Bernadette Bensaude-Vincent

The role of Mendeleev in the construction of the periodic table of chemical elements

Passion for Science

International Symposium

on the occasion of the International Year of the Periodic Table

BOLOGNA, November 6-7, 2019

UNIVERSITÉ PARIS 1
PANTHÉON SORBONNE

CETCOPRA

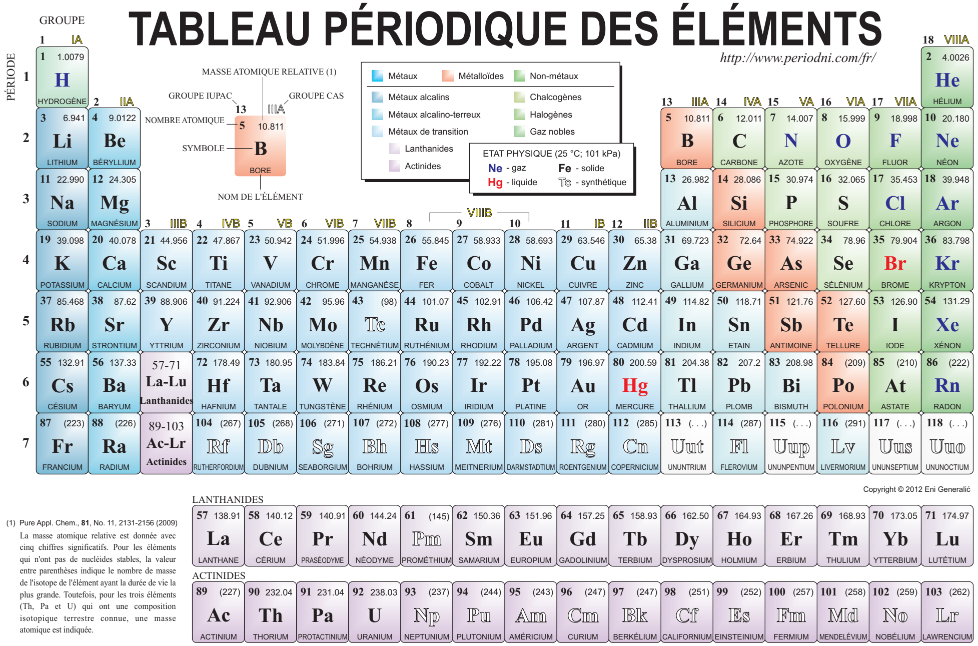
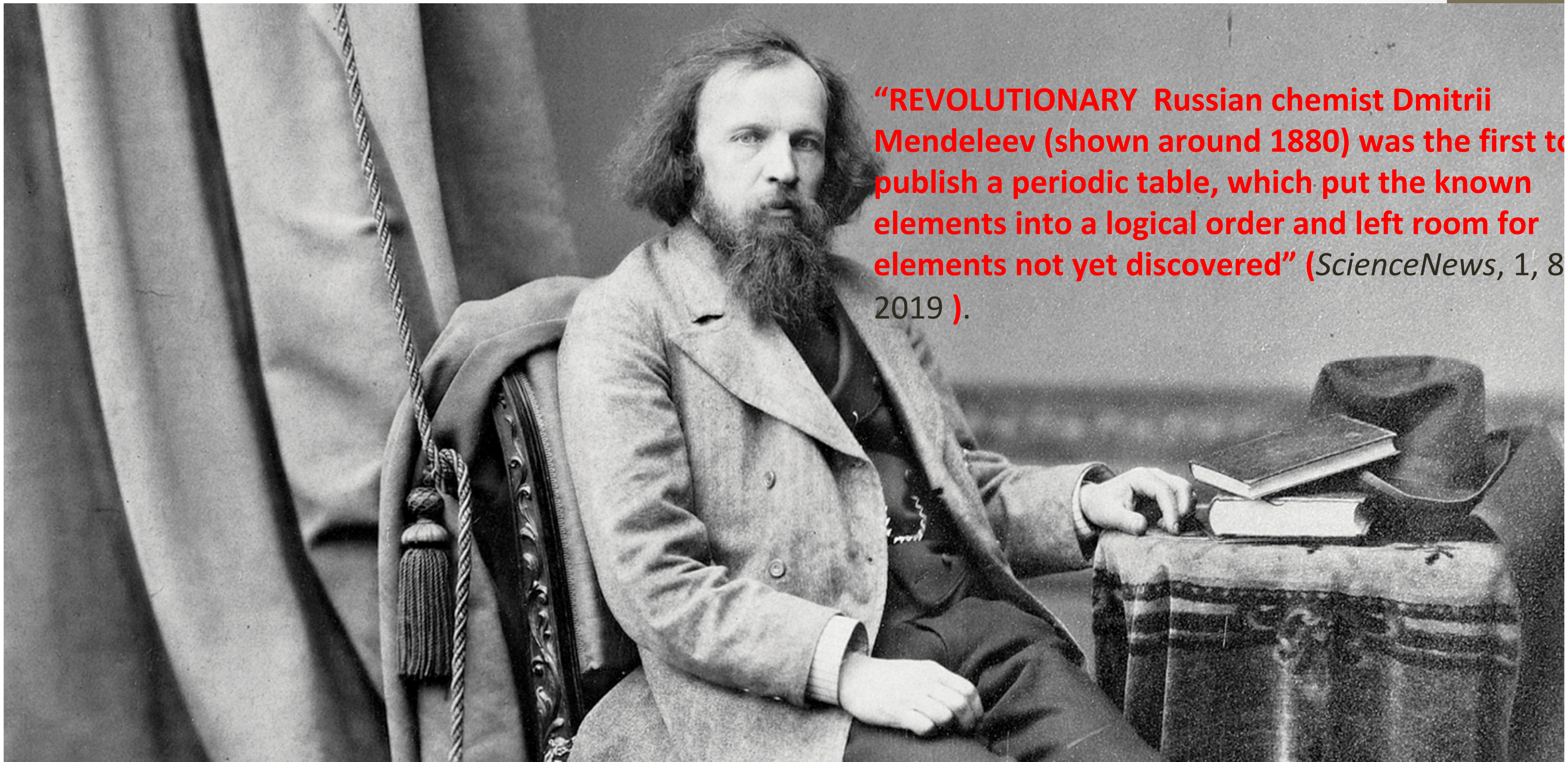


