

THE SAGA OF ATOMIC WEIGHTS

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Who were the first people to think of the concept of atomic weights? How were atomic weights of elements first calculated? In this article, the authors explore the long scientific journey from the origins of the widely used conceptual framework of atomic weights to the debates on the topic prevalent even today.

Introduction

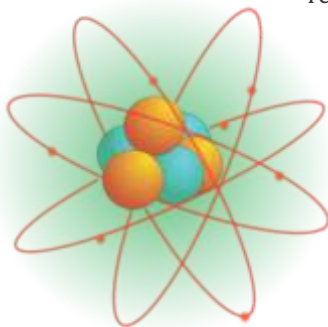
The atomic weight of elements is one single idea that distinguishes Dalton's atomic theory from earlier atomistic ideas about the nature of matter. The concept of atomic weight also makes possible all the quantitative predictions about chemical interactions, and their outcomes. We take the idea of atomic weight as given, and almost never think of it as a conceptual framework which is the result of intense debates beginning in the early nineteenth century. The saga of atomic weights is not only extremely interesting, it also gives us an understanding of the way scientists work. This story takes a winding route, and is enriched by the contributions of several leading scientists of the time. Some of the debate around this concept continues even today.

The beginning

It is well known that ideas of an atom-like particle were present since the ancient times with Kanada in India; and Leucippus and Democritus in Greece, having talked about an ultimate particle. However, the modern atom owes its 'existence' to

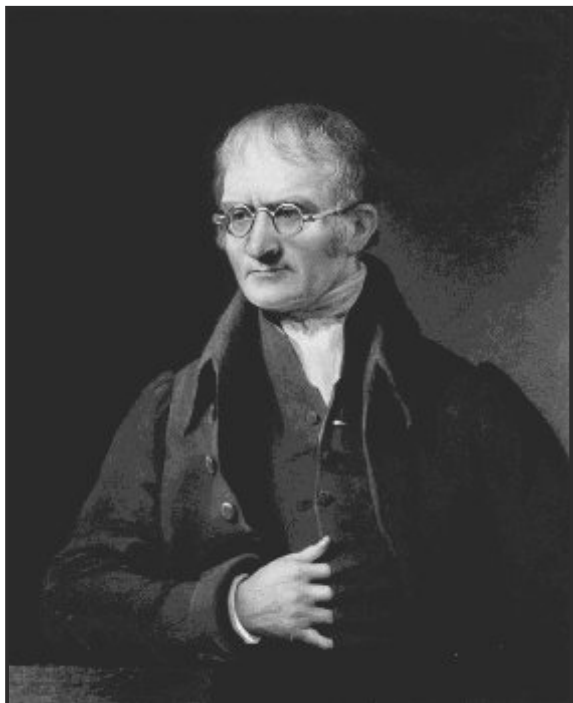
the efforts of several chemists, culminating in Dalton's atomic theory.

In the eighteenth century, chemists started studying chemical phenomena quantitatively, resulting in the postulation of several laws of chemical combination. These included the law of conservation of mass, law of constant proportions, and the law of reciprocal proportions.



John Dalton, looking at these laws, thought that they could be explained only if we assumed matter to be constituted of some ultimate indivisible particles. If he had stopped with this assertion, the modern atom would not be a tool to understand, explain and predict the course of chemical reactions. Dalton enunciated that:

1. All matter is ultimately composed of atoms, which can neither be subdivided nor changed into one-another.
2. Atoms can neither be created nor destroyed.
3. All atoms of the same element have the same weight, and are similar in size and shape etc.
4. Chemical change is the union or separation of atoms as a whole.



British physicist and chemist John Dalton (1766-1844) by Charles Turner (1773-1857) after James Lonsdale (1777-1839) - Public domain. This image is available from the United States Library of Congress's Prints and Photographs division under the digital ID cph.3b12511

These postulates explained the above mentioned empirical laws of chemical combination. Moreover, the theory was interpreted to predict the law of multiple proportions. When this prediction was found to be true, it added strength to Dalton's theory. The theory had secure foundations. It should be noted that all these laws were quantitative statements about chemical reactions, and led to an explanation, which was also quantitative.

Dalton realized this very well. Writing in his 'A New System of Chemical Philosophy' in 1808, referring to the observations made and conclusions derived by Robert Boyle a century earlier, the laws of chemical combination, and especially the law of constant proportion, he said:

"These observations have tacitly led to the conclusion which seems universally adopted, that all bodies ... are constituted of vast numbers of extremely small particles, or atoms of matter, bound together by a force of attraction, which is more or less powerful according to circumstances."

