Dalton’s Atoms and Gay-Lussac’s Laws of Combination

The Regularities of Chemical Combination
Berthollet (1748-1822)

- Collaborated with Lavoisier on chemical nomenclature. Worked with Laplace in Arcueil.
- Shared Laplace’s view that chemical reactions were the result of short-range forces.
- He believed that solutions and alloys were chemical compounds. He believed that compounds could form in any ratio by weight.
  - When Napoleon was in Egypt he was interested to know if Nile water was the same compound by weight as Seine water.
John Dalton (1766-1844)

- He was born into a middle class Quaker family.
- He was self-taught in science and mathematics.
- He taught at a Dissenting Academy in Manchester for most of his career.
- He was a prominent member of the Manchester Literary and Philosophical Society.
Dalton’s work

• Dalton 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.

• He introduced two important laws: the *law of partial pressures*, and the *law of multiple proportions*.

• The laws carried more weight with his contemporaries than the atomic theory.
Dalton’s Newtonianism

- Dalton’s natural philosophy was influenced most strongly by Newton.
- Newton, *Optics*, 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.”
- Newton’s *Principia* had shown that air pressure could be obtained by assuming the particles of air are mutually repulsive. (This was later refuted.)
Partial pressures

• Dalton discovered that the pressure of a mixture of gasses is equal to the sum of the partial pressures of each.

• 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.]

• They did this by exerting some kind of force on the caloric around themselves.
Law of partial pressures

• Dalton, 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.”
Force exerted by different gasses
Dalton’s gasses

Hydrogen gas

Nitrous gas

Carbonic acid gas

4

5

Azote

Hydrogen
Partial pressures
Multiple proportions

• Dalton *hypothesized* 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 oxygen and hydrogen, etc.

• Combined with the atomic theory this meant that one could determine a system of *relative* atomic weights.
The law of simplicity

• Dalton assumed that the simplest compounds were in least numbers (gasses would be individual particles, the lowest ratio was always 1:1, etc).

• This lead him to number of formulas that disagree with ours (gasses are H, O, N; water=HO, etc).

• 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.
ELEMENTS

Simple
1  2  3  4  5  6  7  8
9 10 11 12 13 14 15 16
17 18 19 20

Binary
21 22 23 24 25

Ternary
26 27 28 29

Quaternary
30 31 32 33

Quinquevinary & Sexenary
34 35

Septenary
36 37
The atomic hypothesis

• Dalton first introduced the hypothesis to explain the fact that water *absorbs* gases in specific fractions by volume (1, 1/8, 1/27, etc.).

• Dalton, 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’s Table of relative weights

- Hydrogen 1
- Azote (Nitrogen) 4.2
- Carbone 4.3
- Ammonia 5.2
- Oxygen 5.5 (*)
- Water 6.5
- Phosphorus 7.2
- Phosphuretted hydrogen 8.2
- Nitrous gas 9.3 ….
Dalton, 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.” [Newton’s RR 3.]
Dalton’s atoms

• Dalton’s atoms are the indivisible units of matter. (In fact, he used the term for both 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 as a research program.
Chemical processes

• Dalton, 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.
  – 1 atom of A + 3 atoms of B = 1 atom of F, quarternary.
  &c. &c.”
Problems with atomic weight

- There were a number of practical difficulties associated with the system of atomic or equivalent weights.
- Any system depended on accurate measurements, the selection of a conventional standard weight (H=1, O=10, O=100, etc.) and agreement on the basic formulas of combinations (water=HO, water=H₂O, 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, he went to Paris to attend the École Polytechnique.
• He was a student of Berthollet’s at Arcueil.
• Spent his life in Paris as one of the leading members of the French scientific community.
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:
  – 1 vol. nitric oxide + 1 vol. oxy. = 1 vols. nitric peroxide.
The law of combining volumes

- He was particularly interested in the fact that the volumes involved were *whole number ratios* of each other.

- He generalized these finding 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. (Something which Dalton, and his followers, would not accept.)
Proportions by volumes I

- 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…”
Proportions by volumes II

• … 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

• It was hard for natural philosophers to see how this could be compatible with Dalton’s atomism. (Dalton initially rejected it, citing the rounded figures.) French and English chemists were drawn along national lines.

