4. Core-formed glass Alabastron (6th - 4th century BCE) [M.88.129.10; Courtesy of the Los Angeles County Museum of Art].

DECLINE AND THE RISE TO ROMAN GLASS

After this period of initial development, the glass industry declined for a time until a revival in production beginning in Mesopotamia during 900-700 BCE.[4,7,16] This was followed by the growth of an apparently independent glass industry in Syria and along the Palestinian coast in 800-500 BCE[7] and a revival in Egypt in ca. 500 BCE.[4] This overall resurgence in glass technology is viewed as part of the Iron Age revival that followed the period of turmoil in the Mediterranean in 1200-1000 BCE. Centers of glass production then continued to develop in Egypt, Syria, and other countries along the eastern shore of the Mediterranean Sea,[9] with the Egyptian industry ultimately becoming centralized at Alexandria.[16,56] During this second period of ca. 6th century BCE to ca. 4th century CE, glass was characterized by lower potassium (0.1-1.0 %) and magnesium (0.5-1.5%) content, along with a consistent high concentration of antimony.[16,24,40] Many authors have linked the decreased magnesia and potash content with a change from plant ash to that of natron as the alkali source.[16,40,50,58] Another major change during this period was a shift in emphasis from opaque to clear glass production, with the move to clear and translucent colored glass thought to be due to a shift in viewpoint as much as any specific new advances in technology.[39]

Colorless glass was produced via the careful selection of a silica source of low iron content, coupled with the addition of antimony as a decolorizing agent.[18,31] The use of antimony as an additive was not new and was previously important for the production of opaque glasses. The colorless glasses achieved via the use of antimony are very similar in composition to the previous white opaque glasses, differing only in higher antimony levels (1.95% on average) for the opaque glasses.[28] Although such colorless glass was relatively transparent, the final object may still exhibit a slight yellow tint depending on the extent of Fe(III) content. In addition, the majority of ancient glass contained various undissolved materials and was therefore not as transparent as modern glass.

The conquests of Alexander the Great (d. 323 BCE) during the 4th century BCE brought the Greeks in contact with the cultures of the Near East as far as India.[39,59] As a result, the Greeks began to amass the technological knowledge of the Middle East, as well as that of the Egyptians, Indians, and Chinese.[42] Rome then conquered Greece in the 2nd century BCE, with the entire Mediterranean basin united under Roman rule by 30 BCE.[39] The culture and natural philosophy of the Greeks was thus absorbed by the Romans, including the collected knowledge and technology of glassmaking.

The term "Roman glass" is used to describe the normal composition of glass of the period 4th century BCE to 9th century CE that was produced throughout Syria, Egypt, Italy, and the western provinces.[24] Such glass consists of a composition similar to that of the previous antimony-rich group, although with a large drop in the amount of antimony and significantly higher manganese content. This has led to the conclusion that the primary distinction between Roman glass and the previous antimony-rich glass is the choice of decolorant used to achieve colorless glass.[16,24,60] However, this is somewhat of an oversimplification as it is generally believed that the Roman period is also distinguished by other changes in the raw materials applied to glass production.[37] The primary alkali source for Roman glass is generally held to be natron, most probably obtained from the Wadi Natrun in Egypt.[16,36,37,40,58,61,62] The Romans extensively imported natron from Egypt and it remained the alkali of choice for glass production for the duration of the Roman Empire.[40] In contrast, the silica source of Roman glass is now thought to consist primarily of sand, based on increased alumina (Al_2O_3, 2.3% average), TiO_2 (0.07% average), and Fe_2O_3 (0.5% average) content.[37,62] Furthermore, Pliny the Elder confirms the use of sand in Roman glass in his *Natural History*[63] and this sand-natron glass formulation remained as the standard glass formulation throughout the Roman and Byzantine periods until ca. 850 CE[37].

In addition to the use of manganese as a decolorant, Roman glass also utilized lead salts and other components as additives to the glass formulation.[7,18,36,63] The primary use of lead was as a colorant in the production of yellow opaque glasses,[28] but lead salts were also sometimes intentionally added to either improve the working properties of the melt[36] or to enhance the brightness of the resulting glass.[18] It has also been claimed by some that the uniform calcium content found in the analysis of Roman glasses is evidence of the intentional addition of lime to glass formulations.[7] To support this reasoning, authors have pointed to passages of Pliny the Elder that mention the addition of shells and fossil sand to glass,[63] as well as suggesting chalk or other forms of limestone ($CaCO_3$) that could have acted as convenient sources of lime in addition to burned shells (primarily a mixture of chitin and $CaCO_3$).[7] Still, it has also been pointed out by others that the distinct lack of substantial amounts of such additives in known glass recipes does not really support such claims.[2] Furthermore, as these potential calcium-based additives are not mentioned in the known glassmaking treatises of the Medieval and Renaissance periods, it is generally believed that the role of lime in glass was not yet recognized during the Roman period.[20] It should be pointed out, however, that analysis of the sands used as the Roman silica sources have shown higher calcium content and thus these sands are believed to have acted as a source of lime as well as silica.[37,60,61]

ADVANCED PROCESSING METHODS AND NEW APPLICATIONS

The Roman Empire presented a ready market for high-quality glass objects, which thus encouraged the development of new methods for the manipulation of glass and a more centralized approach to glassmaking.[2] For the first time, the mass production of similar glass objects became an economic goal and new fabrication methods were required to meet this demand. Such efforts began with bending (Fig. 6), a method also known as sagging or slumping.[2,55] The formation of slumped objects began with pouring hot glass onto a flat surface (Fig. 6A), which was then pressed with a flat,

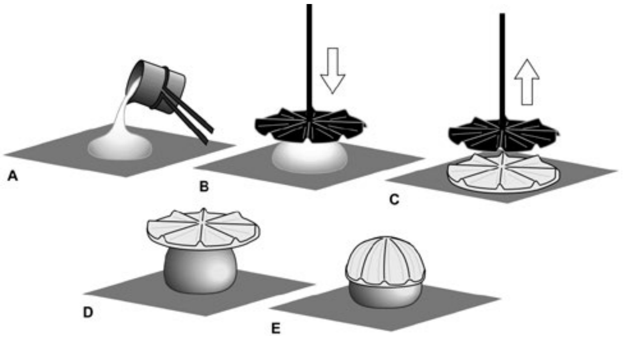

Figure 6. The formation of open-form bowls by sagging glass over convex "former" molds: (A) molten glass is poured onto a flat surface; (B) pressed with a flat, disc-shaped former; (C) cooled to create a glass disc; (D) transferred onto a "former" mold; (E) heated to cause the disc to sag over the mold giving the final bowl shape [adapted from reference 42 with permission from Springer Nature].

