The development of the Periodic Table

There are numerous substances, and they can react with each other in numerous ways. However, even during alchemy, there was a strong belief that substances can be classified. However, the notion of element was a completely different one: the four elements Water, Fire, Earth and Air were described by Aristotle with reference to Empedokles. However, they carry properties instead of being elements in our modern sense. Consequently our chemical element water is not identical with the ancient elementary principle Water, as our water can become solid (and thus has some properties of the principle of Earth, and can be transformed in a gaseous state, thus carries also some principles of Air (see e.g. Priesner 2011).

Elementary property	Cold	Heat
Dry	Earth	Fire
Moist	Water	Air

Thus what we have is the notion of elements, but nor in the sense we use it nowadays. However, there is another idea that can be taken as being relevant to the conceptual development of chemistry that materializes in the Periodic Table: The idea of classifying chemical substances: According to the Aristotelian understanding, gold was the purest of all metals. However, this metal could be degraded, and thus be transformed in less pure substances (This is the basis of the idea of transmutation which alchemist tried to carry out in order to refine metals so that in the end they would have gold again.). It has to be understood that alchemy has to be taken as being the fundamental basis of chemistry, particularly on the level of procedures. Alchemists aimed at composing and separating materials, thus in the end by recombining elementary principles to arrive at new materials and possibly gold.

Thus a development towards the Periodic Table can only be identified when this understanding of transmutation had been overcome in favor of an understanding where some simple substances which cannot be separated by any kind of operation into simpler substances exist and form the basis for compound substances. Probably the first to develop this understanding (or at least to publish a treatise that shows this understanding) was Robert Boyle. In his monograph The sceptical chemist he distinguished chemistry from alchemy and developed an understanding of chemical elements that bears the basis of our notion. He pointed out that “ … I now mean by elements … 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.” (Boyle 1661, 187)[1]

Whilst elements became some sort of standard in chemical argumentation, it remained unclear what elements are and what compound substances are. To give but two examples: air was considered to be an element until well into the 18th century when several chemists started almost simultaneously their study of pneumatics and were able to show that air was a combination of several gases. Until the end of the 18th century, phlogiston was a substance that was accepted by most natural philosophers, however, when Lavoisier established his new chemical theory that went together with a new chemical nomenclature, and the first listing of chemical elements. In Lavoisier’s system phlogiston did not exist anymore, however, he included instead the imponderable (meaning weightless) element calorique together with the equally imponderable lumic that was the substance of light. These elements were kept well into the 19th century and were only omitted when the concept of energy became more and more established.

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[1] See also http://www.chemheritage.org/discover/online-resources/chemistry-in-history/themes/early-chemistry-and-gases/boyle.aspx, last access 06.03. 2012

TABLE OF SIMPLE SUBSTANCES.

Simple ſubſtances belonging to all the kingdoms of nature, which may be conſidered as the elements of bodies.

New Names.	Correſpondent old Names.
Light	Light.
Caloric	Heat. Principle or element of heat. Fire. Igneous fluid. Matter of fire and of heat.
Oxygen	Dephlogiſticated air. Empyreal air. Vital air, or Baſe of vital air.
Azote	Phlogiſticated air or gas. Mephitis, or its baſe.
Hydrogen	Inflammable air or gas, or the baſe of inflammable air

Oxydable and Acidifiable ſimple Subſtances not Metallic.

New Names.	Correſpondent old names.
Sulphur Phoſphorus Charcoal	The ſame names.
Muriatic radical Fluoric radical Boracic radical	Still unknown.

Oxydable and Acidifiable ſimple Metallic Bodies.

New Names.		Correſpondent Old Names.
Antimony	Regulus of	Antimony.
Arſenic		Arſenic.
Biſmuth		Biſmuth.
Cobalt		Cobalt.
Copper		Copper.
Gold		Gold.
Iron		Iron.
Lead		Lead.
Mangeneſe		Manganeſe.
Mercury		Mercury.
Molybdena		Molybdena.
Nickel		Nickel.
Platina		Platina.
Silver		Silver.
Tin		Tin.
Tungſtein		Tungſtein.
Zinc		Zinc.

Salifiable ſimple Earthy Subſtances

New Names.	Correſpondent old Names.
Lime	Chalk, calcareous earth. Quicklime.
Magneſia	Magneſia, baſe of Epſom ſalt Calcined or cauſtic magneſia
Barytes	Barytes, or heavy earth.
Argill	Clay, earth of alum.
Silex	Siliceous or vitrifiable earth.