Chart of Nature

- It contains all of the atomic building blocks found so far
- It provides a framework for future elements.

A revolutionary genius?



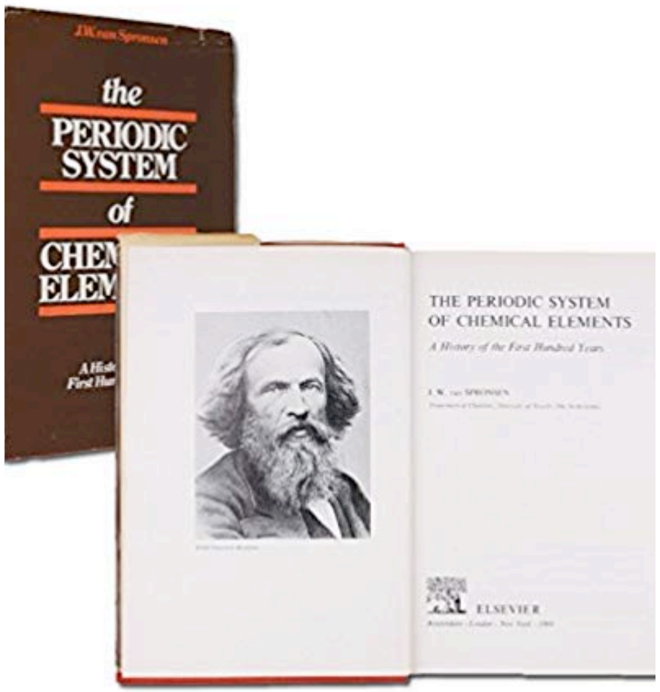
“REVOLUTIONARY Russian chemist Dmitrii Mendeleev (shown around 1880) was the first t publish a periodic table, which put the known elements into a logical order and left room for elements not yet discovered” (*ScienceNews*, 1, 8 2019 **)**.

A prophet?