Figure 7. Ribbed bowl (1st century CE) [81.10.39; Courtesy of The Metropolitan Museum of Art, www.metmuseum.org].

disc-shaped tool (Fig. 6B) to create a glass disc (Fig. 6C). The resulting disc was then transferred onto a "former" mold (Fig. 6D) and the system was reheated to soften the glass disc to the point that the combination of heat and gravity would cause the disc to sag over the mold to give a bowl-shaped glass object (Fig. 6E, Fig. 7). The formed piece was then finished by grinding and polishing in order to remove mold markings or tool marks.[55,64] The large-scale production of slumped objects has been dated to ca. 400 BCE[39] with one of the most common objects made in this way being the distinctive ribbed bowls often referred to as pillar-molded bowls. Such bowls were popular from the 1st century BCE to the 1st century CE and modern glassmakers have illustrated that this is a viable, easily repeatable, and relatively fast method which reproduces all of the characteristics of Roman-era ribbed bowls.[64]

Of course, the most significant new advancement was the introduction of glassblowing during the 1st century BCE,[2,7,23,31,37,53,56,65] a technique now commonly viewed as synonymous with the general working of glass. Although it has been proposed by some to have been invented as early as 250 BCE, there is far too little evidence to support the application of glassblowing at this earlier date.[65] Sometime after 50 BCE, however, blown glass objects had become common and thus the genesis of glassblowing is typically dated to the time period of 50 BCE - 20 CE.[31,65] The origin and development of this technique is typically attributed to craftsmen somewhere in Syria or Phoenicia,[23,39,54,56,65,66] with many scholars favoring the Phoenician city of Sidon (on the coast of Syria) as its point of origin.[31,66] Glassblowing is then thought to have migrated to Rome via craftsmen and slaves after Roman annexation of the area in 63 BCE.[16] The introduction of the revolutionary technique now made possible the creation of an almost endless variety of hollow glass objects.[56] This method allowed the production of very thin, transparent glass, increased the overall versatility of glass significantly, and opened up potentially new applications for glass.[46] In addition, glassblowing could be combined with previous methods to result in new variants such as mold-blowing (Fig. 8),[65] in which glass was blown into a two- or three-piece hollow mold. The product of this method was a hollow, thin-walled vessel and the molds could be re-used indefinitely to allow the mass production of such objects.[65] As a consequence of such advances, the whole character of glass objects changed, with the heavier forms of earlier periods being gradually replaced by thin-walled vessels.[37] Furthermore, the scale of glass production increased dramatically such that it was now possible for the rapid production of simple utilitarian vessels in large quantities, and glass transitioned from prestige objects to household commodities.[7,37]

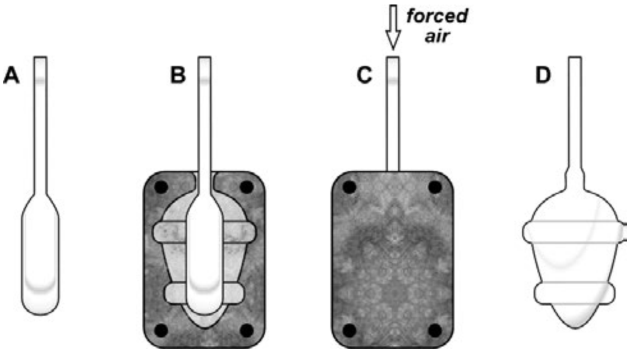

Figure 8. Blow-molding with a two-piece mold: : (A) hollow glass blank; (B) glass blank inserted into mold; (C) mold fastened together and softened glass blown to fill mold; (D) mold disassembled and hollow vessel isolated [reprinted with permission from reference 2. Copyright 2015, American Chemical Society].

One of the new applications of glass introduced by the Romans was the construction of glass window panes as early as the 1st century CE.[67-70] The date of this innovation is supported by window glass in Pompeii structures built or restored after the earthquake of 62 CE, yet preceding the eruption of Vesuvius in 79 CE,[68] with additional examples commonly found in Roman sites in Britain.[69,70] For the most part, however, such early glass windows were quite small, of irregular thickness, and not truly clear or transparent (Fig. 9).[67] Larger glazed windows comprised of multiple glass panes were known, however, such as those used for solar heating of Roman bath houses.[71] Early window panes were fabricated via a variety of different processes,[2,62,67-70,72] the oldest of which was the production of "cast glass" which produced panes of uneven thickness, with one side exhibiting a smooth texture and the other side a pitted, rough finish.[68-70] This seems to have been the prevailing technique up to the 3rd century CE, after which the technique fell into disuse and thus the exact details of making cast glass have been lost.[62,69,70,72] The production of blown window glass (cylinder and crown glass) appeared sometime after the 2nd century CE, with both the cylinder and crown techniques starting to become widespread by the beginning of the 4th century CE.[62,72] It is thought that cylinder-blown glass windows initially existed alongside windows fabricated via the older casting technique.[72]

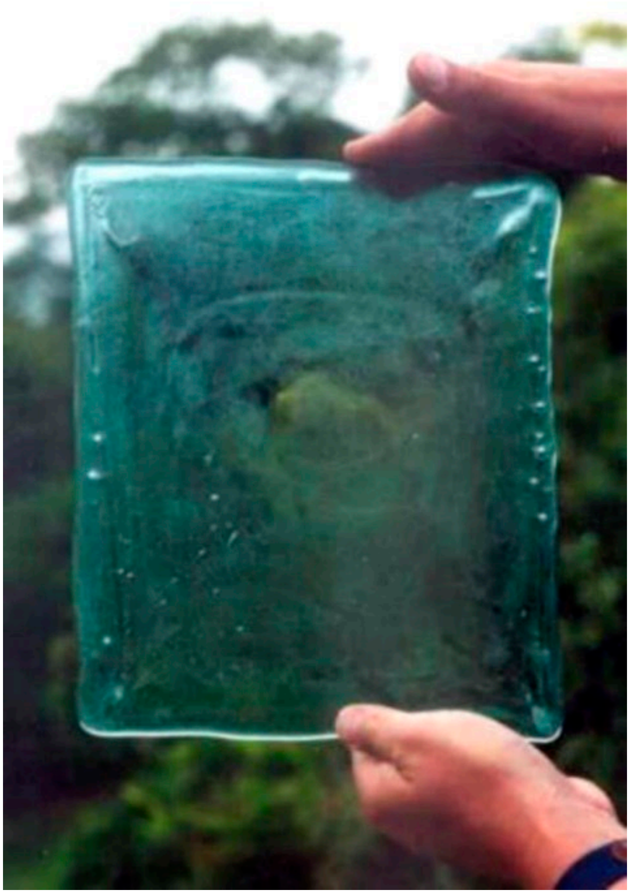
Figure 9. Modern reproduction of Roman window glass (~5 mm thick) [Copyright Mark Taylor and David Hill, used with permission].