"... This conclusion, which appears completely satisfactory; ... we have hitherto made no use of it, and that the consequence of the neglect has been a very obscure view of chemical agency..."

The 'neglect' which Dalton talked about had to do with postulate 3 of his theory. He had a vast amount of data, and on the basis of that meticulous data, he concluded,

"In all chemical investigations, it has justly been considered an important object to ascertain the relative weights of the simples which constitute a compound. But unfortunately the enquiry has terminated here; whereas from the relative weights in the mass, the relative weights of the ultimate particles or atoms of the bodies might have been inferred, from which their number and weight in various other compounds would appear, in order to assist and to guide future investigations, and to correct their results. Now it is one great object of this work, to shew (sic) the importance and advantage of ascertaining the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one more compound particle."

Having said this, Dalton proceeded to calculate the weights of different ultimate particles, i.e., atoms.

Dalton calculates atomic weight

It was amply clear to Dalton that atoms were so tiny that it was futile to attempt to weigh them singly. But, one may surmise that he could have calculated average weights. However, remember that in the beginning of the nineteenth century, all that was known was combining weights of various elements when they reacted with other elements. For example, when hydrogen reacted with oxygen, it was always in the proportion of 1g of hydrogen and 8g of oxygen. But how can you calculate atomic weights of these two elements from this knowledge?

Weights of the two elements involved in the reaction do not tell you anything about the number of atoms of each element participating in the reaction. And there was no way Dalton could

1 Dalton called smallest particle atom, whether of elements or compounds.

determine the number of atoms in, say, 1g of hydrogen or 8g of oxygen.

In other words, you either had to know the formula of water *a priori* or you had to know the number of atoms contained in a specific weight of each element. As one can now appreciate, Dalton had no way of knowing either of the two. But that did not deter him.

Instead, he made certain assumptions to complete the task. The assumptions turned out to be wrong, but his Ingenious logic and improvisation had important consequences.

Let us look at the problem in a more systematic manner. From Dalton's theory, firmly established on a solid ground of chemical arithmetic, the obvious conclusion is that elements enter into chemical reactions as whole atoms. So we can write several formulae for water:

Dalton said

"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, quarternary.
- And so on

The following general rules may be adopted as guides in all our investigations regarding chemical synthesis.

1. When only one combination of two bodies can be obtained, it must be presumed to be a binary one, unless some other cause appears to the contrary.
2. When two combinations are observed, they must be presumed to be a binary and a ternary.
3. When three combinations are observed, they must be presumed to be one binary, and the other two ternary.
4. When four combinations are observed, we should expect one binary, two ternary, and one quarternary, etc."

From the application of these rules, to the chemical facts already well ascertained, he

proceeded in the following manner. According to Dalton, nature was simple. If two elements combine to form a compound, they shall do so in the simple ratio of one atom each. If more than one compound is formed by the combination of the same elements, other ratios may be considered, as given above.

Let's take the example of water.

In the early nineteenth century, only one compound of hydrogen and oxygen was known, viz., water. Thus, using Dalton's method, one atom of hydrogen would combine with one atom of oxygen to give one 'atom' of water. In actual weights, 1g of hydrogen combines with 8g of oxygen to produce 9g of water. So, one can conclude that 8g of oxygen would contain as many atoms of oxygen as there are hydrogen atoms in 1g of hydrogen. Therefore, every atom of oxygen would be 8 times heavier than an atom of hydrogen.

As hydrogen was (and is) the lightest element known, Dalton assumed the weight of a hydrogen atom to be 1 and using this as the unit of atomic weight, he calculated atomic weights of several elements and compound bodies.

1. Hydrogen, its relative weight 1
2. Azote (nitrogen) 5
3. Carbone or charcoal 5
4. Oxygen 7
5. Phosphorous 9
6. Sulphur 13
7. Magnesia 20
8. Lime 23
9. Soda 28
10. Potash 42
11. Strontites 46
12. Barytes 68
13. Iron 38
14. Zinc 56
15. Copper 56
16. Lead 95
17. Silver 100
18. Platina 100
19. Gold 140
20. Mercury 167

The voluminous challenge

This was a time of great activity in chemistry, with many chemists trying to lay the foundations of this nascent science. Thus, despite the reputation

for impeccable logic which Dalton enjoyed, there were, soon, some serious challenges to his table of atomic weights.



