1.1.1: Early Experiments of Atomic Theory

Development of Atomic Theory

Since the ancient times, humans thought of explaining the material world in all of its complexity. The basic idea behind all element theories is that the matter that surrounds us is composed of more simple matter. This matter may be composed of even simpler matter. The most simple matter would be called an element.

The first element theories were one element theories: The greek philosopher Thales thought water was the only element, and everything was a form of water. Anaximenes thought air was the only element, and Heraclitus believed fire was the only element (Figure 1.1.1).

Figure **1.1.1** Thales (640-545 BC) (Attribution: Ernst Wallis et al [Public domain] https://commons.wikimedia.org/wiki/File:Illustrerad_Verldshistoria_band_I_Ill_107.jpg), Anaximenes (585-525 BC) (Attribution: https://commons.wikimedia.org/wiki/File:Anaximenes_of_Miletus_Painting.jpg) and Heraclitus (544 – 483 BC) (Attribution: RoyFokker [CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)]), respectively.

However, with only one element assumed it was difficult to explain the material world in all its complexity satisfactorily. This could be done more satisfactorily by a multi-element theory. The first philosopher who introduced a multi-element theory was Empedocles. He suggested a four-element theory with fire, air, water, and soil as the elements (Figure 1.1.2).

Figure 1.1.2 Empedocles (495 – 435 BC) (Attribution: Thomas Stanley, The history of philosophy, 1655 [Public domain] https://commons.wikimedia.org/wiki/F...Philosophy.jpg)

First atomistic ideas

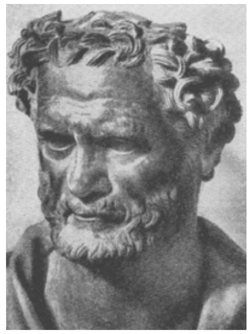

Figure 1.1.3 Democrites (460 – 370 BC) (Attribution: Strannik 92 [CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)] https://commons.wikimedia.org/wiki/File:Demokrit.jpg)

The element theories of Thales, Anaximenes, Heraklitus, and Empedocles were all non-atomistic. This means that they did not include the idea that elements were made of small particles that were indivisible. The first greek philosophers that introduced atomistic element theory were Leukippes, and Democrites (Figure 1.1.3). They assumed that particles cannot be divided into smaller particles infinitely often. Ultimately, after many divisions, one would arrive at particles that could not be further divided, and these particles would be called atoms. Atomistic element theory allows for many different elements which helps to explain the complexity of the material world satisfactorily. However, Leukippes and Democrites did not know how many different elements there were, and how different atoms of different elements were actually distinguished. This question would not be answered until about 2000 years later.

Modern Atomic Theories

Figure 1.1.4 Antoine Lavoisier, the father of modern chemistry, discovered the law of conservation of mass in 1774. (Attribution: Louis Jean Désiré Delaistre (1800–1871); drawing by Julien Léopold Boilly (1796–1874). [Public domain], https://commons.wikimedia.org/wiki/F...sier_color.jpg)

Although the atomistic idea was already known in the antique, it became forgotten for a long time and was only reintroduced about 2000 years later with Dalton's atom hypothesis. What lead to Dalton's atom hypothesis? The first discovery that was important to the development of modern atomic theory was the law of the conservation of mass by Antoine Lavoisier (Fig. 1.1.4). Historically, the conservation of mass and weight was kept obscure for millennia by the buoyant effect of the Earth's atmosphere on the weight of gases, an effect not understood until the vacuum pump first allowed the effective weighing of gases using scales. Until then, in many instances mass seemed to appear or disappear. For example, the mass of wood seems to disappear when it is burned. However, the mass of the wood actually does not disappear it is just converted into the mass of gases, mainly carbon dioxide. When scientists realized that mass never disappeared they could for the first time embark on quantitative studies of the transformations of substances. This in turn led to the idea of chemical elements, as well as the idea that all chemical processes and transformations are simple reactions between these elements. The **law of conservation of mass** states that the mass of a closed system of substances will remain constant, regardless of the processes acting inside the system. An equivalent statement is that matter cannot be created or destroyed, although it may change form. This implies that for any chemical process in a closed system, the mass of the reactants must equal the mass of the products.

Law of Constant Composition

The discovery of the law of the conservation of mass led to the discovery of the law of the constant composition (also called law of definitive proportions) by Joseph Proust (Fig. 1.1.5). This law was the result of chemical analysis that determined the mass ratio of elements in pure substances. It was found that a pure substance always contains exactly the same proportion of elements by mass. For example the element analysis of pure substances containing the elements carbon and oxygen would be either 42.9% carbon and 57.1% oxygen or 27.3% carbon and 72.7% oxygen.

Figure 1.1.5 Joseph Proust (1754-1826) (Attribution: The original uploader was HappyApple at English Wikipedia. [Public domain] https://commons.wikimedia.org/wiki/F...ust_joseph.jpg)

The law was questioned by Proust's fellow Frenchman Claude Louis Berthollet, who argued that the elements could combine in any proportion. The very existence of this debate was because at the time the distinction between pure chemical compounds and mixtures had not yet been fully developed. When two pure compounds of two different elements are mixed, then the mixture can have a continuous mass ratio between the two elements because compounds can be mixed at any ratio. So, for the example in the two compounds between carbon and oxygen, in mixtures of the two there could be carbon to oxygen ratios varying continuously between 27.7 % to 42.9% carbon, and 42.9% to 72.7% oxygen. It was an accomplishment of Proust that he was able to correctly distinguish between pure compounds and mixtures.