It is also during the Roman period that the development of chemical apparatus began sometime towards the end of the 1st century CE.[73-76] Specific known examples at this point in time include the initial distillation apparatus (Fig. 10), the water-bath, and the *kerotakis* apparatus, all credited to the alchemist Maria the Jewess.[73-76] Although glass did find some application in such chemical apparatus, the majority were fabricated from either earthenware (with the interior glazed) or copper.[73,76] Rather, glass was limited to the objects such as the receiving flasks for stills (*bikos*) or other initial types of flasks known as *phials* and *urinals*.[73,76] As glass technology was rising to its initial heights during this time period, it is somewhat surprising that glass-based apparatus for the chemical arts do not seem to have been developed to any significant degree during the Roman period.[22,46,73] The late use of glass for such applications was largely due to the fact that typical soda-lime glasses of this period lacked sufficient chemical durability to be practical for such use.[6] Laboratory glassware must often withstand severe temperature changes in the presence of strong reagents. Thus, for such glassware to be useful, it must not only be resistant to chemical attack, but must also be durable under thermal stress.[22,73] The combination of poor quality, low thermal stability, and the

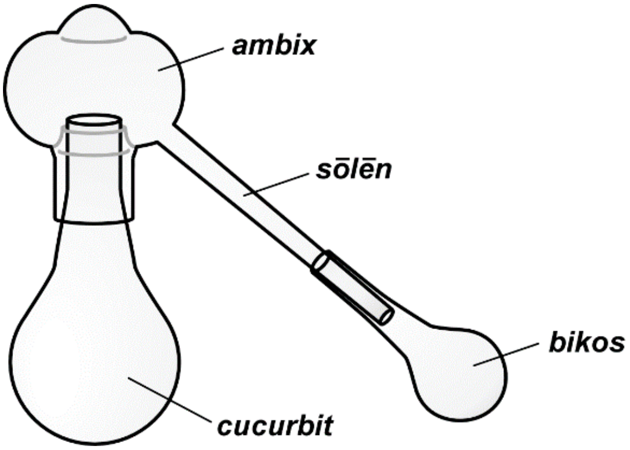

Figure 10. Basic components of the early still [adapted from reference 75 with permission from Springer Nature].

irregular nature of early glasses resulted in the frequent breaking of vessels when used under heat.[77]

VENETIAN GLASS

Centralized glass production came to an end following the fragmentation of the Roman Empire in the 4th century CE, with glassmaking shifting from urban centers to rural locations closer to raw materials and critical sources of fuel. As a consequence, glassmakers became isolated and Eastern and Western glassware gradually acquired distinct characteristics. In addition, this resulted in the loss of more specialized and sophisticated decoration techniques (cutting, polishing, and enameling) and critical techniques such as glassblowing were simplified to their basic essentials.[39] The path of glass in the East continued in the Byzantine Empire long enough to ensure its survival, and aspects of glassmaking that died out in the West were thus kept alive. Furthermore, contact between the Byzantine Empire and the new empire of Islam allowed Islamic glassmakers to add known Roman and Byzantine techniques to their glassmaking activities.[39] As with many chemical arts, this cumulative glassmaking knowledge was then preserved by the world of Islam until the coming of the Renaissance in the West. After the initial Crusades in the 11th century, the center of glass manufacture gradually shifted from glassmakers in the Islamic Empire to the growing glass industry of Venice.[7,56,78]

Venice developed into a city state during the 9th century and grew in importance during the 11th to 13th centuries by exploiting its strategic position at the head of the Adriatic.[39] The strength of the Venetian fleet allowed it to make the most of its advantageous trading position, achieving a virtual dominance of trade with the East. It is believed that the tradition of glassmaking never completely died out in Italy after the fall of Rome and the manufacture of glass had been revived in Venice by the time of the Crusades.[4,46,79] This simple industry was well established by the 9th century and was soon operating on such a remarkably grand scale that it was prospering by 1200.[39,56,80]

It is believed that the Venetians then gained additional glassmaking knowledge via an influx of Eastern expertise, beginning with information transfer from Byzantine glassmakers after the sack of Constantinople in 1204 and enhanced by a critical treaty signed in 1277 between Venice and the Prince of Antioch to facilitate the transfer of technology between the two centers.[39,78,79] This included the transfer of Syrian glassmaking, thus allowing many secrets to be brought to Venice, and a continuous supply of low-cost plant ash for the Venetian glass industry was established in 1366.[81] These factors provided key components that led to the flowering of glass in 14th to 16th century Venice.[78]

As the glass industry grew, the Venetian glassmakers established their own guild in 1268 with a more elaborate guild system to follow in 1279.[39,56] The center of Venice ultimately became dominated by furnaces, the control of which was lost far too often, the resulting fires causing destruction of both critical glasshouses and adjacent neighborhoods. As a solution, the glass industry was ordered to be moved to the island of Murano in 1291, about a mile from Venice.[56,79,80] The glasshouses of Murano are said to have extended for an unbroken mile where thousands of workers toiled to make the glass objects for which Venice became famous (Fig. 11).[56,80]

Until the beginning of the 14th century, the primary source of silica used by the Venetian glassmakers was various local sands.[82,83] In addition to silica, these sands

Figure 11. Venetian wineglass (Murano, 16th century CE) [91.1.1458; Courtesy of The Metropolitan Museum of Art, www.metmuseum.org].