• Conflicts: (1) the densities were off (ex. carbonic oxide (CO) should be denser than oxygen (O*) gas but it was known to be less dense). (2) It would imply that particles of basic gases were splitting (ammonia from 1H+ 3N, nitrous oxide from 2N + 1O).

• These are all due to the fact that they thought simple gasses were made up of individual particles.
Amedeo Avagadro (1776-1856)
Avagadro’s hypotheses

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

• Avagardo proposed that equal volumes of gases at equal temperatures and pressures contain the same number of 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 hypotheses (con’t)

• 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.”
The solution

• He pointed out that if the elemental gases (Hydrogen, Oxygen, Nitrogen, 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. [But Dalton’s law of simplicity would have to be discarded.]

• He also showed that, given the state of chemical knowledge, it was unnecessary to assume further division of the basic gases.
Ahead of its time

• There were a number of reasons why Avagadro’s hypotheses were not taken up at the time.
• His language was confusing, especially his varied terminology for the constituent parts.
• He was a natural philosopher not a practicing chemist so he was seen as outside the research community.
  – His paper included a calculation of the mass of a molecule but no new organization of formulas and weights.
• His views about the bonding of multiple particles of the same type in the elemental gases was contrary to the current theories of chemical affinity.
Berzelius (1779-1848)

- Berzelius was the most influential chemist of the early 19th century.
- He combined the methods of Lavoisier, the theories of Dalton and the electrochemistry of Davy.
- He introduced the modern system of chemical notation based on abbreviating the Latin names for the elements.
- He based his theory of chemical reactions on Davy’s electrochemistry.
M. Berzelius on Oxichlorides with Compound Radicals.

1 at. of acetic acid \( \ldots = 4 C + 6 H + 3 O \)
2 at. of acetic chloride \( \ldots = 8 C + 12 H + 12 Cl \)

\( \bar{A} = C^3 H^6 O^4 \) and \( A CP = C^4 H^6 C^4 \)
\( \bar{A} + A CP = \bar{A} + 4 C + 8 H + 12 Cl + 3 O \)

which contains three times the number of simple atoms, in
the formula of M. Malaguti \( = C^4 H^6 Cl^3 O \).

2. Sulphuretted ether, \( C^4 H^6 S^1 O \), contains, in tripling the
number of simple atoms,
1 at. of acetic acid \( \ldots = 4 C + 6 H + 3 O \)
2 at. of acetic sulphuret \( = 8 C + 12 H + 6 S \)

\( A S^3 = \bar{A} \)

\( \bar{A} + 2 \bar{A} = 12 C + 18 H + 6 S + 3 O \).

3. Chlorosulphuretted ether, = \( C^4 H^6 S Cl^1 O \), 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

\( No. 2 = (\bar{A} + 2 \bar{A}) + (A + 2 A Cl^3) \).

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

\( Bz Cl^3 + Bz (Bz = C^4 H^6) \)

is treated by sulphuret of lead, we obtain \( Bz + 2 Bz \).

4. Chlorinated acetic ether, \( Cl^1 H^1 C^1 O^4 \), gives, on multipli-
ying the number of simple atoms by 1\( \frac{1}{2} \),
2 at. of acetic acid \( \ldots = 8 C + 12 H + 6 O \)
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, chrom-
um, molybdenum, tungsten, and benzoyl, with chlorine and oxygen.

5. Chlorinated formic ether, \( C^6 H^6 Cl^3 O^4 \), of which if we
triple the number of atoms gives

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

\( P = C^3 H^7 (\bar{P} CP + \bar{P}) \)
Berzelius’ Chemical Affinity

• 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.

• Every chemical compound contained a positive and negative part.

• Under this view similar atoms would repel one another.

• This ruled against the advantage of Avagadro’s hypothesis.
Final Remarks

• Here we notice, again, the development of a number of distinct ‘laws’ which allow research to move forward.

• We see a number of research programs advancing despite numerous ‘anomalies,’ or ‘falsifications.’

• We see that important conceptual advances have to be made in the right context (time, place and setting).