

19th-Century Chemistry:

Chemical Atoms and Chemical Laws

Waseda University, SILS,
History of Modern Physical Sciences

Around the Beginning of the Century...

One of the most well-known chemists at the beginning of the 19th century was Claude Louis Berthollet (1748–1822). He had collaborated with Lavoisier on chemical nomenclature and worked with Laplace in Arcueil. He ran a major laboratory and headed up one of the top journals in the field.

Berthollet shared Laplace's view that chemical reactions were the result of short-range forces. He believed that what we call solutions and alloys were also chemical compounds – hence, he believed that compounds could form in *any ratio by weight*.

For example, when Napoleon was in Egypt he was interested to know if Nile water was the same compound by weight as the water of the Seine in Paris.

John Dalton (1766–1844)



- Born into a middle class Quaker family.
- Self-taught in science and mathematics.
- Taught at a dissenting academy in Manchester for most of his career.
- A prominent member of the Manchester Literary and Philosophical Society.
- Carried out original research in meteorology and chemistry.
- *A New System of Chemical Philosophy* (1808) put forward a theory of chemical atoms – indivisible particles of matter that combine in chemical compounds.

Dalton's Newtonianism

Dalton's natural philosophy was influenced strongly by Isaac Newton.

Newton, *Optics*, 1704, Query 31

"It seems probable to me that God in the Beginning form'd matter in solid, massy, hard, impenetrable, moveable Particles, of such sizes and in such Proportion to Space, as most conducted to the End for which he formed them."

Dalton developed this idea into a chemical philosophy, based on the hypothesis of a chemical atom.

He introduced two important laws: the *law of partial pressures*, and the *law of multiple proportions*. He also introduced the idea of the *law of simplicity* – which was later abandoned.

The laws carried more weight with his contemporaries than the atomic theory.

The Law of Partial Pressures

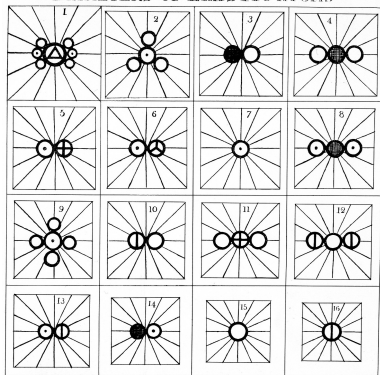
Dalton observed that the pressure of a mixture of gasses is equal to the sum of the partial pressures of each. He argued that this was caused by the action of some kind of force on the **caloric** around the atoms of the gasses.

Because he did not believe that equal volumes of gas under equal pressure have an equal number of particles, he could only make sense of this by explaining that the particles of each gas only acted on other particles of the same gas – we no longer believe this.

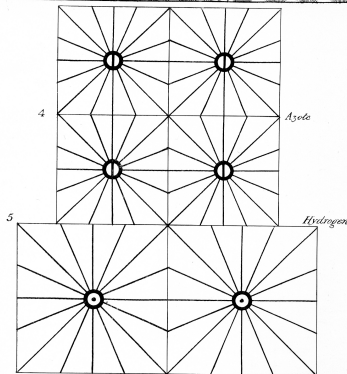
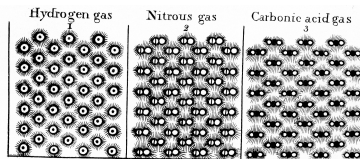
Dalton, "On the Absorption of Gases by Water," 1805

"The elastic or repulsive power of each particle is confined to those of its own kind; and consequently the force of such fluid, retained in a given vessel, or gravitating, is the same in a separate as in a mixed state, depending upon its proper density and temperature."