are thought to have provided considerable alumina, as well as iron oxide, lime, magnesia, and small amounts of manganese.[23] However, it had long been known that the cleaner and whiter the source of silica, the clearer the resulting glass. As a result, these sands were gradually replaced with flint pebbles (a form of the mineral quartz) obtained from nearby river beds. Before use, these pebbles were calcined (heated red-hot in an oxidizing atmosphere), ground, and sieved to form a fine quartz powder that was purer than the sands previously used.[23,39,79,82-85] The resulting material was ~98% silica and became the near exclusive silica source of the Venetian glassmakers for the next several centuries.[82,85]

In terms of the alkali source, the Venetians favored the use of plant ashes imported from the Levant (modern Syria, Israel, Lebanon, and the Sinai in Egypt) as discussed above.[21,82-87] The soda ash imported from the Levant originated from the burning of plants thought to have belonged to the large family of the *Chenopodiaceae*, in particular the plant *salsola kali*.[21,82-87] These Levantine ashes, referred to in Venice and Murano as *allume catino*, were in common use by 1285[82] and were used almost exclusively in Murano until the end of the 1600s.[86] Such ash had high soda content (as much as 30-40%), as well as large quantities of potassium, calcium, and magnesium carbonates.[21,82,85-87] The exclusive use of these ashes was even dictated by the Venetian government, with the use of other plant ashes expressly prohibited,[87] thus highlighting the importance of these ashes to the Venetian glass industry. In addition to specific changes in the raw materials utilized, another significant contribution to the success of Venetian glass was the introduction of new processes for the preparation of the alkali raw materials.[86] The plant ash was shipped to Venice as hard pieces of calcined residue, after which it was pulverized and purified by a series of sieving, filtering, and/or recrystallization steps. These methods removed non-fusible material that would act as particulate matter in the resulting glass, as well as removing other unwanted impurities such as iron and aluminum-containing species.[21,23,84]

The choice of raw materials used by the Venetian glassmakers, coupled with their innovative purification methods, resulted in significantly improved glasses that dominated the industry for hundreds of years. The preparation and purification methods utilized removed unwanted colorants, as well as insoluble, nonfusible components from the resulting glass products. Not only did this result in much clearer glass, but this also removed particles that would have acted as stress points during rapid heating. In addition, the reduced soda content combined with the higher amounts of the stabilizing oxides would result in a material that exhibited both higher chemical durability and less thermal expansion.[18,22,73] As a result, the improved Venetian glass would therefore be more resistant to the action of water, acids, and bases, and would be less affected by rapid temperature changes, thus making it much more favorable for laboratory glassware in comparison to the previous Roman glass. As such, it is not surprising that this time period also exhibited a gradual shift of chemical apparatus from pottery and metal to the greater application of glass.[22,73,76]

MIRRORS, EYEGLASSES, AND LENSES

In addition to the production of higher quality glass, the Venetians also introduced a number of innovations for the production of novel forms of glass objects, beginning with advances in glass mirrors.[88] Although the production of glass mirrors was known to the Romans, these were limited to very small sizes and thus polished metal mirrors were preferred.[46] Critical factors that limited the previous development of glass mirrors was insufficient methods for producing flat, smooth glass that was still clear and relatively thin, as well as the fact that the initial metal backing was commonly lead or tin, and the application of hot metal onto glass typically resulted in thermal shock and cracking or breaking of the underlying glass substrate.[46,89]

This latter limitation was overcome with the innovation of metallic leaf, rather than molten metal, a discovery credited to the Venetians.[80] This was then further advanced in the 13th century, when the Venetians started to use a slow grinding process in order to produce highly polished mirrors.[88] The grinding and polishing needed to create a large, distortion-free surface, however, required the mirror glass to be made thicker than possible using conventional methods for the fabrication of windows. As a solution, panels of the desired thickness were typically produced by a modification of the original "cast glass" method of producing glass panes, after which the glass sheets were painstakingly ground and polished. Finally, the reflecting metal foil was then fixed to one surface to give very high-quality mirrors, although prohibitively expensive. A superior method of coating glass with a tin-mercury amalgam was then developed during the 14th-15th centuries, again typically credited to Venetian glassmakers. Venice had become a center of mirror production by the 16th century and was viewed to produce the best mirrors in the world.[89] Of course, mirrors were a crucial feature in the later development of optics and their application had significant effects on the developing sciences of physics, chemistry, and astronomy. It has been said that without mirrors, the Renaissance and the Scientific Revolution might not have occurred.[90]

Once the Venetian polishing techniques became more common, the manufacture of spherical glass surfaces became much easier, ultimately resulting in the production of eyeglasses.[88] Although various people have been credited with their invention over time,[91-93] available historical evidence has shown all of these to be false attributions and the inventor of eyeglasses is still unknown.[91,92] Available sources support their appearance in Italy sometime between 1286 and 1292,[91,92,94,95] with Pisa typically given as the most likely site of origin.[92-94] Eyeglasses were being produced in Venice by 1300 and were repeatedly referenced in guild regulations during the first two decades of the 14th century.[92,93,96] In fact, Venice became such an important production center for eyeglasses that Venetian spectacle makers left the glassmakers' guild to form their own guild in 1320.[93]

The earliest eyeglasses were comprised of two separate lenses and frames, held together with a central rivet (Fig. 12A).[93,94] These initial spectacles utilized convex lenses (Fig. 12B),[95,96] thus improving vision for the farsighted and used primarily for reading.[92,93] Concave lenses, for the nearsighted, were more difficult to work and did not arrive until the mid-15th century.[94-96] It has been stated that eyeglasses are one of mankind's most beneficial material inventions. Without them, people born with poor vision would be illiterate or have insufficient vision for a skilled trade. Even most people born with normal vision typically lose the ability to focus by their mid-40s.[93,95] As a consequence, it is believed that this single invention effectively doubled the intellectual life span of the average person beginning in the 13th century, significantly impacting society as a whole. Of course, as with mirrors, high-quality lenses were critical for the development of optics, as well as allowing later discoveries such as the microscope and telescope.[88]

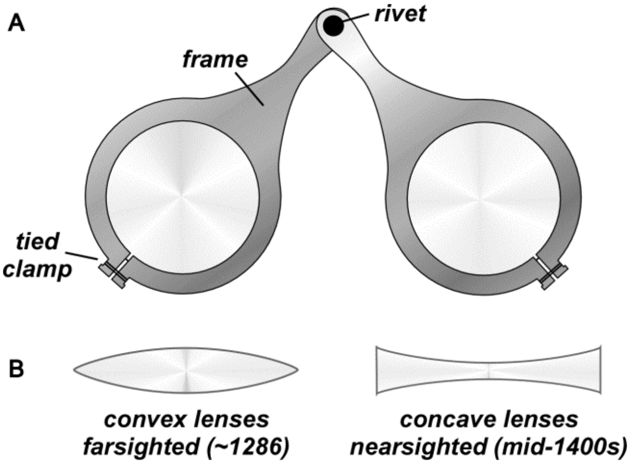

Figure 12. Early eyeglasses design (A) and convex versus concave lenses (B) [adapted from reference 87 with permission from Springer Nature].

