1.5: Modern Atomic Theory and the Laws That Led to It

Learning Objectives

- Correctly define a law as it pertains to science.
- Understand the application of the application of the law of conservation of matter.
- Understand the application of the law of definite proportions
- Understand the application of the law of multiple proportions
- Understand the basis of Dalton's Atomic Theory

With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist A. Lavoisier laid the foundation to the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. While John Dalton is credited for proposing modern atomic theory. Dalton built his theory upon laws previously identified by Lavoisier and Proust as a basis for his atomic theory:

1. Law of Conservation of Mass,
2. Law of Definite Proportions, and
3. Law of Multiple Proportions.

Law of Conservation of Mass

"Nothing comes from nothing" is an important idea in ancient Greek philosophy that argues that what exists *now* has always *existed*, since no new matter can come into existence where there was none before. Antoine Lavoisier (1743-1794) restated this principle for chemistry. This law, which is central is the **law of conservation of matter** (also known as the "law of indestructibility of matter") and states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is *conserved*. According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

> *Law of Conservation Conservation of Mass states that in a chemical reaction, matter is neither created nor destroyed.*

Figure 1.5.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before (Figure 1.5.1). When wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose we had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose we had been able to measure the oxygen used by the fire and the gases produced by the fire. What would we find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

Example 1.5.1

If heating 10 grams of $CaCO_3$ produces 4.4 g of CO_2 and 5.6 g of CaO, show that these observations are in agreement with the law of conservation of mass.

Figure 1.5.1: A sample of calcium carbonate ($CaCO_3$). (Public Domain; Walkerma).

Solution

- Mass of the reactants, $CaCO_3$: $10\ g$
- Mass of the products, CO_2 and CaO: $4.4\ g + 5.6\ g = 10\ g$.

Because the mass of the reactants = the mass of the products, the observations are in agreement with the law of conservation of mass.

? Exercise 1.5.1

a. What is the law of conservation of matter?
b. How does the law of conservation of matter apply to chemistry?

Answer a

The law of conservation of matter states that in any given system that is closed to the transfer of matter, the amount of matter in the system stays constant

Answer b

The law of conservation of matter says that in chemical reactions, the total mass of the products must equal the total mass of the reactants.

The Law of Definite Proportions

Joseph Proust (1754-1826) formulated the **law of definite proportions** (also called the Law of Constant Composition or Proust's Law), which states that if a compound is broken down into its constituent elements, the masses of the constituents will *always* have the same proportions, regardless of the quantity or source of the original substance. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 1.5.1.

Table 1.5.1: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82\text{ g carbon}}{2.78\text{ g hydrogen}} = \frac{5.33\text{ g carbo}}{1.00\text{ g hydrog}}$
B	22.33 g	4.19 g	$\frac{22.33\text{ g carbon}}{4.19\text{ g hydrogen}} = \frac{5.33\text{ g carbo}}{1.00\text{ g hydrog}}$
C	19.40 g	3.64 g	$\frac{19.40\text{ g carbon}}{3.63\text{ g hydrogen}} = \frac{5.33\text{ g carbo}}{1.00\text{ g hydrog}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

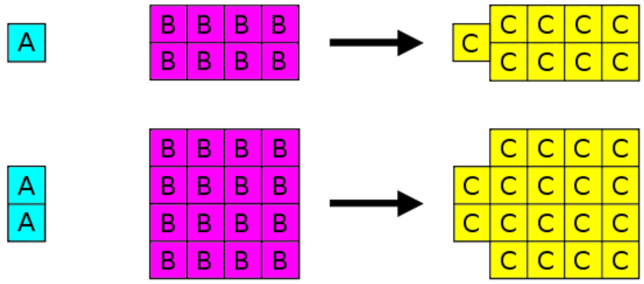

Figure 1.5.2: If 1 gram of A reacts with 8 grams of B, then by the Law of Definite Proportions, 2 grams of A must react with 16 grams of B. If 1 gram of A reacts with 8 grams of B, then by the Law of Conservation of Mass, they must produce 9 grams of C. Similarly, when 2 grams of A react with 16 grams of B, they must produce 18 grams of C.