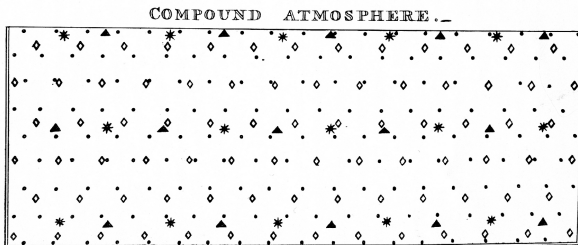
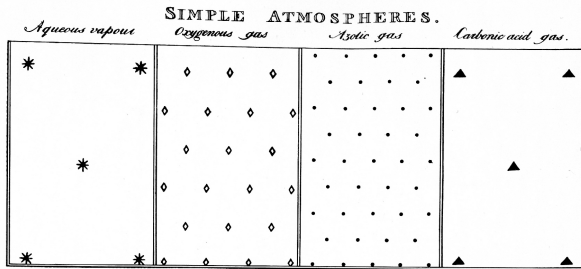
DIAMETERS OF ELASTIC ATOMS



Force exerted by different gasses



Dalton's gasses and the force produced



Dalton's law of partial pressures

The Law of Multiple Proportions

Dalton proposed that each compound was formed from a set combination of individual atoms of each element. This would explain the series of chemical combinations such as the oxides of nitrogen, the combinations of oxygen and hydrogen, and so on. Combined with the atomic theory this meant that one could determine a system of *relative* atomic weights.

Dalton, "On the Absorption of Gases by Water," 1805

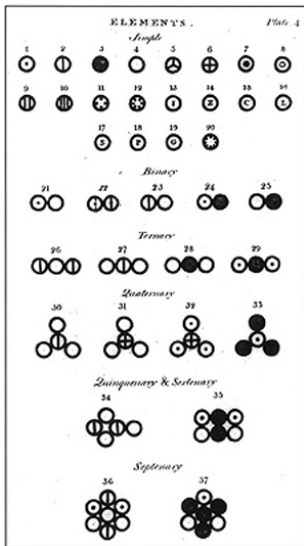
"If 100 measures of common air be put to 36 of pure nitrous gas..., after a few minutes the whole will be reduced to 79 or 80 measures, and exhibit no signs of either oxygenous or nitrous gas. If 100 measures of common air be admitted to 72 of nitrous gas..., there will, as before, be found 79 or 80 measures of pure azotic [nitrogen] gas for a residuum... These facts clearly point out the theory of the process: the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity."

The Law of Simplicity

Dalton assumed that the simplest compounds were in least numbers (gasses would be individual particles, the lowest known ratio was always assumed to be 1:1, and so on).

This lead him to a number of formulas that disagree with ours. (For example, he believed that water was one atom of hydrogen combined with one atom of oxygen.) Nevertheless, using these assumptions and the current literature, he could produce a table of equivalent weights. (He used $H := 1$.)

This law was later abandoned.



Dalton's "table of elements"

1. Hydrogen, 2. Nitrogen, 3. Carbon,
4. Oxygen, 5. Phosphorus, 6. Sulphur,
and so on.

The Atomic Hypothesis

Dalton first introduced the **atomic hypothesis** to explain the fact that water absorbs gases in specific fractions by *bulk*, or weight (1, 1/2, 1/3, 1/8, and so on).

Dalton, "On the Absorption of Gases by Water," 1805

"Why does water not admit its bulk of every kind of gas alike?—This question I have duly considered, and though I am not able yet to satisfy myself completely, I am nearly persuaded that the circumstance 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."

Dalton, *A New System of Chemical Philosophy* (1808)

“Whether the ultimate particles of a body ... are all alike, that is, of the same figure, weight, &c. is a question of some importance... Now it is scarcely possible to conceive how the aggregates of dissimilar particles should be so uniformly the same. If some of the particles of water were heavier than others, if a parcel of the liquid on any occasion were constituted principally of these heavier particles, it must be supposed to affect the specific gravity of the mass, a circumstance not known. Similar observations may be made on other substances. Therefore, we may conclude that the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, &c. In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen, &c.”

Dalton's Atoms and Chemical Processes

Dalton's *atoms* are indivisible units of matter. In fact, however, he used the term for both of what we call atoms and molecules. They are distinguished from each other purely on the basis of weight. For Dalton, *chemical elements* are characterized by being composed of a particular type of atom. This theory establishes an investigation of atomic weights and chemical processes as a research program.

Dalton, *A New System of Chemical Philosophy* (1808)

"If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple: namely,

1 atom of A + 1 atom of B = 1 atom of C, binary.

1 atom of A + 2 atoms of B = 1 atom of D, ternary.

2 atoms of A + 1 atom of B = 1 atom of E, ternary.

1 atom of A + 3 atoms of B = 1 atom of F, quarternary.

3 atoms of A + 1 atom of B = 1 atom of G, quarternary. &c. &c."

