Determining Atomic Weights
The Role of Avogadro's Hypothesis

by Lindsey Novak

Overview

This module focuses on the interconnected concepts of atomic weight, measurement by weight and volume, and the distinction between atoms and molecules of the same element (notably for diatomic gases, such as hydrogan, oxygen and nitrogen). By situating the lesson is its original historical context, it will introduce students to conceptual change in science (and *why* ideas change), as well as to the role of persuasion and politics in science. The lesson begins in the early 1800s in Europe, just after the publication of Dalton's Atomic Theory. Students follow the story of Avogadro and his hypothesis from its introduction in 1811 to its full acceptance in 1858. The students will consider the reasons that Avogadro's hypothesis was not accepted for half a century. Along the way they will be discussing "big picture" issues such as: (a) the role of politics in science and (b) the timing and acceptance of scientific ideas.

Outline

1. Introduction: Chemistry in 19th-century Europe

Let us situate ourselves in the early 1800s in Europe. Chemists were finally in agreement about what constituted an element, thanks to Lavoisier and others. They were beginning to realize that these elements had consistent weights and began to investigate the concept of atomic weights further. They speculated that the elements were made of particles, and the research was aimed at finding out what these particles were, how they combined, and how the atomic weights could be determined.

There were three main schools of thought concerning atomic weights, atoms, and molecules. These theories came from three prominent chemists of the time: Dalton, Gay-Lussac, and Berzelius. We will also meet Avogadro, an Italian chemist who proposed a hypothesis relating to atomic weights.

A. Background – Science in the 1800s (Europe)

- ! Napoleonic Wars and other hostilities between countries discouraged communication between scientists and scientific communities.
- ! Also unwilling to share because scientists wanted the full "rights" to their ideas.
- ! Chemists worked with equivalents; they were said to be more fixed than atomic weights.
- ! Two major trends in chemistry during the early 1800s.
- ! Newtonianism: Universe is interpretable in terms of forces and particles. Sciences should seek to discover fundamental laws. All sciences share a common methodology and theoretical foundation.
- ! Nonreductionist Position: Emphasis on the relationship between chemistry and natural history, especially minerology (Bonner 20).

**Important here to discuss the basic understanding of elements, matter, and particles at the time. Atoms and molecules are not clearly defined; chemists tend to use the terms interchangeably. They used equivalents rather than atomic weights to do calculations (see lab). There is yet no standardized way for measuring the "amount" of an element or compound — whether by weight or volume.

B. Three Main Schools of Thought:

John Dalton (England) – Fig. 1

- ! Dalton's Atomic Theory
- ! First published by Scottish chemist Thomas Thompson (1807). His research criticized for "poor analysis."
- ! Dalton associated atoms with elements.
- ! Each element has its own unique atoms with unique properties including atomic weight.
- ! 1808: Dalton publishes his atomic theory. Includes a list of about 30 elements and the law of multiple proportions.

- Law of multiple proportions: when two elements combine in a series of compounds, the ratios of the weights of one element that combine with a fixed weight of the second are in a ratio of small whole numbers.
- His theory is rather straightforward; implies that atomic weights might all be whole numbers.
- Theory denies possibility of atoms of the same species being attracted to one another.
- Relied on analysis by weight (gravimetric analysis) (Levere 107).

Joseph Louis Gay-Lussac (France) – Fig. 2

- 1808: Gay-Lussac publishes his law of combining volumes for gases: gases combine in volumes that are in ratios of small whole numbers.
- Relied on volumetric analysis
- Convinced that his method of volumetric analysis of gases was more general and straightforward than Dalton's analysis by weight (Levere 109).

**Dalton and Gay-Lussac were not enthusiastic towards each other's work. They didn't see any way that their laws of combining weights and combining volumes could be reconciled. [*Elaborate on the problem of measuring by volume versus weight.*]

Jons Jakob Berzelius (Sweden) – Fig. 3

- Became interested in electrochemistry while in medical school in Sweden. Thesis for his medical degree was about using electric shock therapy to treat various diseases.
- 1807: Appointed professor at Medical College, Stockholm.
- Performed a series of experiments in preparation for writing and publishing a chemistry textbook for medical students.
- Discovered many new elements.
- Found that elements in inorganic substances are bound together in definite proportions by weight (Chem. Heritage Foundation).
- Created a system of symbols to identify elements
- Worked to determine atomic weights of all the known elements.
- ~1810: Berzelius is advocating his theory of **electrochemical dualism**: he derived his own formulas for compounds by looking at the properties of chemical reactions.
- Compounds can be decomposed by electric current. Separated elements found at poles of electrolytic cells.
- Proposes that atoms are charged.
- Problem: different reactions suggest different formulas for the same substance.
- Theory denies possibility of like atoms being attracted to one another. Claims that in order for atoms to be attracted to each other they had to have opposite or significantly different electrical characters.