Figure 1 Lavoisier's list of elements
http://www3.ul.ie/~childsp/CinA/Issue43/cianct6.jpg
last access 30-08-13

It gets evident that – even though he did not use a systematic – Lavoisier classified his elements into metals, non metals, earthly substances, and simple substances. This organization is based on the properties of the elements: materials with similar behavior in chemical reactions were classified as similar. However, this organization of elements is still very simple and should probably not be considered as a classification. Yet, there is another aspect which is crucial in Lavoisier's work with respect to the development of the Periodic Table: he analyzed chemical reactions quantitatively; in this respect he formulated the law of the conservation of mass according to which the masses of the educts in a chemical reaction equals the masses of the products.

Possibly the first to develop a classification of chemical elements was the pharmacist Johann Wolfgang Döbereiner (1780-1849). Being not formally trained as a chemist, he still got an appointment in 1810 at the University of Jena. However his training enabled him to perform chemical operations in his laboratory as well as in his teaching. From his experiments, he noted that there are several groups of three chemical elements that behave very similar to each other in reactions. He could find several combinations of elements, and there were always three elements. Moreover, these elements did not just react similarly, but they had also some fundamental connections: Most notably, calcium, strontium, and barium did not just show a similar behavior; moreover, their masses had a certain ratio, the mass of strontium being the mean of the ones of calcium and barium. Döbereiner called these triplets 'triads'. In an article published in the Annalen der Physik, Döbereiner referred to measurements by Berzelius that showed that a similar ratio occurred in the triad formed by the elements chlorine, bromide, and iodine. In the end, Döbereiner war able to form ten triads which covered thirty out of the 53 elements that were known at that time.

Some German chemists tried in the following years to expand this systematization; particularly Gmelin expanded Döbereiner's system by allowing groups of more than three elements. However, in the end the system became not accepted.

Some thirty years after Döbereiner's attempt to systematize chemical elements, other chemists developed different kinds of classification. Among them were Jean Baptiste André Dumas and Max von Pettenkofer, who both argued that a mathematical expression can be found for the atomic weight of elements with similar chemical behavior. Other chemists argued that the chemical stoichiometric relation of several substances is related to their masses and thus an indication of an ordering principle – e.g. CH4, NH3, OH2, and FH.

Compared to these researchers, the French Alexandre-Emile Béguyer de Chancourtois made one step further. He ordered the chemical elements in a sort of spiral according to their atomic mass – a structure he called ‘vis tellurique’. In doing so, he observed that – placing the elements in a row with growing atomic masses and with adequate dimensions of the spiral, some chemical elements that stood in this construction above each other showed remarkable similarities in their behavior.

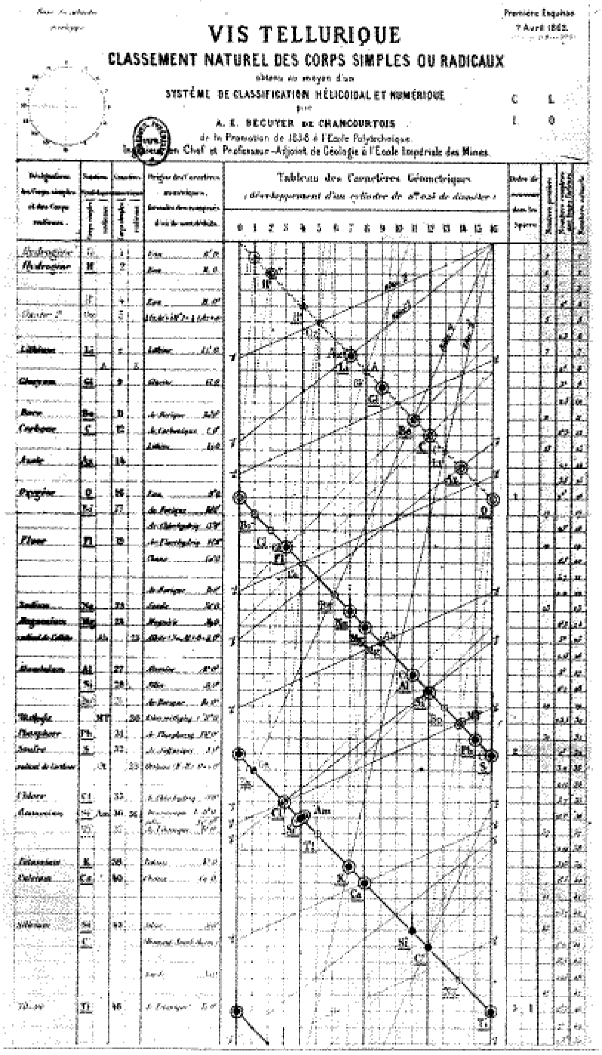

Figure 2 Chancourtois order of the elements http://upload.wikimedia.org/wikipedia/