FROM WALDGLAS TO BOHEMIAN GLASS

Glass in the West followed a different path following the fragmentation of the Roman Empire.[78] Under Roman rule, glasshouses had been established in the western provinces of Gaul and Britannia prior to the 3rd century CE, including sites at Boulogne, Trier, Cologne, Manchester, and Leicester.[7,16,56] By ~500 CE, the Western Empire fell to German tribes and although glassmaking essentially ceased in the West for a period, the established glasshouses survived and the knowledge of glass production was not completely lost. Reduced access to raw materials unavoidably produced glass exhibiting the character of the local silica and flux used and made it no longer possible to achieve colorless glass.[39] Such northern glass produced in the Middle Ages was sometimes referred to as *Waldglas* (forest glass), and was commonly dark green or brown due to contained impurities.[23,97]

A critical raw material for the production of high-quality soda lime glass was the natron imported from Egypt. However, without suitable access to the previously imported soda, several northern glasshouses started to use the ash of wood logs as the primary flux for glass production as early as 800 CE.[16,18,98,99] Beech was most commonly used for this purpose, although other species such oak, spruce, and birch were also used.[98,100] In comparison to the previously discussed soda-rich ashes obtained from plants grown near the sea or in salty soil, inland species typically provide ash higher in potash (K_2CO_3).[23] Thus, the ash of the various trees used was very low in soda, but all exhibited significant potash content (up to 37%) along with very high levels of calcium.[21,99] Thus by the 10th century CE, glass in the northern glasshouses was produced from a combination of the tree ash and local sands to give a potash-lime formula.[16,18,24,100] Chemical analysis of northern glasses of this time period have revealed high potassium and calcium content (11.8 and 17.9%, respectively) coupled with low sodium (1.63%), although potash-lime glass produced from 780-1000 CE was also quite variable and not as consistent as later glasses.[99]

In comparison to soda-lime glass, potash-lime glasses exhibited significantly different physical properties. For example, the application of potash as the flux could reduce the melting point of the silica to low as 750 °C, compared to the value of ca. 1000 °C achieved with soda.[101] In addition, potash-lime glass was heavier and harder than soda-lime glasses, which made it better for cutting and engraving, although it was also typically not as clear. Due to its lower melting temperature and the simple availability of trees in the Northern European forests, potash-lime glass could be inexpensively mass-produced, making it very desirable, particularly for the production of windows.[99,100]

Such northern potash-lime glass is often viewed as reaching its greatest heights with the material known as Bohemian glass. Although it is named after the Bohemian forests where it was developed, it is typically viewed as a German glass, as its origin stems from efforts by Rudolph II, Emperor of Germany and King of Bohemia, to start an establishment in Prague to make cut glass in imitation of rock-crystal.[97,102] As such, he recruited famous engravers of rock-crystal to Prague in the late 16th century, most critical of which was a German named Lehmann who came to Prague in 1590.[97] Glassworks had been established in the Bohemian and Silesian forests as early as the 15th century, but the glass produced was typical of other northern glasshouses and primarily copied Venetian glass forms.[97,98,102] Lehmann, however, developed a new style of glass-cutting and engraving that served as the basis of Bohemian forms. To facilitate the cut glass, heavier and thicker forms were developed, with the first such Bohemian glasses being white glass cut in facets and engraved with images. At a later period, both colored and colorless glass were also made.[97,102] A new Bohemian glass was then introduced in 1683 under the name of *Kreideglas* (chalk glass), which is the first verified glass that used lime as a significant component. This reputedly improved glass is ascribed to Michael Müller, developed in his factory in southwest Bohemia,[20] and the analyses of Bohemian glasses dated to the end of the 17th century are consistent with the use of lime.[98]

It was not long before Bohemian glass competed successfully with Venetian glass and, by 1730, it had completely supplanted Venetian glass in terms of artistic form.[97,102] Furthermore, it was in the early period of the 19th century that the chemical laboratory underwent what has been described as the "*glassware revolution*".[103] As such, what started with the gradual replacement of other materials (copper and pottery) with Venetian glass had now transitioned to a laboratory consisting primarily of chemical glassware, the majority of which was now produced from Bohemian glass.

CONCLUSION

The introduction of borosilicate glass in the 1880s ultimately ended the reign of the simpler soda-lime and potash-lime glasses, with brands such as Pyrex offering greater thermal and chemical stability and thus dominating most practical applications of glass.[104] Still, many of the everyday innovations commonly associated with glass began with these simpler formulations, including windows, glass mirrors, eyeglasses and lenses, and of course, chemical glassware. Needless to say, silicon in the guise of such silica-based glasses had unimagined impact on science and society, long before the element was ultimately isolated in the early 19th century.

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Mendeleev at Home[1]

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Abstract. Dmitri Mendeleev was "at home" at the St. Petersburg State University for forty years. The museum set up in his former place of work/living quarters is well worth a visit.

Keywords. Mendeleev Museum, Mendeleev Archives, personal effects, memorabilia, laboratory equipment.

INTRODUCTION

Situated along the banks of the Neva River is St. Petersburg State University, just a short walk over the Dvortsovyy Bridge from the Hermitage Museum. Founded in 1724 by decree of Czar Peter the Great, the university still occupies the massive building designated by Peter as the "Twelve Colleges." And it is here, on the street now called Mendeleevskaya liniya, that the Mendeleev Museum and Archives (Figure 1) is located.