Dalton's First Table of Relative Weights

Hydrogen	1	(by definition)
Azote [Nitrogen]	4.2	(!, based on NH not NH ₃)
Carbone or charcoal	4.3	
Ammonia	5.2	
Oxygen	5.5	(!, based on HO not H ₂ O)
Water	6.5	
Phosphorus	7.2	
Phosphuretted hydrogen	8.2	
Nitrous gas	9.3	
...	...	

Most of these weights are considerably different from modern values. Some of this is due to the incorrect *law of simplicity* in setting NH for ammonia, HO for water, and so on.

Dalton did not do his own experiments to determine the weights – he relied on the published literature.

Difficulties with the Concept of Atomic Weight

There were a number of practical difficulties associated with the early systems of equivalent atomic weights.

Any system depended on (a) accurate measurements, (b) the selection of a conventional standard weight ($H := 1$, $O := 10$, $O := 100$, etc.) and (c) assumptions about the basic formulas of combinations (water $:= HO$, water $:= H_2O$, etc.).

Hence there were a number of different systems with different results.

Joseph Louis Gay-Lussac (1778–1850)

Gay-Lussac grew up during both the French and the chemical revolutions. When his father (a wealthy lawyer) was imprisoned during the revolutionary period, the son went to Paris to attend the École Polytechnique. He later became a student of Berthollet at Arcueil.

He spent his life in Paris as one of the leading members of the French scientific community.

He disagreed with Dalton, and proposed a *law of combining volumes*, which he believed contradicted Dalton's work.



Gay-Lussac & Biot in a balloon

The Law of Combining Volumes

Gay-Lussac was interested in the fact that certain gasses decrease in volume when they combine. In 1808, he carried out a series of experiments and rounded his numbers to show that:

2 vols. carbonic oxide + 1 vol. oxy. = 2 vols. carbonic acid gas.

2 vols. nitrogen + 1 vol. oxy. = 2 vols. nitrous oxide.

1 vol. nitric oxide + 1 vol. oxy. = 1 vols. nitric peroxide.

3 vols hyd. + 1 vol. nitrogen = 2 vols. ammonia.

He was particularly interested in the fact that the volumes involved were whole number ratios of each other. He generalized these findings to a physical law: "The compounds of gaseous substances with each other are always formed in very simple ratios, so that representing one of the terms by unity, the other is 1, or 2, or at most 3." He pointed out that this law, combined with the atomic hypothesis, implied that equal volumes of gas at the same temperature and pressure contain the same number particles.

Proportions by Volume

Gay-Lussac, 1809

"Gases always combine in the simplest proportions when they act on one another; ... 1 to 1, 1 to 2, or 1 to 3. It is very important to observe that in considering weights there is no simple and finite relation between the elements of any one compound; it is only when there is a second compound between the same elements that the new proportion of the element that has been added is a multiple of the first quantity. Gases, on the contrary, in whatever proportions they may combine, always give rise to compounds whose elements by volume are multiples of each other. Not only, however, do gases combine in very simple proportions, as we have just seen, but the apparent contraction of volume which they experience on combination has also a simple relation to the volume of the gases, or at least to that of one of them."

Reconciling the Theories

$$\frac{w_{E1}}{w_{E2,1}}, \frac{w_{E1}}{w_{E2,2}}, \frac{w_{E2,1}}{w_{E2,2}} = \frac{m}{n}, \text{ but } \frac{v_{E1}}{v_{E2}} = \frac{m}{n}, \text{ where } m, n \in \{1, 2, 3, \dots\}$$

It was hard for natural philosophers at that time to see how the laws of Dalton and Gay-Lussac could be reconciled. Dalton initially rejected Gay-Lussac's work, citing the rounded figures. French and English chemists were drawn up along national lines.

Conflicts: (1) The densities were off (for example carbonous acid gas (then and now CO) should be denser than oxygen gas (then O, but now O₂) but it was known to be less dense). (2) Reconciling the theories would imply that particles of basic gases were splitting apart. That is, it would imply that Dalton's Law of Simplicity was wrong – but there were good reasons at the time for thinking that this could not be the case.

Avagadro's Solution

The problem was actually solved already in 1811, but no one noticed until 1858.