> *Law of Definite Proportions states that in a given type of chemical substance, the elements are always combined in the same proportions by mass.*

The Law of Definite Proportions applies when elements are reacted together to form *the same* product. Therefore, while the Law of Definite Proportions can be used to compare two experiments in which hydrogen and oxygen react to form water, the Law of Definite Proportions can *not* be used to compare one experiment in which hydrogen and oxygen react to form water, and another experiment in which hydrogen and oxygen react to form hydrogen peroxide (peroxide is another material that can be made from hydrogen and oxygen).

Example 1.5.2: Water

Oxygen makes up 88.8% of the mass of any sample of pure water, while hydrogen makes up the remaining 11.2% of the mass. You can get water by melting ice or snow, by condensing steam, from river, sea, pond, etc. It can be from different places: USA, UK, Australia, or anywhere. It can be made by chemical reactions like burning hydrogen in oxygen.

However, if the water is **pure**, it will **always** consist of 88.8 % oxygen by mass and 11.2 % hydrogen by mass, irrespective of its source or method of preparation.

The Law of Multiple Proportions

The **law of multiple proportions** (sometime call Dalton's Law) states that if two elements form more than one compound between them, then the ratios of the masses of the second element which combine with a fixed mass of the first element will always be ratios of small whole numbers. Many combinations of elements can react to form more than one compound. In such cases, this law states that the weights of one element that combine with a fixed weight of another of these elements are integer multiples of one another. It's easy to say this, but please make sure that you understand how it works. Nitrogen forms a very large number of oxides, five of which are shown here.

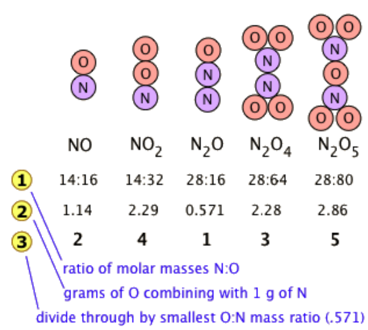

Figure 1.5.3: Law of Multiple Proportions applied to nitrogen oxides (NO_x) compounds. (CC-BY; Stephen Lower)

- Line ① shows the ratio of the relative weights of the two elements in each compound. These ratios were calculated by simply taking the molar mass of each element, and multiplying by the number of atoms of that element per mole of the compound. Thus for NO_2, we have (1 × 14) : (2 × 16) = 13:32. (These numbers were not known in the early days of Chemistry because atomic weights (i.e., molar masses) of most elements were not reliably known.)
- The numbers in Line ② are just the mass ratios of O:N, found by dividing the corresponding ratios in line 1. But someone who depends solely on experiment would work these out by finding the mass of O that combines with unit mass (1 g) of nitrogen.

- Line is obtained by dividing the figures the previous line by the smallest O:N ratio in the line above, which is the one for N_2O. Note that just as the law of multiple proportions says, the weight of oxygen that combines with unit weight of nitrogen work out to small integers.
- Of course we just as easily could have illustrated the law by considering the mass of nitrogen that combines with one gram of oxygen; it works both ways!

> *The law of multiple proportions states that if two elements form more than one compound between them, the masses of one element combined with a fixed mass of the second element form in ratios of small integers.*

Example 1.5.3: Oxides of Carbon

Consider two separate compounds are formed by only carbon and oxygen. The first compound contains 42.9% carbon and 57.1% oxygen (by mass) and the second compound contains 27.3% carbon and 72.7% oxygen (again by mass). Is this consistent with the law of multiple proportions?

Solution

The *Law of Multiple Proportions* states that the masses of one element which combine with a fixed mass of the second element are in a ratio of **whole** numbers. Hence, the masses of oxygen in the two compounds that combine with a fixed mass of carbon should be in a whole-number ratio.