This remarkable museum was originally the apartment designated for the university's professor of chemistry and laboratory curator. In that capacity, Dmitri Mendeleev (1834–1907) lived here with his wife, Anna Popova-Mendeleeva, during his professorial tenure from 1866 to 1890. It was here that he wrote many of his scientific papers.[2] After his death in 1907 the university and the Russian Chemical Society purchased his personal library, archives, and some furniture from his widow. These effects formed the basis of the museum that was established there only four years later in 1911.

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[1] This essay is reprinted (with added photographs and references) with the kind permission of the Science History Institute, Philadelphia, PA, USA. https://www.sciencehistory.org/distillations/magazine/mendeleev-at-home, last accessed 12 March 2019.

[2] Mendeleev was never elected to the Russian Academy of Sciences, which would have supplied the living quarters, research facilities, etc. for life. Although he was, admittedly, the most famous Russian scientist both at home and abroad, his nomination was turned down by the so-called "German Party," which, in 1881, elected Friedrich Konrad Beilstein (1838-1906) instead. In response, the Russian Chemical Society, of which Mendeleev was one of the founders, drew up a statement that said, in part: "The indisputable value of the services of this candidate, whose equal cannot be found in Russian science, and his reputation abroad, make his rejection entirely incomprehensible." H. M. Leicester, *J. Chem. Educ.* **1948**, *25*, 439.

Figure 1. Plaque at the Entrance of the Mendeleev Museum and Archives. Courtesy of Jan and Mary Kochansky. It reads: "Here the great Russian chemist Dmitrii Ivanovich Mendeleev taught, worked and lived from 1850-1890."[3]

CENTRAL ATTRACTIONS

The central attractions of the museum are the three rooms that were originally Mendeleev's living room, dining room, and study. The first room contains memorabilia associated with his childhood and youth, as well as photographs of family members, artists, scientists, architects, and close colleagues who gathered for socializing and conversation each Wednesday evening. (As a chemist, Mendeleev acted as an adviser to artists and architects on the composition of pigments and of building materials.)

Figure 2. Mendeleev photographs and memorabilia. Photograph courtesy of Roger Rea.

The second room, which in Mendeleev's lifetime served as a dining room, is devoted to recording Mendeleev's life before he came to St. Petersburg University, including his study at the Main Pedagogical Institute in St. Petersburg from 1850 to 1855 and his work trip to Heidelberg from 1859 to 1861. Also recorded in the second room is his discovery of the periodic law in 1869. Here the visitor can view his stand-up desk (he was a very tall man for the times) and some of his monographs on a variety of subjects, such as mineralogy, isomorphism, and specific volume. These monographs reflect Mendeleev's early interest in connecting internal properties to external form. There are also some examples from his mineral collection and the wooden models of crystalline forms that he constructed himself.

The third, and most evocative room, is Mendeleev's reconstructed study, where everything remains as it was during the last years of his life. Here one can see, among other items, a group of photographs of Mendeleev with the discoverers of some of his "eka-elements" (elements whose future discovery Mendeleev predicted in 1869): Lars Fredrik Nilson (1840-1899), who discovered scandium in 1879;[4] Paul-Émile Lecoq de Boisbaudran (1838-1912), who discovered gallium in 1875;[5] and Clemens Winkler (1838-1904), who discovered germanium in 1886.[6]

MENDELEEV'S MAJOR CONTRIBUTIONS TO CHEMISTRY

The museum also conserves Mendeleev's personal archives. This famous collection has as its base a cataloging system developed by Mendeleev himself and consists of over 35,000 titles, encompassing manuscripts, draft

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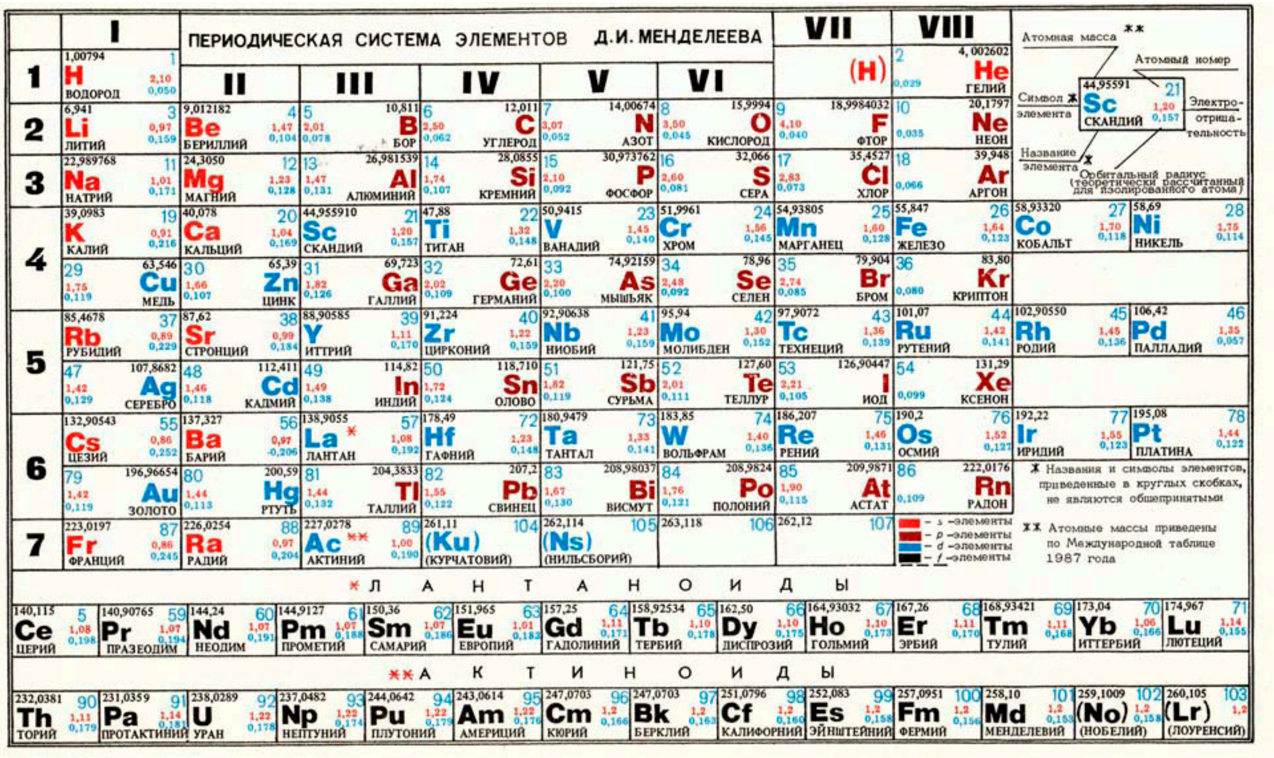
[3] Translation courtesy of David Lewis, University of Wisconsin, Eau Claire, WI, USA

[4] Nilson, L. *C. R. Chim.* **1879**, *88*, 642.