Amedeo Avagadro (1776–1856), an Italian natural philosopher, proposed that equal volumes of gases at equal temperatures and pressures contain the same number particles, no matter how many fundamental parts these particles contained.

Avagadro paid particular attention to the way the volumes of gasses could decrease in combination. He introduced the conceptual difference between *molecule* and *atom*, although his actual terminology was quite confusing on the issue.

Avagadro's Two Hypotheses

Avagadro, "Essai d'une manière de déterminer...", 1811

"The first hypothesis ... is the supposition that the number of *integral molecules* [molecules] in any gas is always the same for equal volumes, or always proportional to the volumes...

We suppose, namely, that the *constituent molecules* [molecules] of any simple gas whatever (i.e., the molecules which are at such a distance from each other that they cannot exercise their mutual action) are not formed of a solitary *elementary molecule* [atom], but are made up of a certain number of these molecules united by attraction to form a single one."

Hence, if the elemental gases (Hydrogen, Oxygen, etc.) came in **pairs of atoms**, all the difficulties could be resolved and both the law of combining volumes and of multiple weights would be upheld. He also proved that it was unnecessary to assume further division of the basic gases.

Ahead of its Time...

For various reasons Avagadro's proposal was not taken up at the time: (1) His language was confusing. (2) He was a natural philosopher not a practicing chemist so he was seen as outside the research community – for example, his paper included a calculation of the mass of a molecule but no new organization of formulas and weights. (3) His views about the bonding of multiple particles of the same type was contrary to theories of chemical affinity that were prevalent at that time.

Indeed, his ideas contradicted those of Jöns Jacob Berzelius (1779–1848), one of the most influential chemists of the early 19th century, who had written a series of popular textbooks. Berzelius's views combined the practical chemistry of Lavoisier, the philosophical theories of Dalton, and the electrochemistry of Davy.

Berzelius' Chemical Affinity

8 M. Berzelius on Oxichlorides with Compound Radicals.

1 at. of acetic acid ... = 4 C + 6 H + 3 O
 2 at. of acetic chloride ... = 8 C + 12 H + 12 Cl
 $(\bar{A} = C^1 H^6 O^3 \text{ and } A C^2 = C^4 H^6 Cl^2) \bar{A} + A C^2 = 12 C + 18 H + 12 Cl + 3 O$
 which contains three times the number of simple atoms, in the formula of M. Malaguti = $C^4 H^6 Cl^2 O$.

2. Sulphuretted ether, $C^4 H^6 S^1 O$, contains, in tripling the number of simple atoms,

1 at. of acetic acid = 4 C + 6 H + 3 O
 2 at. of acetic sulphuret = 8 C + 12 H + 6 S
 $(A S^1 = \bar{A}) \quad \bar{A} + 2 \bar{A} = 12 C + 18 H + 6 S + 3 O.$

3. Chlorosulphuretted ether, $C^4 H^6 S^1 Cl^1 O$, the number of simple atoms being multiplied by 6, contains two atoms of acetic acid, two atoms of acetic sulphate, and two atoms of acetic chloride, which may be represented by the combination of an atom of No. 1. and an atom of

No. 2 = $(\bar{A} + 2 \bar{A}) + (\bar{A} + 2 A C^2)$.

It is probable that in treating the acetic oxichloride (No. 1) by sulphuret of lead, we shall obtain No. 2 or No. 3, as the decomposition may be more or less complete; just as when

$Bz C^2 + \bar{B}z$ ($Bz = C^4 H^{10}$)

is treated by sulphuret of lead, we obtain $\bar{B}z + 2 \bar{B}z$.

4. Chlorinated acetic ether, $C^4 H^6 C^1 O^4$, gives, on multiplying the number of simple atoms by 12,

2 at. of acetic acid ... = 8 C + 12 H + 6 O
 1 at. of acetic chloride = 4 C + 6 H + 6 Cl

$A Cl + 2 \bar{A} = 12 C + 18 H + 6 Cl + 6 O$

This combination is proportional to those of sulphur, chromium, molybdenum, tungsten, and benzoyle, with chlorine and oxygen.