- in 1869 only 63 of the 105 elements known in 1969=> discovery of the periodic law extremely improbable

- With so few pieces of the puzzle in hands, how did Mendeleev manage to construct a whole picture ?
- (François Dagognet, 1969)

Neither revolutionary…nor Prophet

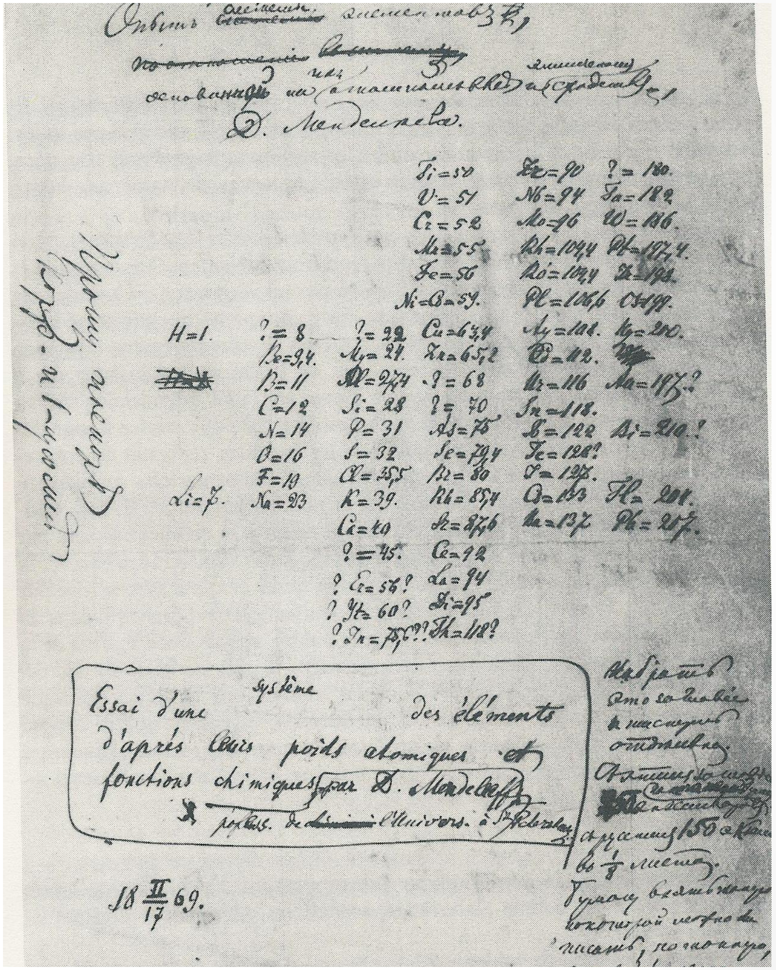


Mendeleev = one among 6 independent co-discoverers

- Alexandre Béguyer de Chancourtois (1862) *vis tellurique*
- John Newlands (1864) law of octaves
- William Odling (1864) system of 57 of the 60 elements known in 1964+ vacant spaces)
- Gustav Hinrichs spiral(1867) “natural classification based on spectral lines”
- Julius Lothar Meyer (1864 and 1868) system including all known elements.

Why Mendeleev's Table?

- Contemporary system is quite different from Mendeleev's table
- Apart from nationalistic claims (cf St Petersburg conference)
- Individual discovery or collective endeavour & world heritage



Overall argument

- More normal science than revolutionary discovery
- Mendeleev’s originality: clear definition of what was to be ordered (element *vs* simple substance) = key in the process of construction of the periodic system
- Feedback of the periodic system on the definition of chemical element

Demographic pressure

Facing an increasing number of simple substances

Avant 1700	1700-1800	1800-1850	1850-1900
antimoine	azote	aluminium	actinium
argent	béryllium	baryum	argon
arsenic	bismuth	bore	césium
carbone	chrome	brome	dysprosium
cuivre	cobalt	cadmium	gadolinium
étain	fluor	calcium	gallium
fer	hydrogène	cérium	germanium
mercure	manganèse	chlore	hélium
or	molybdène	erbium	holmium
phosphore	nickel	iode	indium
plomb	oxygène	lanthane	krypton
soufre	platine	lithium	néodyme
	strontium	magnésium	néon
	tellure	niobium	polonium
	titane	osmium	praséodyme
	tungstène	palladium	radium
	uranium	potassium	rhodium
	yttrium	rubidium	ruthénium
	zinc	sélénium	samarium
	zirconium	silicium	scandium
		sodium	thallium
		tantale	thullium
		thorium	xénon
		vanadium	ytterbium