commons/5/57/Telluric_screw_of_De_Chancourtois.gif, last access 30-08-13

Another researcher who developed a systematization of the growing number of chemical elements was the British John Alexander Reina Newlands who published his work also in the 1860ies. Newlands observed that “ ‘If the elements are arranged in order of their equivalents [ie relative atomic masses in today’s terminology] with a few transpositions, it will be seen that elements belonging to the same group appear in the same horizontal line. Also the numbers of similar elements differ by seven or multiples of seven. Members stand to each other in the same relation as the extremities of one or more octaves of music. Thus in the nitrogen group phosphorus is the seventh element after nitrogen and arsenic is the fourteenth elements after phosphorus as is antimony after arsenic. This peculiar relationship I propose to call The Law of Octaves'.”[2] Newland related this structure of the elements to the musical octaves. This kind of combining musical and scientific systems of classification is not as uncommon as it seems nowadays: Kepler used a similar approach for the planets in the solar system in his Harmonia Mundi. Seemingly, Newland had no conception of the underlying principles , yet, he was able to indicate that there might be some hidden systematics behind the behaviour of the chemical elements. Even though he structured the elements according to their masses, he was well aware that there are some irregularities (where two elements with similar atomic masses are at the ‘wrong position’ when their chemical behaviour is compared to the ones in the other octaves). Consequently, Newland made these elements change their place in his systematisation, thus using no longer only the atomic mass as the strudturing parameter. However, his approach did not gain much acceptance, yet, it can be seen as an indicator that chemists were thinking more and more about classification of chemical elements.[3]

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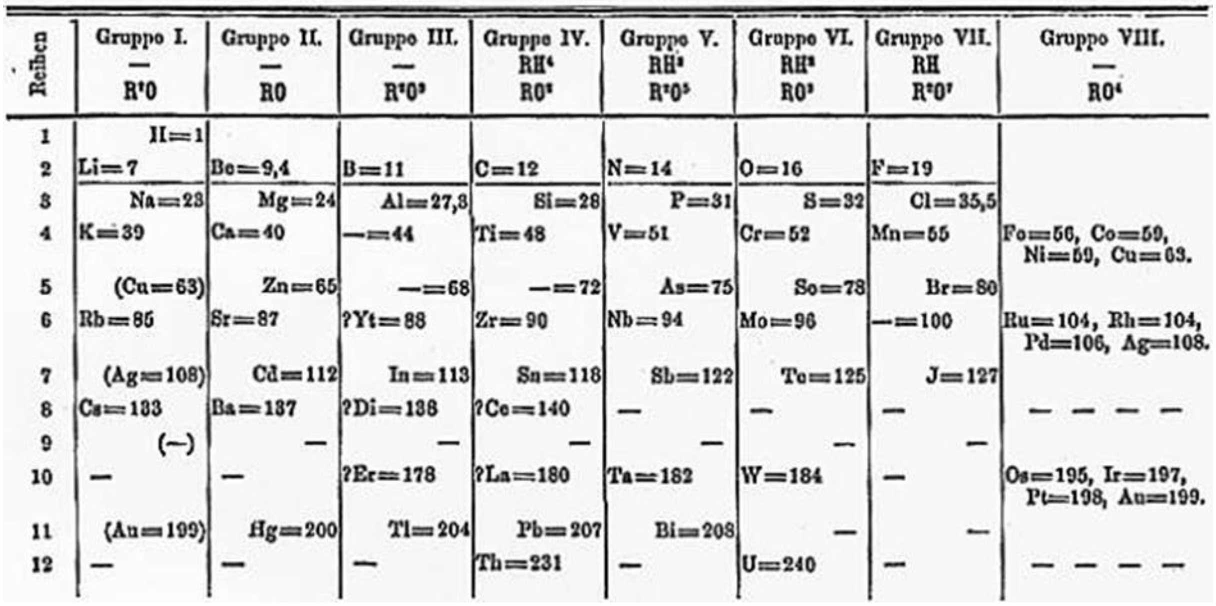
[2] Newland, quoted from http://www.rsc.org/Education/Teachers/Resources/periodictable/pre16/develop/newlands.htm, last access 22.03. 2012. It has to be noted that the noble gases were not known at that time.

[3] It has to be understood that most chemists just arranged the elements in alphabetical order or put together metals and non-metals. A key step towards developing the Periodic System lies in the understanding that a principle to arrange the elements lies in their chemical behavior combined with their atomic masses.