5. Chlorinated formic ether, $C^2 H^4 C^1 O^4$, of which if we triple the number of atoms gives

2 at. of formic acid = 4 C + 4 H + 6 O
 1 at. of formic chloride ... = 2 C + 2 H + 6 Cl
 2 at. of acetic acid = 8 C + 12 H + 6 O
 1 at. of acetic chloride ... = 4 C + 6 H + 6 Cl

$P = C^2 H^4 (\bar{P} C^4 + 2 \bar{P}) + (A C^2 + \bar{A}) = 18 C + 24 H + 12 Cl + 12 O$

For Berzelius *atoms* had distinct electrical natures, as did *radicals* (groups of atoms that act in various ways as units), which accounted for their tendencies to combine in certain ways and not in others. Hence, every chemical compound contained an electropositive and an electronegative part, and similar atoms would repel one another. This made it difficult to believe that two atoms of the element could combine to form the molecules of gases.

He also introduced a system of chemical notation based on abbreviating the Latin names for the elements.

A State of Confusion

In 1812, H. Davy had speculated that there would be very few actual elements – maybe one or two. By the 1840s, however, the number had reached 48. There were a number of different systems for denoting the elements (Dalton's circles, Berzelius letters, the old alchemical symbols, and so on), and disagreement about some of the fundamental compounds and weights.

In 1860, August Kekulé convened an international conference in Karlsruhe (near Stuttgart) in order to try to address some of these issues and to arrive at a disciplinary consensus.

- Around 140 chemists attended, including almost all of the world's more prominent chemists.
- A relatively unknown chemist, Stanislao Cannizzaro (1829–1910), presented a paper which he had published in an obscure journal two years earlier.

Cannizzaro's Proposal

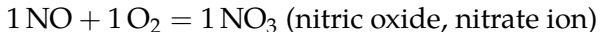
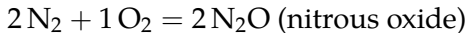
Cannizzaro was an atomist who believed in the identity of the chemical and physical atom – based on the new dynamic theories of heat.

His paper – “Sunto di un corso di filosofia chimica,” *Il Nuovo Cimento*, 1859 – laid out clearly how the differences between Gay-Lussac and Dalton could be resolved using Avagadro's hypotheses. He, then, explained the historical and theoretical reasons why this was not accepted at the time. He situated his work in the context of the work of the important chemists of the early 19th century and showed how it reconciled all of their ideas.

At the Karlsruhe Conference, his lecture summarized his paper, in French; and he handed out offprints to the chemists at the conference.

Atoms and Volumes

Using the Avagadro's hypotheses, Cannizzaro went on to make claims about what was happening at the atomic level:



This allowed a standardization of the chemical formulas, which lead to single system of atomic weights.

These *formulas* and newly calculated *weights* were included in Cannizzaro's paper. These were the sorts of ideas and techniques in which practicing chemists were interested.

A New Reception

Many chemists were convinced of the utility of the new system on the spot, others were convinced when they read the paper in their own time. J.L. Meyer gave a personal account of his encounter with Cannizzaro's paper:

J.L. Meyer

"[I] received a copy which I put in my pocket and read on my way home... The scales seemed to fall from my eyes. Doubts disappeared and a feeling of quiet certainty took their place."

The new system was adopted very quickly into textbooks – such as J.L. Meyer's *Die modernen Theorien der Chemie*, 1862.

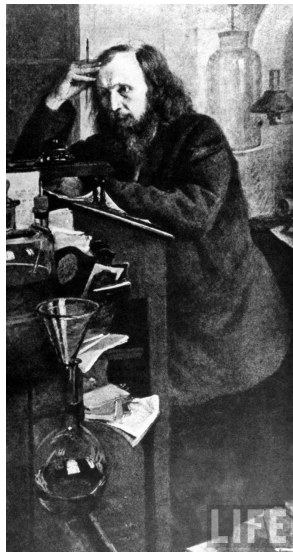
Nevertheless, although most chemists could see the advantages of talking about *chemical atoms*, many still rejected the idea of the *physical atom*.

Dmitry Mendeleev (1834–1907)

Mendeleev grew up in Siberia – his mother's 17th child. His father was a gymnasium teacher who died of tuberculosis, after which his mother supported the family by managing a glass works factory.

He was educated at Main Teachers' Training College and then the University of St. Petersburg, where he went on to spend his professional life.

His left-wing political views caused him some trouble early on, nevertheless, he became one of Russia's most prominent scientists.