Teaching Pressure

- Course of general chemistry taught at St Petersburg University beginning in 1867
- Writing a textbook => Principles of Chemistry (1871). How to order the chapters?
- Ch 1: water, Ch 2: composition of water, Ch 3: Oxygen, Ch 4: ozone. Dalton's Law,
- Ch 5:Nitrogen & Air, Ch 6: Hydrogenated compounds of N, Ch 7: atoms & molecules, Ch 8: carbon & hydrocarbons, Ch 9: Compounds of C, O & N
- Ch 10: table salt NaCl. Berthollet's Law. Ch 11: Halogens
- Ch 12: Na, Ch 13: K, Rb, Cs, Li, Ch 14: Equivalents, Mg, Ca, Sr, Ba, Be
- Ch 15: analogies between elements. Periodic Law

Teachers' dilemma

Chemistry professors' puzzle since Lavoisier.

- How to reconcile didactic constraints with natural order?
- From simple to complex => Which simple substances? Alphabetic order?

- Taking into account all properties (natural classification) or one single criterion (artificial classification)?

Natural *vs* artificial classifications

Ampère's natural classification (1816)

- Gazolytes (Anthacides, borides, thionides, arsenides)
- Leucocytes (argirides, calcides, cassitérides, téphralides, zirconïdes)
- Chroïcolytes (titanides, cérides, chromides, sidérides)

Thenard's artificial classification (1813-16)

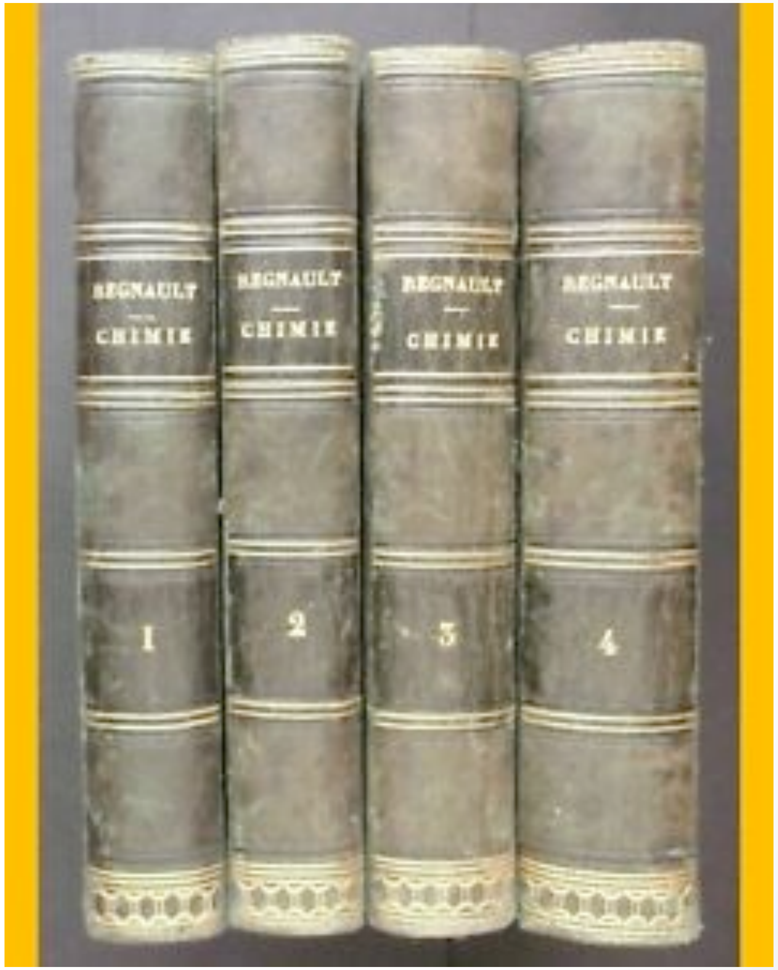
- One single criterion (oxygen reactivity) applied everywhere

Table 2: La classification des métaux de L.J. Thenard D'après le *Traité de chimie élémentaire*, 4e éd. 1824, t.. I, 288–289

Sections	**Métaux**
1	Mg, Be, Y, Al, Th, Zr, Si
2	Ca, Sr, Ba, Li, Na, K
3	Mn, Zn, Fe, Sn, Cd
4	(a) As, Mo, Cr, W, Columbium (b) Sb, U, Ce, Co, Ti, Bi, Cu, Te, Ni, Pb
5	Hg, Os
6	Ag, Pd, Rh, Pt, Au, Ir.