[5] P.-É. Lecoq de Boisbaudran, *C. R. Chim.* **1875**, *81*, 493.

[6] Winkler, C., *J. prakt. Chem.* **1887**, *36*, 177.



ПЕРИОДИЧЕСКАЯ СИСТЕМА ЭЛЕМЕНТОВ Д.И. МЕНДЕЛЕЕВА

	I	II	III	IV	V	VI	VII	VIII		
1	1,00794 1 H ВОДОРОД 2,10 0,050						(H)	4, 002602 2 He ГЕЛИЙ 0,029		
2	6,941 3 Li ЛИТИЙ 0,97 0,159	9,012182 4 Be БЕРИЛЛИЙ 1,47 0,104	10,811 5 B БОР 2,01 0,078	12,011 6 C УГЛЕРОД 2,50 0,062	14,00674 7 N АЗОТ 3,07 0,052	15,9994 8 O КИСЛОРОД 3,50 0,045	18,9984032 9 F ФТОР 4,10 0,040	20,1797 10 Ne НЕОН 0,035		
3	22,989768 11 Na НАТРИЙ 1,01 0,171	24,3050 12 Mg МАГНИЙ 1,23 0,128	26,981539 13 Al АЛЮМИНИЙ 1,47 0,131	28,0855 14 Si КРЕМНИЙ 1,74 0,107	30,973762 15 P ФОСФОР 2,10 0,092	32,066 16 S СЕРА 2,60 0,081	35,4527 17 Cl ХЛОР 2,83 0,073	39,948 18 Ar АРГОН 0,066		
4	39,0983 19 K КАЛИЙ 0,91 0,216	40,078 20 Ca КАЛЬЦИЙ 1,04 0,169	44,955910 21 Sc СКАНДИЙ 1,20 0,157	47,88 22 Ti ТИТАН 1,32 0,148	50,9415 23 V ВАНАДИЙ 1,45 0,140	51,9961 24 Cr ХРОМ 1,56 0,145	54,93805 25 Mn МАРГАНЕЦ 1,60 0,128	55,847 26 Fe ЖЕЛЕЗО 1,64 0,123	58,93320 27 Co КОБАЛЬТ 1,70 0,118	58,69 28 Ni НИКЕЛЬ 1,75 0,114
	63,546 29 Cu МЕДЬ 1,75 0,119	65,39 30 Zn ЦИНК 1,66 0,107	69,723 31 Ga ГАЛЛИЙ 1,82 0,126	72,61 32 Ge ГЕРМАНИЙ 2,02 0,109	74,92159 33 As МЫШЬЯК 2,20 0,100	78,96 34 Se СЕЛЕН 2,48 0,092	79,904 35 Br БРОМ 2,74 0,085	83,80 36 Kr КРИПТОН 0,080		
5	85,4678 37 Rb РУБИДИЙ 0,89 0,229	87,62 38 Sr СТРОНЦИЙ 0,99 0,184	88,90585 39 Y ИТТРИЙ 1,11 0,170	91,224 40 Zr ЦИРКОНИЙ 1,22 0,159	92,90638 41 Nb НИОБИЙ 1,23 0,159	95,94 42 Mo МОЛИБДЕН 1,30 0,152	97,9072 43 Tc ТЕХНЕЦИЙ 1,36 0,139	101,07 44 Ru РУТЕНИЙ 1,42 0,141	102,90550 45 Rh РОДИЙ 1,45 0,136	106,42 46 Pd ПАЛЛАДИЙ 1,35 0,057
	107,8682 47 Ag СЕРЕБРО 1,42 0,129	112,411 48 Cd КАДМИЙ 1,46 0,118	114,82 49 In ИНДИЙ 1,49 0,138	118,710 50 Sn ОЛОВО 1,72 0,124	121,75 51 Sb СУРЬМА 1,82 0,119	127,60 52 Te ТЕЛЛУР 2,01 0,111	126,90447 53 I ИОД 2,21 0,105	131,29 54 Xe КСЕНОН 0,099		
6	132,90543 55 Cs ЦЕЗИЙ 0,86 0,252	137,327 56 Ba БАРИЙ 0,97 -0,206	138,9055 57 La * ЛАНТАН 1,08 0,192	178,49 72 Hf ГАФНИЙ 1,23 0,148	180,9479 73 Ta ТАНТАЛ 1,33 0,141	183,85 74 W ВОЛЬФРАМ 1,40 0,136	186,207 75 Re РЕНИЙ 1,46 0,131	190,2 76 Os ОСМИЙ 1,52 0,127	192,22 77 Ir ИРИДИЙ 1,55 0,123	195,08 78 Pt ПЛАТИНА 1,44 0,122
	196,96654 79 Au ЗОЛОТО 1,42 0,119	200,59 80 Hg РТУТЬ 1,44 0,113	204,3833 81 Tl ТАЛЛИЙ 1,44 0,132	207,2 82 Pb СВИНЕЦ 1,55 0,122	208,98037 83 Bi ВИСМУТ 1,67 0,130	208,9824 84 Po ПОЛОНИЙ 1,76 0,121	209,9871 85 At АСТАТ 1,90 0,115	222,0176 86 Rn РАДОН 0,109		
7	223,0197 87 Fr ФРАНЦИЙ 0,86 0,245	226,0254 88 Ra РАДИЙ 0,97 0,204	227,0278 89 Ac ** АКТИНИЙ 1,00 0,190	261,11 104 (Ku) (КУРЧАТОВИЙ)	262,114 105 (Ns) (НИЛЬСБОРИЙ)	263,118 106	262,12 107			