Thus for every 1 g of the first compound there are 0.57 g of oxygen and 0.429 g of carbon. The mass of oxygen per gram carbon is:

$$\frac{0.571 \text{ g oxygen}}{0.429 \text{ g carbon}} = 1.33 \frac{\text{g oxygen}}{\text{g carbon}}$$

Similarly, for 1 g of the second compound, there are 0.727 g oxygen and 0.273 g of carbon. The ration of mass of oxygen per gram of carbon is

$$\frac{0.727 \text{ g oxygen}}{0.273 \text{ g carbon}} = 2.66 \frac{\text{g oxygen}}{\text{g carbon}}$$

Dividing the mass of oxygen per g of carbon of the second compound:

$$\frac{2.66}{1.33} = 2$$

Hence the masses of oxygen combine with carbon in a 2:1 ratio which s consistent with the Law of Multiple Proportions since they are whole numbers.

John Dalton and the Atomic Theory

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 1.5.4), is a fundamental concept that states that all elements are composed of atoms. Previously, an atom was defined as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of the human pinkie (about 1 cm).

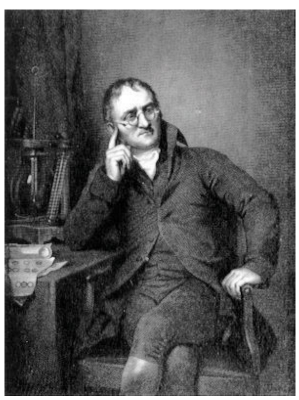

Figure 1.5.4: John Dalton was an English scientist who enunciated the modern atomic theory.

Dalton's ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means "indivisible" or "uncuttable.") Dalton had something that the ancient Greek philosophers didn't have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. When Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

Dalton's Theory was a powerful development as it explained the three laws of chemical combination (above) and recognized a workable distinction between the fundamental particle of an element (atom) and that of a compound (molecule). Six postulates are involved in Dalton's Atomic Theory:

1. All matter consists of indivisible particles called atoms.
2. Atoms of the same element are similar in shape and mass, but differ from the atoms of other elements.
3. Atoms cannot be created or destroyed.
4. Atoms of different elements may combine with each other in a fixed, simple, whole number ratios to form compound atoms.
5. Atoms of same element can combine in more than one ratio to form two or more compounds.
6. The atom is the smallest unit of matter that can take part in a chemical reaction.

Deficiencies of Dalton's Theory

In light of the current state of knowledge in the field of Chemistry, Dalton's theory had a few drawbacks. According to Dalton's postulates,

1. The indivisibility of an atom was proved wrong: an atom can be further subdivided into protons, neutrons and electrons. However an atom is the smallest particle that takes part in chemical reactions.
2. According to Dalton, the atoms of same element are similar in all respects. However, atoms of some elements vary in their masses and densities. These atoms of different masses are called isotopes. For example, chlorine has two isotopes with mass numbers 35 and 37.
3. Dalton also claimed that atoms of different elements are different in all respects. This has been proven wrong in certain cases: argon and calcium atoms each have an same atomic mass (40 amu).
4. According to Dalton, atoms of different elements combine in simple whole number ratios to form compounds. This is not observed in complex organic compounds like sugar ($C_{12}H_{22}O_{11}$).
5. The theory fails to explain the existence of allotropes (different forms of pure elements); it does not account for differences in properties of charcoal, graphite, diamond.

The importance of Dalton's theory should not be underestimated. He displayed exceptional insight into the nature of matter and his ideas provided a framework that was later modified and expanded by other. Consequentiually, John Dalton is often considered to be the father of modern atomic theory.

References

1. Petrucci, Ralph, William Harwood, Geoffrey Herring, and Jeffry Madura. General Chemistry. 9th ed. Upper Saddle River, New Jersey: Pearson Prentince Hall, 2007
2. Moore, John. Chemistry for Dummies. John Wiley & Sons Inc, 2002.
3. Asimov, Isaac. A Short History of Chemistry. , CT.: Greenwood Press, 1965.
4. Patterson, Elizabeth C. John Dalton and the Atomic Theory. Garden City, NY: Doubleday, 1970
5. Myers, Richard. The Basics of Chemistry. Greenwood, 2003
6. Demtröder, Wolfgang. Atoms, Molecules and Photons: An Introduction to Atomic- Molecular- and Quantum Physics. 1st ed. Springer. 2002

Summary

This section explains the theories that Dalton used as a basis for his theory: (1) the Law of Conservation of Mass, (2) the Law of Constant Composition, (3) the Law of Multiple Proportions.