The first challenge to Dalton's method came from some elegant experiments on combinations of gases, conducted mainly by Joseph Gay-Lussac. Whereas Dalton mainly used the weights of reacting elements to construct the formulae, and calculate atomic weights, Gay-Lussac (1778-1850) was studying the volumes of reacting gases. On the basis of numerous experiments, he arrived at the law of combining volumes: at a given pressure and temperature, gases combine in simple proportions by volume. If any of the products are gaseous, they also bear a simple whole number ratio to that of any gaseous reactant. For example, 2l of hydrogen combine with 1l of oxygen to give 2l of water vapour. The ratio of these volumes is 2:1:2.

The volume ratios for some reacting gases are given below:

Reaction Volume Ratios for Reactants

Hydrogen + Oxygen → Water **2:1**

Hydrogen + Chlorine → Hydrogen Chloride **1:1**

Carbon Monoxide + Oxygen → Carbon Dioxide **2:1**

Methane + Oxygen → Water + Carbon Dioxide **1:2**

Gay-Lussac did not infer anything from these results, although the conclusion was staring him in the face. If elements combine as atoms, and the volumes of combining gases bear a simple ratio, there must be some relationship between volume and the number of atoms.

Berzelius (1779-1848) interpreted Gay-Lussac's law to mean that equal volumes of gases, under identical conditions of temperature and pressure, have the same number of atoms. Since Dalton had already proposed the idea that simple whole numbers of atoms join together to give compounds, then if a given volume of hydrogen has, say 1000 atoms, it will combine with 1000 atoms of chlorine. Since this amount of chlorine occupies the same volume as hydrogen, it follows that under similar conditions of temperature and pressure, equal volumes of any gas will contain the same number of atoms.

Applied to the reaction of hydrogen and oxygen, the idea will appear thus

Hydrogen + oxygen → water

2 vol + 1 vol → 2 vol

2n particles + 1n particle → 2n particles

If we assume n to be equal to 10, Berzelius would conclude that 2 vol of hydrogen would contain 20 atoms of hydrogen, and 1 vol of oxygen would have 10 atoms of oxygen. Thus, according to Berzelius, the number of atoms of hydrogen and oxygen in water would be in the ratio of 2:1; the formula of water would thus be H₂O (and not HO, as assumed by Dalton), and every atom of oxygen would be 16 times as heavy as a hydrogen atom.

Berzelius' interpretation provided a simple method to determine atomic weights: make various gases react separately with one volume of hydrogen, and measure the volume of gases which combine completely with one volume of hydrogen.

The contradiction

Dalton, obviously, had great doubts about Berzelius' conclusion, as it seemed to contradict the central postulate of his atomic theory, viz., the indivisibility of elemental atoms. Let us continue with the example of water to illustrate this point. We will start by writing the equation for dissociation of water vapour into its elements:

Water vapour → Hydrogen + Oxygen

2 vol → 2 vol + 1 vol
2 atoms → 2 atoms + 1 atom
1 atom → 1 atom + 1/2 atom

The problem is starkly clear – If one atom of water is dissociated (or inversely if one atom of water is created), one will get (or need) half an atom of oxygen; thus, Berzelius' proposal seemed to go against the indivisibility of atoms, and thus was unacceptable to Dalton.

The battlefield of atomic weights

Not just Dalton and Berzelius, many others too came up with their own ways of calculating and reporting atomic weights. They differed in their methods, experimental results, and units for comparison; among other things (for example Berzelius decided to assume the atomic weight of Oxygen to be 100). There was a time when it became impossible to read published research accounts due to the multiplicity of atomic weights and formulae based on the same. It is reported that acetic acid had something like 13 formulae. In this situation, many chemists stopped using atomic weights, and went back to reporting only combining weights. Some people, including leading chemists like Dumas and Wohler, even suggested abandoning the whole idea of atoms, as being too abstract and confusing.

A solution neglected for half a century

We may all have heard of the Italian chemist Amedeo Avogadro, for his hypothesis that replaced the word atom with molecule in Berzelius' proposal (which, if you do not remember, suggested that at a given pressure and temperature, all gases contain the same number of atoms). It almost appears that Avogadro was engaging in semantics. On the contrary, he was expressing something very profound about the nature of elements and chemical combinations, which was to revolutionise thinking in chemistry, in addition to solving the riddle of atomic weights, and the apparent contradiction between Gay-Lussac's results and Dalton's atomic theory.