- Berzelius is well-respected and influential. His electrochemical theory is widely accepted. (Levere 112).
- Wrote *Textbook of Chemistry*. Widely read, several editions published, translated into five languages.
- 1821-1848: Wrote and published series of "Annual Reports" where he summarized and critiqued the most important scientific achievements of the year.
- Classified minerals based on chemical characteristics.
- "The research of Berzelius was characterised by systematic diligence, chemical instinct and experimental precision unparalled by other 19th-century researchers" (European Association for Chemical and Molecular Sciences).

Question [1]: As a chemist in Europe in the early 1800s, which theory do you find more plausible? What criteria do you rely on to make that decision? What other information would you like to have about each school of thought? Do you see any way to combine, integrate or accommodate these differing theories with one another?

2. Amedeo Avogadro

** Meet Amedeo Avogadro, an Italian chemist/physicist who proposed a hypothesis that seemed to reconcile Dalton's and Gay-Lussac's theories.

Amedeo Avogadro – Fig. 4

- Born Aug. 9, 1776 – Italian
- Father Filippo Avogadro worked in the judicial system of the Kingdom of Sardinia.
- Family was of high social status.
- Likely was educated at home under the supervision of priests. (Little known about his primary education.) Attended the schools of Turin for his secondary education. BA in 1792.
- Entered the Faculty of Law at the University of Turin.
- Brother Felice became a judge, two other brothers chose military careers.
- Graduated from the U of Turin in 1796 and went on to work in the legal profession.
- Started his scientific education ~1798. Probably read about science extensively in his leisure.
- 1804: became member of the Academy of Sciences of Turin after the submission of 2 essays on electricity.
- 1800-1806 did lots of work on electricity.
- Hard to explain shift from legal to scientific interests (rare during this time).

- "Although Avogadro worked for over a quarter of a century within the French scientific tradition, he derived no benefit from its favorable circumstances. He remained isolated; he did not belong to any group or academic *clique*." p. 17
- He had limited correspondence with other scientists at the time.
- 1809: appointed prof. of "positive philosophy" (math/physics) at the former Royal College of Vercelli. Spent 11 yrs. there.
- 1809: 6 pg. note by Avogadro published in *Journal de Physique*
    - claims, contrary to the grat Lavoisier, that oxygen is not 'the principle of acidity'
    - introduced series of considerations on concept of alkalinity/acidity (Morselli 5)

Avogadro's New Hypothesis

Avogadro's work with gases led him to propose in 1811 that:

equal volumes of gases at the same temperature and pressure contain equal numbers of particles.

What kinds of particles is he talking about? These particles could be single or multiple, or simply the smallest particles of whatever gas he worked with (oxygen, carbon dioxide, etc.).

< Here students may profit from doing a lab that weighs gases. >

[*Be careful not to refer to H_2 or O_2 — as their diatomic status is not yet known!*]

Avogadro worked extensively with gases and claimed that his hypothesis was based on the "unity and economy of nature."

But Avogadro is not a very reputable chemist. Prior to proposing his hypothesis, Avogadro also developed a modified theory of caloric, or heat as a substance, and wrote extensively about it. He continued to support this theory even as it became increasingly obsolete.

His experimental results are not consistent. While Avogadro has determined the correct atomic weight for about 25 compounds and a few elements, he has gotten literally hundreds wrong, according to everyone else's measurements.

Question [2]: How does Avogadro's new perspective fit with the three existing schools of thought (of Dalton, Gay-Lussac and Berzelius) ? Does it agree with all, some, or none of them? How does Avogadro's proposed concept [and his reputation] change your own view of what theory to adopt? What other information would you like to have?

3. From Avogadro to Cannizzaro

A consequence of Avogadro's new hypothesis is that:

> *Combination by volumes in the ratio of small whole numbers implied the combination by particles in the ratio of small whole numbers* (Levere 110).

This reconciles Dalton's law and Gay-Lussac's law. Yet Avogadro's hypothesis is not widely accepted. Why not? Well . . .

1. It calls for the acceptance of atoms of the same species that are attracted to each other.
   Consider Gay-Lussac's results for the composition of water. He found that two volumes of hydrogen combine with one volume of oxygen to give two volumes of water vapor. According to Avogadro that implies that two particles of hydrogen combine with one particle of oxygen to give two particles of water vapor. BUT that's only possible if each particle of oxygen can be divided into two parts. For Dalton, Gay-Lussac, and Berzelius atoms of the same species cannot be attracted to each other (Levere 111).

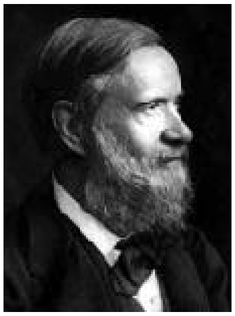
2. His hypothesis has limited applicability.
   Avogadro has been working primarily with gases. But we do not know much about gases (now, in the early 1800s). Chemists are more concerned with determining the relative atomic weights of the known elements. The older tradition of working with gases has been in decline since 1815. Avogadro's work simply isn't pertinent to modern chemistry (Fisher).