1850s Textbooks: Hybrid classifications

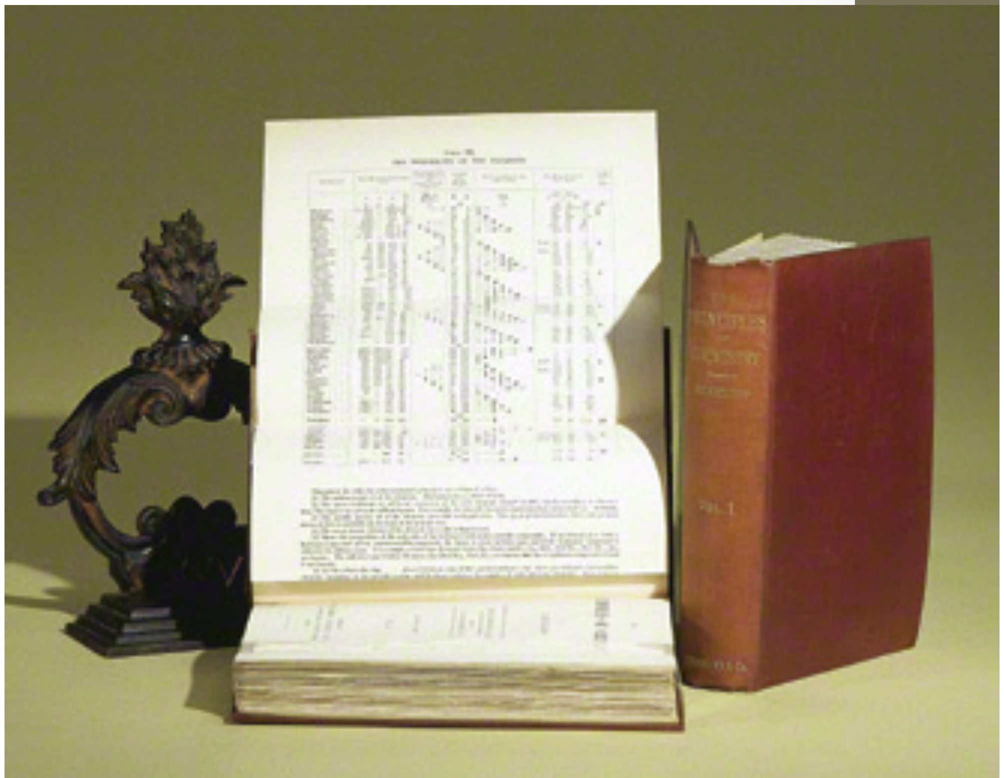
- Artificial for metals (revised version of Thenard's)
- Natural for non-metals (Jean-Baptiste Dumas)



1871: Mendeleev 's *Principles of Chemistry*

Introduction:

alphabetic list of simple substances with reference to Lavoisier.