So, what did Avogadro say, and why was it neglected for fifty years? In short, Avogadro proposed that elements can, and do often, exist as compound atoms. In his paper published in 1811, Avogadro hypothesized that the ultimate particles are of two kinds – atoms and molecules. His most 'preposterous' suggestion was that even elements could exist as molecules. On the basis of this, he



Picture of Amedeo Avogadro (1776–1856), the Italian scientist – Public Domain. From a drawing by C. Sentier, executed in Torino at Litografia Doyen in 1856. Edgar Fahs Smith collection.

was able to make the famous change, we now know as Avogadro's hypothesis: at a given temperature and pressure, all gases contain equal number of molecules (which may consist of more than one atom).

According to Avogadro, the above reaction between hydrogen and oxygen can be understood as follows:

Hydrogen + oxygen → water

2 vol + 1 vol → 2 vol

2n molecules + 1n molecules → 2n molecules

1 molecules + 1/2 molecules → 1 molecules

In effect, what he said was that both hydrogen and oxygen existed as molecules, and that these molecules contained two atoms each of their respective elements. Thus, in the last reaction, what was splitting was a molecule of oxygen, not an atom of the same element. This was in keeping with Dalton's theory. If one accepted this suggestion, things become a lot less complicated.

It is said that this seminal paper remained in oblivion for so long, because it was published in Italian, in an obscure journal, and Avogadro's presentation was very crude. However, to be fair to the chemists of the day, one must note that Avogadro had no theoretical basis for this

suggestion. It was common understanding during those days that elements react with each other because of their opposite charges. This made it difficult, if not impossible, to place the idea of atoms of the same element coming together to give you a molecule. This may be another reason for the neglect. It is obvious that instead of providing a new theoretical insight into the nature of matter, Avogadro's attempt was made to reconcile Dalton's theory and Berzelius' interpretation of Gay-Lussac's experimental results.

The idea of atomic weight was such a fundamental and practically useful idea that chemists were not willing to give it up, and go back to alchemic ways. Thus many other attempts were made to make this idea workable.

Other attempts

A) Dulong and Petit Method

One such method was proposed by Pierre Dulong (1789-1838) and Alexis Petit (1791-1820). In 1819, they discovered a relationship which could be stated in the form of a law: the atomic weight of a metal multiplied by its specific heat is approximately equal to 6.4.

Since the specific heat of a metal can be determined experimentally, this law can be used to find the approximate atomic weights of metals. At least it can be used to ascertain the correct value from among various competing values determined experimentally. Let us take a brief look at an example.

The approximate atomic weight of silver, calculated from its specific heat is 113.3. From an actual experiment involving reaction of weighed quantities of silver and oxygen, it was found that they react in the ratio of 13.51:1. If we assume that one atom of silver reacts with one atom of oxygen, this means that an atom of silver is 13.51 times as heavy as an oxygen atom. This gives a value of 216.16 (16×13.51) as the atomic weight of silver.

Using data on its specific heat, we have the approximate atomic weight of silver as 113.3, which is roughly half the weight obtained above. Hence, the formula of silver oxide is Ag_2O , and the atomic weight of silver is $216.16 / 2 = 108.08$.

B) Victor Meyer method

Victor Meyer basically refined existing techniques to find vapour densities, and applied Berzelius'

method to compare atomic weights. He was able to extend the method to vapours, in addition to gases.

You can see the basic problem in determining atomic weights. While we make a measurement on macroscopic amounts of reactants, we want to draw some conclusions about the relative masses of individual atoms. Suppose, we have one box containing bananas weighing 500g and another box containing oranges weighing 1kg. With this data in hand, we can hardly compare weight of one banana and weight of an orange. However, if we assume that each of them contains a dozen of each fruit, then we may say that each orange is twice as heavy as a banana. With atoms, we cannot know, we can make only assumptions.

As was mentioned in the beginning, atomic weights are useful because they give us a way to understand and predict the course of chemical reactions.

From what has been said above, you can appreciate the confusion and turmoil the problem of atomic weight must have created in the first half of nineteenth century. One chemist, who was deeply concerned about this problem, was August Kekule. He called a conference of chemists from across nations to resolve just this riddle, as he felt that this continuing confusion will stall the progress of science. This first global conference of chemists was held in Karlsruhe (Germany) in 1860.