3. As noted earlier, Avogadro is not a very reputable chemist.
   There are problems with his caloric theory, as well as his determinations of atomic weights. Also, Avogadro's hypothesis goes against Dalton, Gay-Lussac and — most importantly — Berzelius. Berzelius is very well-respected and considered the authority on this subject (Fisher).

<u>What happens next?</u>

- Avogadro's hypothesis pretty much gathers dust. Let's fast-forward to 1838.
- ~1838 Gerhardt and Laurent derive atomic weights using combined gas volumes and other properties. They use part of Avogadro's hypothesis to find atomic weights, but their hypothesis is not accepted because it also goes against Berzelius's theory.
- 1848: Berzelius dies.
- Dobereiner observes triads.
- Scientists become increasingly familiar with the numerical patterns and regularities in atomic weights.
- Organic chemistry emerges as a branch of chemistry, reviving the study of gases.
- The phenomenon of allotropy is being investigated.
- Chemists then begin to accept Gerhardt and Laurent's ideas.
- Scientists become increasingly more accurate due to improved methods of measurement and calculation.

Stanislao Cannizzaro – Fig. 5



- Italian chemist.
- 1858: writes a paper showing how Avogadro's Hypothesis resolved many problems with finding atomic and molecular weights. Also explained how it helped bring together work on atomic heats and vapor densities. [*Elaborate for honors or advanced class*.] Clarified the difference between an atom and a molecule — and the possibly problematic consequence that some gases must be ***diatomic***. [*Elaborate!*]
- His paper is ignored at first.
- Then he presents his paper at a conference in Karlsruhe, Germany. Many people hear it.

Question [3]: Does Cannizzaro resolve all the problems with Avogadro's initial hypothesis? Given this information, would you be willing to support Avogadro's Hypothesis (with Cannizzaro's contributions)? What other information would you like to have?

4. Epilogue

Unlike Avogadro's hypothesis in 1811, Cannizzaro's ideas were widely accepted. Mostly, his explanation was more complete than Avogadro's. Cannizzaro's work was based on three main points:

1. The equal numbers hypothesis (Avogadro's Hypothesis)
2. The idea that some elementary molecules must contain more than one particle (especially that gas molecules such as hydrogen, oxygen and nitrogen may be ***diatomic***).
3. The idea that the atom is the smallest quantity of an element found in any molecule containing that element.

**Avogadro did not propose (2) or (3) (Fisher).

Some chemists were immediately persuaded; others read his paper on the way home from the conference and came to agree with Cannizzaro. This was a major turning point for the acceptance of Avogadro's Hypothesis (Levere 115).

After the acceptance of Avogadro's Hypothesis (with Cannizzaro's contributions), chemists had a firm grasp on the concept of atomic weights. By 1860 there was no more disagreement about whether certain atomic weights should be halved or doubled, and there was a working set of atomic weights based on accurate analyses. Now that elements had been assigned atomic weights, it was time to decide how to organize the elements. Enter Mendeleev and the periodic table.

Question [4]: Why did it take 50 years for Avogadro's Hypothesis to be accepted? How did science change over that half a century? Should Avogadro's method have been accepted right away? Why or why not?

Editor's Note: Of course, Avogadro is perhaps now more renowned for the eponymous "Avogadro's number" than for his hypothesis about equal volumes of gases. Ironically, perhaps, Avogadro never proposed a specific number of molecules for a particular weight-equivalent (or mole) of a substance. That number was postulated and ascertained late in the 1800s, and named in honor of Avogadro for having found an intimate connection between the amount of a substance (for a gas, easily measured by volume) and the number of particles, or molecules.

References

"Avogadro's Number." New Jersey SAS. 15 Oct. 2008 <http://www.njsas.org/projects/atoms/avogadro.php>.

Bonner, John K. *Amedeo Avogadro: A reassessment of his research and its place in early nineteenth century science*. Diss. Johns Hopkins University, 1974. Ann Arbor, MI: Xerox University Microfilms, 1974.

Fisher, Nicholas. "Avogadro, the chemists, and historians of chemistry." *History of Science* (1982).

Giunta, Carmen. "Equal Numbers in Equal Volumes: Avogadro." *Elements and Atoms.* 1 Dec. 2008 <http://web.lemoyne.edu/~giunta/ea/avogadroann.html>.

"Jons Jakob Berzelius." *Chemical Heritage Foundation*. 2005. <http://www.chemheritage.org/classroom/chemach/electrochem/berzelius.html>

"Jons Jakob Berzelius." *European Association for Chemical and Molecular Sciences*. 2005. < http://www.euchems.org/Distinguished/19thCentury/berzelius.asp>

Levere, Trevor H. *Transforming Matter: A History of Chemistry from Alchemy to the Buckyball*. New York: Johns Hopkins UP, 2001.

Morselli, Mario. *Amadeo Avogadro*. New York: Springer, 1984.

Images

All images available from Wikipedia (public domain).
Fig. 1 – John Dalton
Fig. 2 – Joseph Louis Gay-Lussac
Fig. 3 – J.J. Berzelius
Fig. 4 – Amedeo Avogadro
Fig. 5 – Stanislao Cannizzaro