*ЛАНТАНОИДЫ

140,115 5 Ce ЦЕРИЙ 1,08 0,198	140,90765 59 Pr ПРАЗЕОДИМ 1,07 0,194	144,24 60 Nd НЕОДИМ 1,07 0,191	144,9127 61 Pm ПРОМЕТИЙ 1,07 0,188	150,36 62 Sm САМАРИЙ 1,07 0,186	151,965 63 Eu ЕВРОПИЙ 1,01 0,182	157,25 64 Gd ГАДОЛИНИЙ 1,11 0,171	158,92534 65 Tb ТЕРБИЙ 1,10 0,178	162,50 66 Dy ДИСПРОЗИЙ 1,10 0,175	164,93032 67 Ho ГОЛЬМИЙ 1,10 0,173	167,26 68 Er ЭРБИЙ 1,11 0,170	168,93421 69 Tm ТУЛИЙ 1,11 0,168	173,04 70 Yb ИТТЕРБИЙ 1,06 0,166	174,967 71 Lu ЛЮТЕЦИЙ 1,14 0,155

**АКТИНОИДЫ

232,0381 90 Th ТОРИЙ 1,11 0,179	231,0359 91 Pa ПРОТАКТИНИЙ 1,14 0,181	238,0289 92 U УРАН 1,22 0,178	237,0482 93 Np НЕПТУНИЙ 1,22 0,174	244,0642 94 Pu ПЛУТОНИЙ 1,22 0,179	243,0614 95 Am АМЕРИЦИЙ 1,22 0,176	247,0703 96 Cm КЮРИЙ 1,2 0,166	247,0703 97 Bk БЕРКЛИЙ 1,2 0,163	251,0796 98 Cf КАЛИФОРНИЙ 1,2 0,160	252,083 99 Es ЭЙНШТЕЙНИЙ 1,2 0,158	257,0951 100 Fm ФЕРМИЙ 1,2 0,156	258,10 101 Md МЕНДЕЛЕВИЙ 1,2 0,153	259,1009 102 (No) (НОБЕЛИЙ) 1,2 0,158	260,105 103 (Lr) (ЛОУРЕНСИЙ) 1,2

Атомная масса **
Атомный номер
Символ * элемента
Электро-отрицательность
Название * элемента
Орбитальный радиус (теоретически рассчитанный для изолированного атома)

44,95591 21 Sc СКАНДИЙ 1,20 0,157

* Названия и символы элементов, приведенные в круглых скобках, не являются общепринятыми

🟥 – s -элементы
🟫 – p -элементы
🟦 – d -элементы
⬛ – f -элементы

** Атомные массы приведены по Международной таблице 1987 года

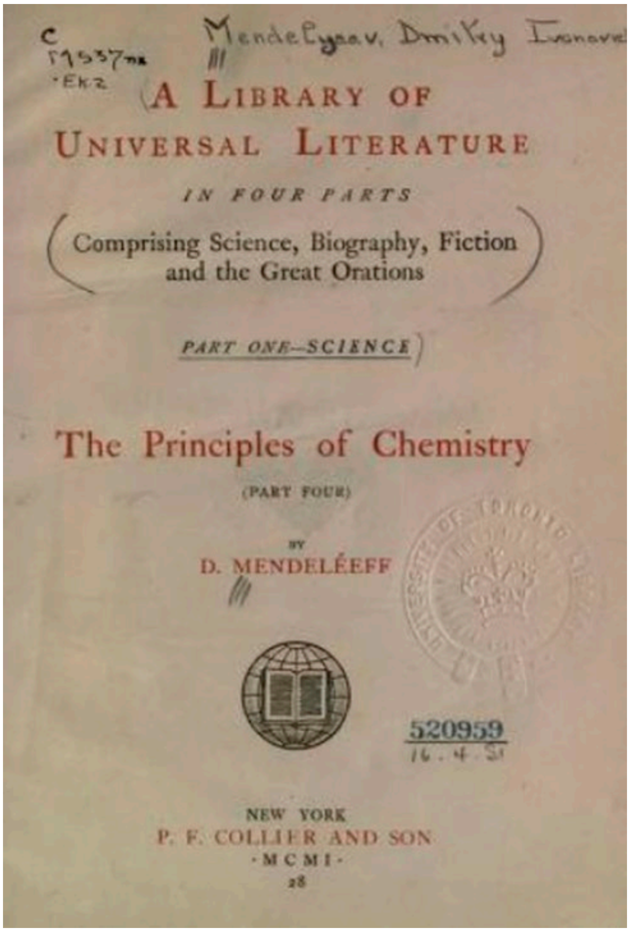
Figure 3. A Russian Periodic Table showing elements 104 and 105 as kurchatovium and nielsbohrium respectively. Courtesy of Mary and Jan Kochansky.

Figure 4. Mendeleev's Study. Photograph courtesy of Margaret Comaskey.

Figure 5. Mendeleev's Apparatus for Measuring Gas Densities. Photograph courtesy Roger Rea.

documents, letters, telegrams, diaries, notebooks, laboratory registers, expenditure accounts, and correspondence with Russian and foreign scientists. In addition, over 200 scientific instruments, many of them built specifically for Mendeleev, are housed here. There is also a world map that shows all the places Mendeleev visited (including northwestern Pennsylvania) as part of his scientific travels.

Although Mendeleev is best remembered for his discovery of the periodic law, his other major achievements were authorship of a major textbook, *Principles of*



Mendelyeev, Dmitry Ivanovi

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Figure 6. Title Page of a 1901 American reprinting of the the English edition of Mendeleev's "Principles of Chemistry."[7]

Figure 7. Mendeleev Monument (Ilya Ginzburg, 1930). On the wall behind is the famous giant version of the Periodic Table. The building is the former Bureau of Weights and Measures where Mendeleev was Director. It now houses the Mendeleev All-Russian Institute of Meteorological Research. Photograph: Mary Virginia Orna.

Chemistry (which included the periodic law), his studies on the elasticity of gases, and his studies of solutions as associations, to say nothing of his far-ranging eclectic interests in a variety of other fields. A visit to this museum evokes an appreciation for all of his interests in one small space.

If the Mendeleev aficionado's curiosity has not been satisfied with this museum chock-full of memorabilia, a short subway ride to the Technological Institute (via line 1 or line 2) will bring him or her face to face with the famous cigar-smoking Mendeleev statue at the foot of the giant periodic table built into the wall of one of the university buildings. From the viewpoint of this explorer, it is well worth the journey.

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[7] Mendeleev's "Principles of Chemistry." https://archive.org/details/principlesofchem00menduoft/page/n4 , last accessed 21/03/2019.

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