C) Enters Cannizzaro

The Karlsruhe conference should be seen as an effort to come to a consensus. It would have failed, had not a young school teacher, named Stanislav Cannizzaro, intervened at the right moment.

Cannizzaro's main contribution was to attract the attention of the conference participants to the 1811 paper by Avogadro and propose that it presented a neat method of determining atomic weights. The method is given here as it highlights the fact that the problem of atomic weights was resolved through application of logic and statesmanship.

Cannizzaro's method

In the conference, Stanislav Cannizzaro circulated a note in which he applied Avogadro's hypothesis to select the correct weights for the atoms of different elements. He postulated that:

- All atoms of any element have a definite weight.

- Since molecules, such as a hydrogen molecule or a water molecule, contain a definite numbers of atoms, they must have definite weights, which we refer to as formula weights.
- These formula weights contain one atomic weight (or a whole-number multiple of that atomic weight) for each element present.

Based on these postulates, he proposed a method to calculate atomic weights, following the steps given below:

- According to Avogadro, the molecular formula of water is H₂O.
- If all gases have an equal number of molecules in equal volumes, their densities will be proportional to their molecular weights, i.e. $M \propto D$ or $M = kD$, where k is a constant, M is the molecular weight, and D is the density of the given gas.
- If we know the molecular weight of a gas, we can calculate the constant k from its density. For example, hydrogen has a molecular weight of 2 and oxygen 32. Therefore:

Gas | Molecular weight | Density | $k=M/D$

Hydrogen | 2 | 0.09 | 22.25

Oxygen | 32 | 1.43 | 22.4

- Thus the average value of the constant k is 22.33 (average of 22.25 and 22.4)
- To calculate the atomic weights of carbon and chlorine, we have to find out the molecular weights of the various gaseous compounds of carbon and chlorine, from their densities.(by applying $M=kD$)

Compound	Density (g/l)	Molecular weight (M ₂)	Weight percentage			Amount in one molecule (calculated from molecular weight and percentages)			Probable formula
			Carbon	Hydrogen	Oxygen	Carbon	Hydrogen	Oxygen	
Methane	0.715	16.0	74.8	25	-	12	4.00	-	CH ₄
Ethane	1.340	29.9	79.8	20	-	23.9	6.04	-	C ₂ H ₆
Carbon dioxide	2.88	64.3	37.2	7.8	55	23.9	5.62	25.04	CH ₂ O
Methanol	5.34	110.1	10.05	0.8	89.1	12.2	1.01	136.2	CH ₃ O
Carbon tetrachloride	6.83	152.6	7.8	-	92.9	11.01	-	141	CCl ₄

- Let us see how the above information is derived from data. Step 4 (of applying the equation $M=kD$) gives 16 as the molecular weight of methane. The percentage of carbon in methane (column 2) is 74.8. That is, 100g of methane has 74.8g of carbon. Therefore, 16g

of methane (one mole of methane) contains $(74.8/100) \times 16 = 12g$ of carbon. The other values in the table have been calculated in a similar manner.

- We have calculated the amount of every element in one mole of each of the compounds. Next, we look at the minimum amount of an element present in these compounds. We can see that one mole of each compound has different amounts of carbon. The minimum amount of carbon in one mole of its compounds is 12g. From this, we take the atomic weight of carbon as 12 because we assume that these compounds contain at least one atom of carbon. If later studies give us compounds whose 1 mole contains 6g or 4g of carbon, we will have to revise the atomic weight of carbon. Till then, the atomic weight of carbon can be taken as 12.
- Likewise the atomic weights of other elements can be calculated.

Further developments

With the Karlsruhe Conference, the matter seemed to have been settled. However, the discovery of isotopes provided a new set of challenges to the idea of a unique atomic weight for each element. They led to the idea of elements having fractional atomic weights.

Recently the International Union of Pure and Applied Chemists have had to deal with another problem. It was found that atomic weights of some elements differ according to where and how the element is obtained. This had to do with differing isotopic compositions of elements in different places and environments. The suggested solution for this is that from now onwards, atomic weights will be reported as a range rather than as a single value.

We are not going into the details of all these developments, but it must be clear, by now, that the atomic weights reported in the periodic table we have all been using, have not been easy to arrive at. Ultimately, it was the actual process of counting atoms and molecules (Avogadro number) that has given us the answer that we think of as the final one, today. But is this the last we'll hear of this?

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