Mendeleyev's Work

Mendeleyev was a prolific researcher and writer in all areas of 19th-century chemistry and industry. He worked both to make chemistry a theoretical science and to find new practical applications of chemistry for the Russian economy and industrial use. He wrote a number of books and reports on the utilization of Russia's vast natural resources.

He is most remembered as the discoverer of the *periodic law of the chemical elements*, which he arrived at in the 1860s as he was working on a new textbook. In the process of writing this book, he decided to try to derive a pattern among the known elements by relating their basic properties.

Chemical Groups

At this time, a number of different groups of elements were recognized by differentiating them on the basis of weight and their tendencies to combine in certain ways with other elements – what we call their valence. These differentiations formed *natural* groups of elements based on their chemical properties.

Alkali metals: lithium, sodium, potassium, rubidium, cesium.
They react violently with water and oxygen.
Similar affinities.

Halogens: fluorine, chlorine, bromine, iodine. Nonmetallic, react violently, form salts and (non-O)acids with H. Similar affinities.

Alkaline earths: beryllium, magnesium, calcium.

A sulfur group: sulfur, selenium, tellurium.

A phosphorus: phosphorus, arsenic, antimony, bithmuth.

Mendeleyev's Procedure

Mendeleyev wrote down each element on a little card along with its atomic weight, its chemical properties and its most common compounds. He then grouped certain elements together based on their *natural properties*. By moving the cards around, he could study the underlying patterns that began to emerge.

He noticed that in each group which shared chemical properties there was a clear ascending pattern in the values of their atomic weights. He placed the group of the *halogens* next to the *alkali metals* and saw that each element of the halogens weighed about the same amount less than the corresponding element in the alkali metals – equal differences of weight. He filled out this pattern as much as possible.

Mendeleyev realized that the chemical properties were somehow *directly related to weight* and that there was some sort of pattern of repetition.

This led to the belief that the chemical properties must be based on some more fundamental, physical properties.

1869-1870 Mendeleyev's Table

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$Ca = 40.1$
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 $V = 50.9$
 $Cr = 52.0$
 $Mn = 54.9$
 $Fe = 55.8$
 $Co = 58.9$
 $Ni = 58.7$
 $Cu = 63.5$
 $Zn = 65.4$
 $Ga = 69.7$
 $Ge = 72.6$
 $As = 74.9$
 $Se = 77.6$
 $Br = 79.9$
 $Kr = 83.8$
 $Rb = 85.5$
 $Sr = 87.6$
 $Y = 88.9$
 $Zr = 91.2$
 $Nb = 92.9$
 $Mo = 95.9$
 $Tc = 98.9$
 $Ru = 101.1$
 $Rh = 102.9$
 $Pd = 106.4$
 $Ag = 107.9$
 $Cd = 112.4$
 $In = 114.8$
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ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

	Tl = 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	Pl = 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
C = 12	Si = 28	? = 70	Sn = 118
N = 14	P = 31	As = 75	Sb = 122
O = 16	S = 32	Se = 79,4	Te = 128?
F = 19	Cl = 35,5	Br = 80	I = 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
		?Yl = 60	Th = 95
		?In = 75,6	Dl = 118?

Д. Менделѣевъ

The first published periodic
table of the elements

Mendeleyev announced the law in 1869 to the Russian Physical Chemical Society. J.L. Mayer published a German version in the early 1870s.

The first table had a number of blank slots and called into question a number of established atomic weights. In placing an element into the table, Mendeleev placed it with its proper natural group rather than on the basis of its then-established relative weight. This led to some corrections in established weights (ex., for Au [gold]) – but in at least one case he was wrong (ex., Bi [bismuth]), due to isotopic effects.

Mendeleyev's Announcement, I

Mendeleyev

- “1. The elements, if arranged according to their atomic weights, exhibit a *periodicity of properties*.
2. Chemically analogous elements have either similar atomic weights (Pt [platinum], Ir [iridium], Os [osmium]), or weights which increase by equal increments (K [potassium], Rb [rubidium], Cs [cesium]).
3. The arrangement according to atomic weight corresponds to the valence of the element and to a certain extent the difference in chemical behavior, for example Li [lithium], Be [beryllium], B [boron], C [carbon], N, O, F [fluorine] ...
5. The magnitude of the atomic weight determines the properties of the element. Therefore, in the study of compounds, not only the quantities and properties of the elements and their reciprocal behavior is to be taken into consideration, but also the atomic weight of the elements.”