Lavoisier's definition

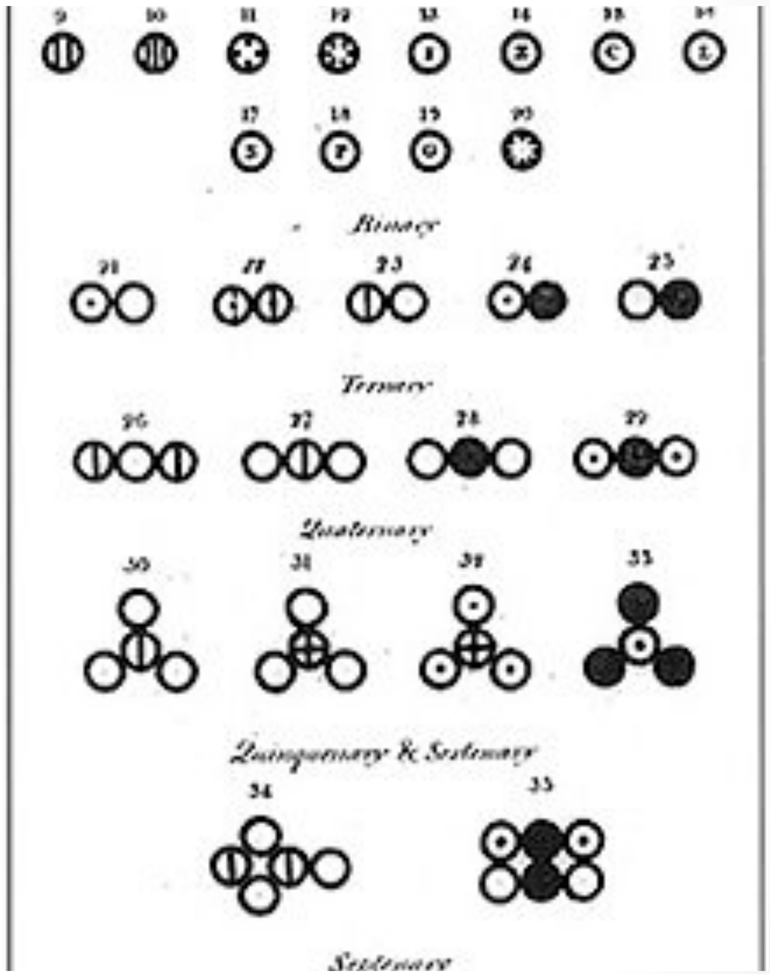
Elements= "all the substances into which we are able to reduce bodies by decomposition. [...] since these principles cannot be separated, rather since we have not hitherto discovered the means of separating them, *they act with regard to us as simple substances*, and we ought never to suppose them compounded until experiment and observation has proved them to be so" (Lavoisier 1799, xxiii).

- Negative criterion deprived the element of positive features=> weak explanatory power of individual behaviour.
- reorganized chemistry along the simple/compound axis
- generated doubts about the simplicity of chemical elements => quest for a reduction of the multiplicity of elements.

Impact of Dalton's atomic theory

- Atomic weight gradually provided a positive attribute to definition of elements

- Speculations about the number of elements William Prout's hypothesis: simple bodies emerged from one single, primary element, hydrogen.



Impetus for classifications based on on atomic weights.

- Looking for arithmetic relations (Johan Döbereiner (1819)

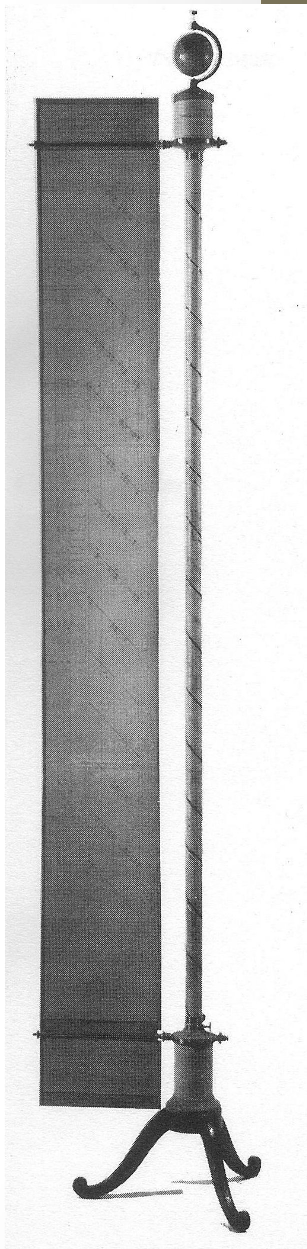
Br=Cl+ 1/2 ; Na= Li+K/2 ; Se= S+Te/2)

- Looking for analogies to detect family features and establish a family tree

Béguyer de Chancourtois

- Vis tellurique (*CRAS*, 1862)

“ c’est seulement par la prise en considération de la loi de Prout que j’arrive à une théorie parfaitement démontrée”



Mendeleev’s alternative approach

- Against Prout’s hypothesis (“obscurantism”, “torments of alchemy”)

- Searching unity in a *general law* rather than in matter itself:

Conceptual clarification

"[I]t 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 the 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" (Mendeleev's lecture notes
St Petersburg University 1867, quoted in Kaji 2002, 6).