The Law of Multiple Proportions

Figure 1.1.6 John Dalton 1766-1844 (Attribution: Charles Turner [Public domain] https://commons.wikimedia.org/wiki/F...les_Turner.jpg)

John Dalton (Fig. 1.1.6) discovered the law of multiple proportions by close analysis of Proust's law of constant composition. He noticed that if two elements form more than one compound between them, then the ratios of the masses of the second element which combines with a fixed mass of the first element will be the ratios of small whole numbers, also called integer numbers. Let us see what is the meaning of the law of the multiple proportions by an example:

Example 1.1.1.1

The first compound contains 42.9% by mass carbon and 57.1% by mass oxygen.

The second compound contains 27.3% by mass carbon and 72.7% by mass oxygen.

Show that the data are consistent with the Law of Multiple Proportions!

Solution

In 100 g of the first compound (100 is chosen to make calculations easier) there are 57.1 g O and 42.9 g C.

The mass of O per gram C is:

57.1 g O / 42.9 g C = 1.33 g O per g C

In 100 g of the second compound, there are 72.7 g O and 27.3 g C.

The mass of oxygen per gram of carbon is:

72.7 g O / 27.3 g C = 2.66 g O per g C

Dividing the mass O per g C of the second (larger value) compound by the mass O per g C of the first compound gives:

2.66 : 1.33 = 2 : 1

2 and 1 are both integer numbers.

Dalton's Atom Hypothesis

Dalton argued that atoms could explain the law of the multiple proportions. If one assumed that elements were made of the same type of indivisible particles, that are identical in mass and all properties then, because these particles can only come in integer numbers, different atoms can be combined to form compounds also only in integer numbers. Thus, in a pure compound atoms of unlike elements would be combined in small whole number ratios. Consequently a given compound always has the same relative number and types of atoms. Chemical reactions would involve reorganization of atoms, but the atoms would retain their identity. Atoms could be rearranged in a chemical reaction but not created or destroyed.

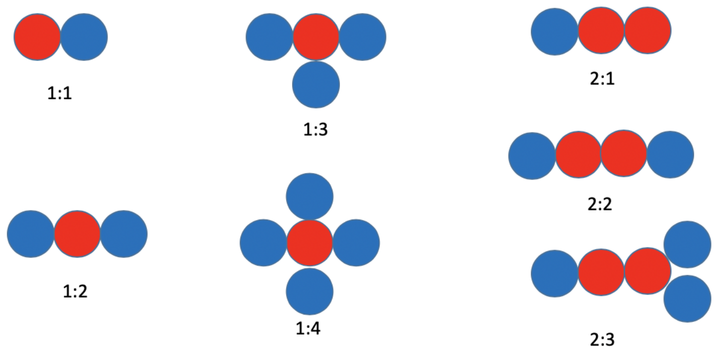

Figure 1.1.7 Illustration of the law of the multiple proportions for two generic, different atoms (red and blue balls).

Figure 1.1.7 is a simple illustration how atoms can explain the law of multiple proportions. The blue and red balls symbolize different atoms of different elements. It is possible to combine a red atom with one, two, three, or four blue atoms to make four different compounds. It is for example also possible to combine two red atoms with one, two or three blue atoms. In all of these compounds as well as in all other thinkable ones, the blue and red atoms can only be combined in integer numbers.

Dalton's Atom Symbols

Dalton also thought of symbols for the atoms of the different elements. The symbols are different from the element symbols that are used today, but the concept is the same. You can see some of them in Figure 1.1.8. For example oxygen is represented by a white ball, while carbon is symbolized by a black ball. You can also see that Dalton already combined atom symbols of different elements to illustrate compounds. For example he combined one white ball with one black ball to indicate carbon monoxide, while he combined two white balls with one black ball to indicate carbon dioxide. In this case he correctly identified the ratios of atoms in the two compounds. However, you can see that this is not always the case. For example, he combined one hydrogen atom (white ball with a dot in the middle) with one oxygen atom to indicate the composition of water. However, as we know today, a water molecule has two hydrogen atoms and one oxygen atom. Why has he been right with the carbon-oxygen compounds, but wrong about the water? The answer is that at the time he could determine the atom ratios only from the law of the multiple proportions. At the time there was only one compound known that was made of hydrogen and oxygen, water, so he assumed the simplest atom ratio of 1:1. If he had known hydrogen peroxide, which has the composition H_2O_2, and thus half as much hydrogen per oxygen, he would have probably correctly assigned the correct hydrogen to oxygen ratio to water. In the case of the carbon oxides, he assigned the compositions correctly because both carbon monoxide and carbon dioxide were known at the time.

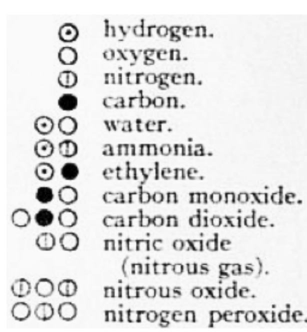

Figure 1.1.8 Dalton’s atom symbols (Attribution: Encyclopædia Britannica, 1911 [Public domain] https://commons.wikimedia.org/wiki/F...an_symbols.png)