Mendeleyev's Announcement, II

Mendeleyev

"6. One can *predict the discovery* of many new elements, for example analogues of Si [silicon] and Al [aluminum] with atomic weights of 65-75. [exa- silicon, exa-aluminum.]

7. A few atomic weights will probably require correction; for example Te [tellerium] cannot have the atomic weight 128, but rather 123–126. [He was wrong, due to isotopes.]

8. From the above table, some new analogies between elements are revealed. Thus Ur [now, indium (In)] appears as an analogue of B [boron] and Al [aluminum], as is well known to have been long established experimentally."

The Periodic Law

Mendeleyev realized that the chemical properties are a *function* of weight and that the certain sets of properties are repeated at regular intervals.

Mendeleyev

“In proportion to the increase in atomic weight elements at first acquire entirely new, changing properties, then these properties recur in a new period, in a new line and row of elements and in the same sequence as in the preceding row. Thus the law of periodicity may be expressed as follows: *the properties of the elements, and thus the properties of simple or compound bodies of these elements, are dependent in a periodic way on the magnitude of the atomic weights of the elements.*”

New Predictions

On the basis of empty places in the table, Mendeleev went on to predict the discovery of new elements. He stated their atomic weight and described their basic properties.

Eka-Aluminum: “In all relations ought to show the transition from the properties of aluminum to those of [indium]. [It] ... will be more volatile than aluminum... It may be hoped that it may be discovered by *spectral analysis*.”

Eka-Boron: The weight “must be approximately 44... Its oxide must have the formula Eb_2O_3 and will be basic but not very active.”

Mendeleev predicted that experimental chemists would soon find elements having these characteristics and expected weights.

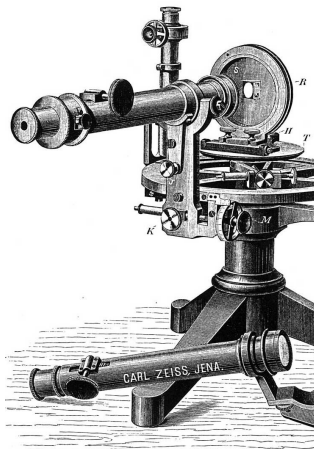
Mendeleyev

“The whole essence of theoretical knowledge in chemistry lies in the abstract conception of the elements. To find their fundamental properties, to determine the reasons for their differences and similarities, and then on the basis of this knowledge to forecast the properties of new bodies formed by the elements – that is the path along which our science advances firmly ... and there still remains much to be done. The main interest in chemistry is in the study of the principle qualities of the elements.”

The Use of the Spectrograph

Throughout the 1850–1870s, chemists used the spectrograph both to analyze compounds and discover a number of new elements. Many of these newly discovered elements were useful to Mendeleyev in discovering the periodic law.

By the time Mendeleyev was working on the table, it was an established part of chemical practice.



A spectrograph made by
the Zeiss company

Mendeleyev's Predictions

In 1875, Lecoq de Boisbaudran (1838–1912) discovered a new element in zinc ore from the Pyrenees. He reported that it had exactly the properties predicted by Mendeleyev for eka-Aluminum. He called it *Gallium*, Ga.

Within two years, eka-silicon (*Germanium*, Ge) had been found; and the predicted element next to calcium was isolated as well (*Scandium*, Sc).

The successful outcome of these precise and novel predictions convinced chemists that Mendeleyev's table organized the elements in some fundamental way even though the physical, or small-scale, structure of the elements was still unknown.

Overview

- Dalton and Guy-Lussac derived laws of chemical reactions, which were in fact claims about *general regularities*. This led to work on tables of relative weights.
- As first it was difficult for chemists to see how these regularities might work together, because of preconceived notions about chemical affinities.
- Until the middle of the century chemists were not impressed with theoretical speculations about atoms or the weights of assumed molecules.
- Cannizzaro showed how Avagadro's hypotheses could be used to make all this into a coherent system.
- Mendeleyev's law – which he regards as fundamental – made specific prediction about the existence of as-of-yet unknown elements. It also made claims that some measurements had been made incorrectly.