3 distinctive features

- conservation > composition
- Abstract *and* material entity
- No mention of atoms

1871 Building a conceptual framework

Just as the words ‘molecule’, ‘atom’, and ‘equivalent’ were used interchangeably, even as recently as the time of Laurent and Gerhardt, so now the terms ‘simple substance’ and ‘element’ are often confounded with one another. However these terms must be sharply distinguished in order to avoid confusion in chemical philosophy. *A simple body is something material, a metal or a metalloid*, endowed with physical and chemical properties. The idea of a simple substance corresponds to that of a molecule […] But in opposition to this, the *term ‘element’ designates those material particles that form simple bodies* and *compounds* and *determine the manner in which they behave* in terms of their physical or chemical properties. The word ‘element’ calls to mind the idea of an atom..” (Mendeleev, 1871, 2).

Simple substances		Molecules
------------------------	=	-------------
Elements		Atoms

Elements as true individuals

Mendeleev's philosophical convictions:

- Against Prout's hypothesis of primary matter (H) as the origin of all other elements. Elements as true individuals

- Atomic weights= identifiers or markers of the *individual* properties of each element rather than markers of the genealogy of elements through their arithmetic relations.

Elements or atoms?

- Mendeleev not always clear. “By replacing the expression ‘atomic weight’ with ‘elementary weight’ one could, it seems to me, avoid the concept of atoms when speaking of elements” (1871)

- Endorsed atomic theory (distinction between atoms & molecules) sine the karlsruhe Conference (1860)

- atoms = not structural units of matter, but units of chemical combination characterized by their capacities to bind with others, i.e. by their atomicity or valence.

Impact of conceptual distinctions on the construction of the periodic table

- Elements as true individuals = condition of *discovery of periodic law* through comparison of dissimilar elements
- Li=7; Be=9,4; B=11; C=12; N=14; O=16; F=19
- Na=23; Mg=24; Al=27,4; Si=28; P=31; S=32; Cl=35,5
- K=39; Ca=40; - Ti=50; V=51:

- Distinction between simple body and element= condition of *predictions.* Simple bodies only exist when isolated *vs* abstract elements can be anticipated and properties deduced from those of neighbour elements

Feedback of the periodic table on the concept of element

A reinforcing process

“Kant said that there are in the world ‘two things, which never cease to call for the admiration and reverence of man: the moral law within ourselves and the stellar sky above us’. But when we turn our thoughts about the nature of the elements and the periodic law, we must add a third subject, namely: *‘the nature of the elementary individuals that we discover around us’*. Without them the stellar sky itself is inconceivable; and in the atoms we see at once their peculiar individualities, the infinite multiplicity of individuals, and the submission of their seeming freedom to the general harmony of nature” (Mendeleev 1879).

=> Element *individualized* by its position in the network of the periodic system.

Elements as “places” in the periodic system

Periodic table confers a “right” to existence

1894: Argon (39.9) no vacant place = > Mendeleev’s objections

1904 Mendeleev denied existence of radioactive elements =>
An Attempt towards a Chemical Conception of Ether (1904)

E(ther)
Co
H He

Isotopes rescue the periodic system

- Carbon-14, Ur-238 = challenges for the periodic system

- 1913, Frederick Soddy ‘isotopes’ (same location) rescued

both the periodic system and Mendeleev’s view of elements
as chemical individuals.

- 1914, Henry Moseley suggested the revision of the periodic law as a function of *atomic numbers* instead of atomic weights.
- 1921, IUPAC definition of element

To sum up

- Ambiguity element/simple substance was obstacle to the classification of elements

- Mendeleev's conceptual clarifications allowed inclusion of all known elements and predictions of unknown ones

- Feedback of the periodic system on the definition of chemical element (as distinct from atoms)

Epistemic remarks:

- concepts are more than linguistic units indispensable for exchanging information in scientific practices.
- Scientific concepts =solutions to theoretical puzzles => should be understood in their context of emergence.

Mendeleev’s discovery?

Nothing like a eureka!
Modest work of clarification for teaching

Conceptual work distinguishes Mendeleev’s from rival systems

Celebrating the **co-construction**
of the notion of chemical element
and the periodic system.