At the end of the 1860ies, two different researchers independently came up with a very similar approach to arrange the chemical elements: Lothar Meyer uand Dmitri Mendeleev. Meyer first published his account in December 1869 in the Annalen für Chemie und Pharmazie, Mendeleev published a detailed paper in 1871 in the same journal without any reference to Meyer's work. Yet, it turned out that this was not Mendeleev's first publication of his understanding, he had already published a description of his work in March 1869 in a Russian journal and thus could claim priority rights.

aluminium, eka-boron, and eka-silicon) were identified and named gallium, scandium and germanium.

This shows the new quality of the approach of Mendeleev: The open positions in Mendelejew's system, where no element could be placed, served as predictor for elements that had not been noticed until then. All the previous attempts to create an order for the chemical elements had not had the potential for such a prediction. Both, Meyer and Mendeleev modified in the following years their Table of Elements (cf. Häusler 1990). Probably both re-



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 3 Mendeleev's structuring of the elements.

http://upload.wikimedia.org/wikipedia/commons/5/55/Mendelejevs_periodiska_system_1871.png,

last access 30-08-13

Evidently, there are some differences between Mendeleev's Table of Elements and the modern Periodic Table. A main difference results from the non existing differentiation between main group and secondary group elements. Additionally, there are no noble gases – they did not exist in either Mendeleev's or Mayer's system.[4] Moreover, the system contains some open positions: Mendeleev's system consisted three additional, suspected element which had the atomic masses of 45, 68, and 70 respectively. A few years later these fictitious elements (which Mendeleev called eka-

searchers independendly came to very similar systematisations of the elements, consequently, the Royal Society London awarded the Copley medal to both of them.

At this point one may ask why in the 1860ies that many chemists came up with different schemes to classify the elements. One probably very relevant aspect in this respect was the outcome of the collaboration of Robert Wilhelm Bunsen and Gustav Robert Kirchhof. They developed the spectroscopic method which enabled researchers to identify several new elements. The more elements were known to chemists, the easier it became to find substances that behaved similar.

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[4] Even though Helium was identified in the solar spectrum, it was not known on Earth at that time. Only at the end of the 19th century, the first identification of a noble gas as a chemical element was described.

Yet, despite this success, there were still some open questions: One was whether more elements existed – actually the detection of the noble gases showed that there was an entire group of elements that had to be added into the system (and which could be integrated into the existing system). However, could there be more elements? An answer to that question was produced by the British physicist Henry Moseley. He demonstrated that a relation existed between the wavelength in the X-ray spectum and the atomic number. From this relation, Moseley concluded: "There are here three possible elements still undiscovered" (Moseley 1913, 713). In some sense, Moseley acts very similar to Mendeleev – he was able to find another mathematical relation that described properties of the atoms, however, there were some gaps in his system of elements. Like Mendeleev, he used these gaps to predict the existence of three new elements, which were later identified as technetium, promethium, and rhenium. However, Moseley's result was even more complex than Mendeleev's – he was not only able to predict the existence of three new elements, he was also able to make an argument that no other element could be found unless it would be heavier than gold.

Having gone that far, there was still one aspect that was irritating in the system: Even though the elements could be arranged according to their chemical and physical behaviour. However, the masses – which were initially one method to arrange the elements – were not constantly increasing, there were a few elements where the atom was lighter than the previous one. Moreover, the masses were not integer multiples of the atomic mass of hydrogen. A solution to this problem was produced by the work of Frederick Soddy and Francis W. Aston. Soddy was able to demonstrate that several radioactive substances consisted of isotopes, atoms with identical chemical properties but (slightly) different masses. Aston develop a device in which he could produce a beam of ionized atoms. this beam was brought into a magnetic field, the deflection was related to the charge and the mass of the atoms. This mass spectrometer, how the device was called, enabled Aston to identify hundreds of isotopes in non-radioactive elements. At the same time, he could demonstrate that most of the elements were a mixture of atoms that had identical chemical properties but different masses. These different atoms were called isotopes, the masses of the isotopes were (almost) integer multiples of the masses of the hydrogen atom, the masses of the elements were the weighted average of the masses of the isotopes.

To summarize, different experimental strategies and conceptual understandings can be identified with respect to the development of our understanding of the Periodic Table: Initially, manipulation of substances was the basis of developing classifications. Only when these had been developed, systematic analysis became successful that – together with the quantitative approach and the different understanding of gases (both established in particular at the end of the 18th century) led to a new systematisation of elements. Whilst this system was still purely empirical, a more thorough conceptual understanding has to be taken into consideration when we look at the development of the modern Periodic System of Elements that includes a conceptual understanding of matter. This models enables a conceptual description of matter for which the Periodic Table is a formal structure that no longer is just an empirically formulated system of systematisation, but the outcome of a complex conceptual understanding.

Note:

Certain aspects that were discussed in this historical background are related to the one on atomism and vice versa.

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